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TDLAS-based *in-situ* monitoring of syngas composition from a pressurized, oxygen-blown, entrained-flow coal gasifier

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A real-time sensor to monitor the quality of the product synthesis gas (syngas) from coal gasification is an important need for successful deployment of integrated gasification combined cycle (IGCC) power generation systems. A new multi-species real-time sensor was developed and demonstrated to monitor the syngas energy content (lower heating value (LHV) and/or the Wobbe index) of syngas from the pilot-scale (1 ton/day), high-pressure (up to 18 atm), entrained-flow, oxygen-blown, slagging coal gasifier at the University of Utah.   The mole fractions of CO, CO_2, CH_4 and H_2O were monitored simultaneously using tunable diode laser absorption spectroscopy (TDLAS) with four fiber-coupled lasers tuned to transitions near 2325, 2017, 2290 and 1352 nm, respectively. There are two challenges for *in-situ* laser absorption sensing in syngas flows: (1) collision-broadening of the absorption spectrum at elevated pressure (10-50 atm) and (2) transmission attenuation by particulate scattering. A sensor strategy using 1f-normalized wavelength-modulation spectroscopy with 2f-detection (WMS-2f/1f) was developed to surmount these challenges. The sensor transitions were selected to optimize the measurement of the four species at syngas pressures up to 20 atm and a temperature near 400K, and the spectral constants and the collisional-broadening coefficients were measured to enable accurate simulation of the absorption lineshapes. The prototype sensor was constructed and performance tested on synthetic syngas with known composition in the laboratory at Stanford.   Field measurements were then conducted in the Utah gasifier where simultaneous multi-species measurements of CO, CO_2, CH_4 and H_2O mole fractions were performed at various operating conditions with a time resolution of ~3s. For an oxygen-blown gasifier, the major species of the syngas can be determined from measured CO, CO_2, H_2O, and an assumption that the balance is H_2. For an air-blown system or for systems with significant added N_2 (used in the Utah gasifier for inert purge and cooling flows), a separate monitor of either H_2 or N_2 is required. To determine the energy content of the syngas, the important minor species CH_4 must also be monitored (H_2S must also be measured for high sulfur coals). Using the known N_2 flow rate, the LHV and Wobbe Index determined in the wet syngas flow are in good agreement with dry values determined from gas sampling and GC analysis. Thus the prototype sensor demonstrated here has good promise for improved control of gasifier syngas quality.

1. Introduction

Coal is used as a solid hydrocarbon fuel for generation of electricity; however, the combustion of coal results in atmospheric emission of greenhouse and acid rain-causing gases such as CO_2, SO_2 and NO_x. Integrated gasification combined cycle (IGCC) power generation represents one of the cleanest methods of harvesting energy from coal [1] when coupled with highly efficient CO_2 and sulfur sequestration processes. The coal gasifier is an integral part of the IGCC system, which converts coal into synthesis gas (syngas) comprised mainly of CO, CO_2 and H_2. The CO_2 is typically extracted from this mixture resulting in a significant reduction in greenhouse gas emission. Continuous observation of the syngas composition is useful to indicate the extent of reaction in the gasifier, the heating value of the output syngas and hence the overall health of the gasification system. Conventionally, the gas is extracted and preconditioned (depressurized, cooled, dehumidified and filtered of particulates) to analyze the components of the syngas with industrially available sensors. These steps introduce significant time delays and may alter the syngas composition. The need for direct real-time syngas composition monitoring is among the most serious challenges faced by the control

and instrumentation of gasifiers as identified by the US Department of Energy [2]. Here we demonstrate the use of TDL absorption sensing to monitor syngas composition from a pilot-scale, oxygen-blown gasifier. The key features of the TDL-based sensors include fast response, non-intrusive nature and sensitive species-specific detection capabilities. Some of the problems of developing an optical sensor unique to the gasification environment are:

1. A particulate-laden environment with extremely low transmission [3].
2. The high pressure of efficient gasification processes [1] produces collision broadening of the absorption transition leading to a decreased peak signal and an absence of the non-absorbing baseline typically used with direct absorption spectroscopy.

These problems were overcome by the use of a 1f-normalized WMS-2f technique that has been demonstrated previously to be effective in high pressure and noisy environments [4,5]. In this method, the injection current of the diode laser is modulated sinusoidally at a frequency of 10 kHz producing a simultaneous variation in laser output intensity and frequency. The signal transmitted through the absorption medium is analyzed at the integer multiples of the modulation frequency; hence the terminology 1f, 2f, 3f ... This technique is well-known for noise rejection in the detection of trace species [6-8] and has been used at Stanford University in noisy environments [9-11]. This normalization technique accounts for the variations in non-absorption losses of the transmitted laser intensity [4,5,11].

The prototype sensor used here has four lasers for detection of CO, CO_2, CH_4 and H_2O tuned to transition frequencies of 4301, 4957, and 4367 (Nanoplus), and 7394 (NEL) cm^{-1} (2325, 2017, 2290, and 1352 nm). The remainder of the gas is assumed to be H_2, thus accounting for the major species in the syngas. With this information, the heating value and the Wobbe index of the syngas can be monitored as a part of a real-time control loop. This article describes the results from the field measurement campaign where these sensors were implemented in a fully operational entrained-flow, oxygen-blown, slagging pilot-scale coal gasifier at the Institute for Clean and Secure Energy, University of Utah.

2. Sensor Fundamentals

The sensors were first developed and tested in controlled test cells [12]. The selection of the spectroscopic transitions for optimal detection of the gases and the laser modulation parameters were discussed in that work. The fundamentals of laser absorption with WMS-2f detection will be summarized here to orient the reader. Following that, the apparatus for practical implementation of the TDLAS sensors for the detection of CO, CO_2, CH_4 and H_2O in a pilot-scale entrained-flow gasifier exhaust will be discussed.

2.1. Absorption sensing

The laser radiation was directed across the syngas flow channel and the transmitted light was intercepted by a photodetector. The transmission coefficient (τ) of a monochromatic light beam at frequency v though the gas is related to the spectral absorbance as given by the Beer-Lambert relation:

$$\tau(v) = \frac{I}{I_0} = e^{-\alpha(v)} \tag{1}$$

where I_0 is the incident beam intensity, I is the transmitted beam intensity and α is the spectral absorbance for a pressure P, path length L, mole fraction of the ith absorbing species x_i, transition linestrength $S_{i,j}$ and lineshape function $\phi_{i,j}(v)$ of the jth transition, as defined by the expression

$$\alpha(v) = P \cdot L \cdot \sum_{i,j} x_i \cdot S_{i,j} \cdot \phi_{i,j}(v) \tag{2}$$

The above expression assumes uniform gas composition and temperature along the laser line of sight (LOS).

For wavelength modulation spectroscopy (WMS), the laser is modulated by sinusoidally varying injection current at angular frequency $\omega = 2\pi f$ which results in an intensity and frequency response as follows:

$$I_0(t) = \bar{I}_0 [1 + i_1 \cos(\omega t + \psi_1) + i_2 \cos(2\omega t + \psi_2)] \tag{3}$$

$$v(t) = \bar{v} + a \cos(\omega t + \psi) \tag{4}$$

where, v is the frequency of light at time t, $\bar{v}$ is the center frequency, a is the modulation depth, ψ is the initial phase of the frequency modulation, I_0 is the unabsorbed beam intensity, $\bar{I}_0$ is the average intensity at the center frequency, i_1 is the linear (1f) intensity modulation amplitude, i_2 is the second-order (2f) intensity modulation amplitude and ψ_1 and ψ_2 are the initial phases of the 1st and 2nd order intensity modulation.

Due to the sinusoidal modulation of the laser wavelength at a frequency ω, the transmitted intensity is also periodic in ω, and can be expressed as a Fourier series expansion as follows:

$$\tau(t) = \sum_{k=0}^{\infty} H_k \cos(k\omega t) \tag{5}$$

where H_k is the kth Fourier coefficient of the expansion and can be expressed as:

$$H_k = \frac{1}{(1 + \delta_{k0})\pi} \int_{-\pi}^{\pi} \tau(\bar{v} + a\cos\theta) \cdot \cos(k\theta) d\theta \tag{6}$$

By combining equations (1), (3) and (5) we get the transmitted laser intensity:

$$I(t) = \bar{I}_0 \left[1 + i_1 \cos(\omega t + \psi_1) + i_2 \cos(2\omega t + \psi_2) \right] \left[\sum_{k=0}^{\infty} H_k \cos(k\omega t) \right] \tag{7}$$

The WMS technique involves the extraction of the harmonics of the above signal at integral multiples of the modulation frequency ω. This is achieved by using a digital lock-in amplifier where the above signal obtained from the detector is multiplied by $\cos(n\omega t)$ or $\sin(n\omega t)$ and then using a low-pass filter for the X and Y components respectively, of the nf signal [5,12]. Here, the 1f and 2f signals were used. The final expression for the 1f-normalized WMS-2f magnitude is given by [5]:

$$S_{2f/1f} = \sqrt{\left[\left(\frac{X_{2f}}{R_{1f}} \right)_{raw} - \left(\frac{X_{2f}}{R_{1f}} \right)_{bg} \right]^2 + \left[\left(\frac{Y_{2f}}{R_{1f}} \right)_{raw} - \left(\frac{Y_{2f}}{R_{1f}} \right)_{bg} \right]^2} \tag{8}$$

where R_{1f} is the vector sum of the X and Y components of the 1f signal. This normalization scheme cancels the unknown variations in mean signal intensity that accounts for the majority of random fluctuations in the average signal due to laser noise and non-absorption transmission losses resulting in a robust sensor applicable in harsh environments.

The sensors for CO, CO_2, CH_4 and H_2O consist of lasers operating at wavelengths targeting interference-free species-specific transitions at 2325, 2017, 2290 and 1352 nm, respectively [12]. That work also summarized a method for estimating the lower heating value (LHV) and the Wobbe index from the major species composition of syngas. Below is a brief summary of that discussion.

The lower-heating value (LHV) of a fuel is one of the most widely used properties to compare the heat release from burning different fuels. It is the amount of energy released when a specific amount of fuel is burnt to completion at 25°C and 1 atm and the combustion products are returned to the same temperature and pressure condition with saturated water vapor.

In general, the syngas-like mixtures are primarily composed of CO, CO_2, CH_4, H_2O and H_2 along with many trace species such as H_2S, NH_3, etc. The laser absorption sensors described here can measure all primary components except

H_2, which is assumed to be the balance. This assumption provides a path to infer the lower heating value (in MJ/kg C) of the syngas as:

$$LHV = \sum_{i=CO,CH_4,H_2} x_i LHV_i \qquad (9)$$

where x_i is the mole fraction and LHV_i is the lower heating value (when in pure state) of the species i. Note the assumption of a H_2 balance for our measurement is valid only for oxygen-blown gasifiers which have only low concentrations of fuel nitrogen in the syngas stream. For air-blown systems or systems with significant nitrogen purge, N_2 must also be accounted in the syngas mixture. Note also for high sulfur coals the heating value of the H_2S must also be included.

Another parameter of importance, when dealing with modern gaseous fuels is the Wobbe Index (WI), which is a measure of interchangeability of fuels. It is expressed as:

$$WI = \frac{HHV}{\sqrt{G_s}} = \frac{\sum_{i=CO,CH_4,H_2} x_i HHV_i}{\sqrt{G_s}} \qquad (10)$$

where HHV_i is the higher heating value of the species i in a pure state and G_s is the specific gravity of the gaseous fuel with respect to dry air at 25°C and 1 bar.

2.2. Apparatus

The prototype diode laser absorption gas sensor for gas composition / heating value designed and tested in the laboratory at Stanford University was demonstrated for practical applicability in the entrained-flow coal gasifier at the Institute for Clean and Secure Energy at the University of Utah.

A. The gasifier

The gasifier can be broken down into four main sections as shown in Fig. 1:

Section 1. Reactor core: The coal slurry and oxygen is fed through the nozzle at the top of this section. The water in the slurry instantly vaporizes upon introduction to the hot reactor core (1300K-1700K). The coal undergoes devolatilization, pyrolysis and finally gasification. The section 1 mostly hosts the partial oxidation reactions. This region is characterized by extremely high particulate density and slag formation.

Section 2. Pre-quench section: After the reacted gas mixture exits the reaction core, it is cooled down by a spray of liquid water directly into the flow. This reduces the temperature to 600K-1000K. The gas composition "freezes" corresponding to equilibrium at this temperature.

Section 3. Post-quench section: The syngas, after being quenched to a much colder temperature by the water sprays in the previous section, bubbles out through a column of liquid water and conveyed through a pipe. At this location, the temperature of the gas is in the range 340K-400K.

Section 4. Post-filtration section: The syngas is passed through a filtration unit to remove the particulates (unreacted coal, soot or ash) from the flow. The temperature does not drop significantly between section 3 and this point. The difference is around 20 K. The overall temperature range is 320K-380K.

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Fig. 1. Schematic of the entrained flow gasifier at the Institute for Clean and Secure Energy at the University of Utah. The sections 1-4 are identified in the diagram.

B. Free space beam multiplexing

The four lasers for the detection of CO, CO_2, CH_4 and H_2O operate at widely separated wavelengths ranging from 1350 to 2325 nm, which is beyond the bandwidth of typical fiber combiners. However it was useful to direct the four beams onto a single detector. The four beams are launched in parallel through the gas medium and collected by an aspheric uncoated CaF_2 lens of 50 mm focal length as shown in Fig. 2. The entire optical assembly was rigidly mounted on an optical breadboard to ensure stability of the optical components.

Fig. 2. Free-space quadruple beam multiplexing

C. Optical access to the syngas

The optical access for the TDL light consists of 1" thick sapphire windows (diameter of 1" and 0.5" at sections 3 and 4 respectively) sealed by teflon gaskets. Sapphire was chosen as the window material due to its superior IR transmission

capability and physical strength. The thickness of the windows ensured safe operation for pressures up to 100 bar. To avoid water condensation on the windows, the window housing was heated by collar heaters to maintain the window temperature (about 150°C) above water vapor saturation.

Section 3 is the pre-filtered stage of the quenched syngas exhaust, where the gas is saturated with water vapor with a considerable amount of suspended particulate. After the filtration stage, most of the particles are removed from the flow as it passes the windows at section 4. The four sensors utilize transitions with varying degrees of sensitivity to their respective concentrations [12]. The CO and H_2O sensing was more sensitive than the CO_2 and CH_4 owing to the product of transition linestrength and relative concentration in the syngas. A way to increase the sensitivity is to increase the absorption path length. But, with the increase in the optical path length, the laser beam extinction due to the particulates in the flow also increases. Therefore the optical path length in section 3 could not be increased beyond about 8 cm without severely degrading the signal-to-noise ratio. A photograph of this arrangement is shown in Fig. 3. However, this problem is overcome in section 4, where the extinction due to the particulates was greatly reduced. Therefore, the CO and H_2O sensors and the CO_2 and CH_4 sensors were clustered together in the shorter (8.3 cm) and the longer optical path (17.9 cm) sections respectively (See Fig 4a and 4b). The CO and H_2O could not be used on the longer path without decreasing the dynamic range.
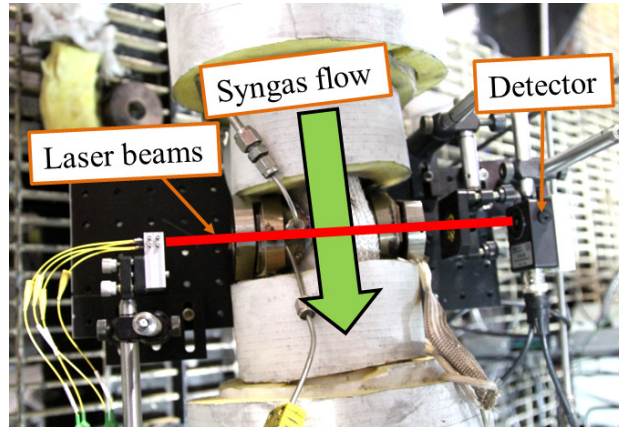

Fig. 3. Photograph of the optical access assembly in Section 3

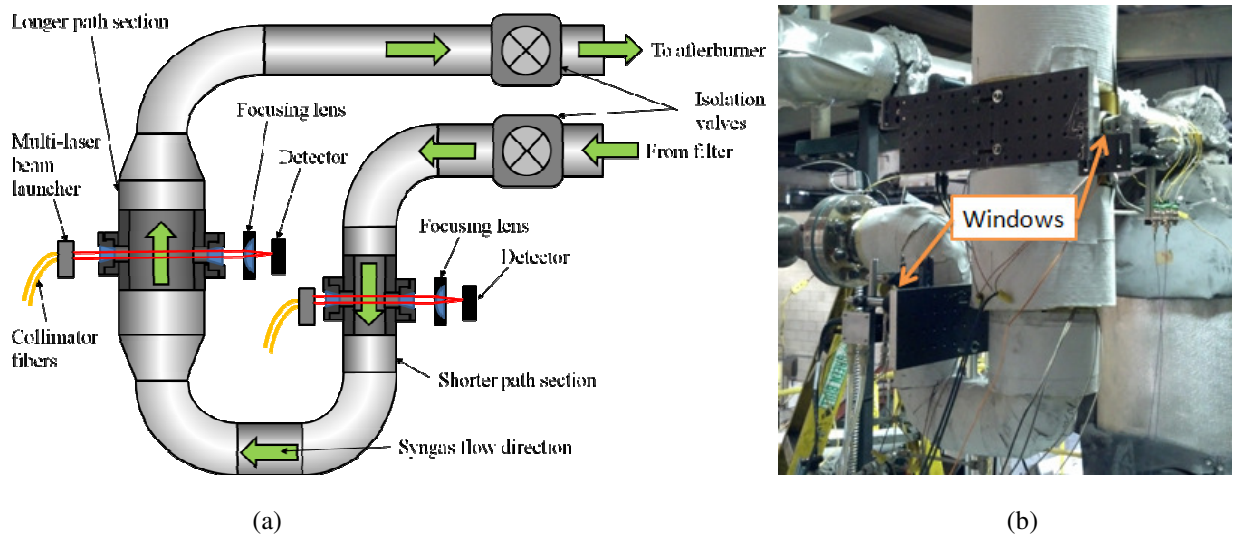(a)   (b)

Fig. 4. (a) Schematic and (b) Photograph of the optical access assembly in Section 4

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D. Lasers and control system

The sensors use four lasers for detection of CO, CO_2, CH_4 and H_2O at the center frequencies of 4301, 4957, and 4367 (Nanoplus), and 7394 (NEL) cm^{-1} (2325, 2017, 2290, and 1352 nm). All four lasers were housed in 14-pin butterfly packages and their outputs were pigtail-fiber coupled. The transmission of extended NIR light beyond 2 µm wavelength through silica based fibers suffers wavelength dependent loss. Thus, fiber lengths were limited to less than 2 m. The lasers, along with the laser current / temperature controllers and the data acquisition (DAQ) system, were placed on a portable cart located about 1 m away from the optical access windows. The DAQ was controlled by an ethernet cable from the control room situated about 90 ft away. A schematic is shown in Fig. 5.
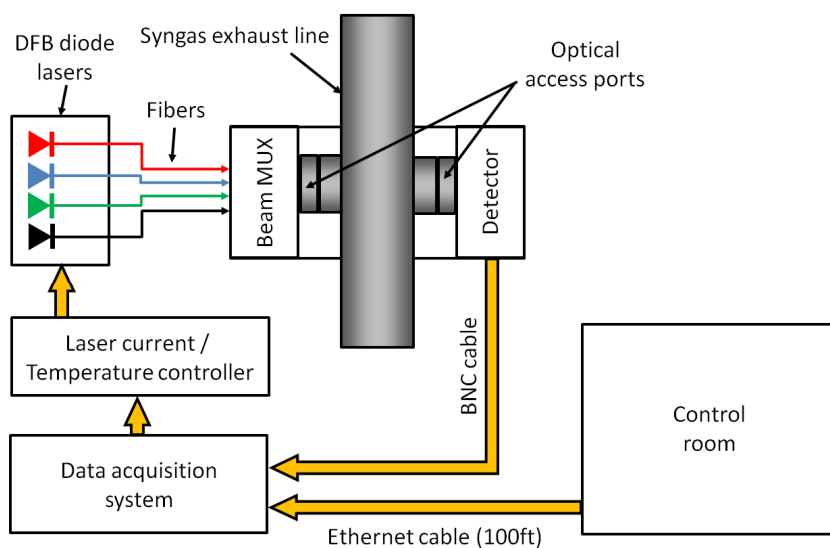
Fig. 5. Schematic illustrating the components of the sensor including the controller and the DAQ in relation to the syngas exhaust pipe

3. Results and Discussion

This section summarizes the measurements obtained during a field measurement campaign at the Institute for Clean and Secure Energy (ICSE), University of Utah, Salt Lake City, Utah during the first week of May 2012. These results can be divided into two segments: a) Sensor field validation and b) Simultaneous time-resolved multi-species concentration measurements.

3.1. Field validation of sensor performance

The coal gasifier represents an extremely harsh environment that has the potential to produce unknown interfering species at the selected laser wavelengths. To investigate the possibility of interference, a wide wavelength range scan of each laser was taken around each of the transitions. A full comparison of measurement and simulation of the shape of the WMS lineshapes reveals the identity of the absorber. Similar measurements previously identified interference by NH_3 in the gas mixture, which led to an alternate selection of a transition devoid of NH_3 interference for CH_4 detection. Such measurements were performed successfully for CO, CO_2, CH_4 and H_2O and compared to the expected WMS lineshape as shown in Fig. 6. Agreement of the 1f-normalized WMS-2f lineshapes with the simulated spectra confirms the identity of the absorbing species and a high signal to noise ratio of the obtained signals and verifies the absence of inteference.
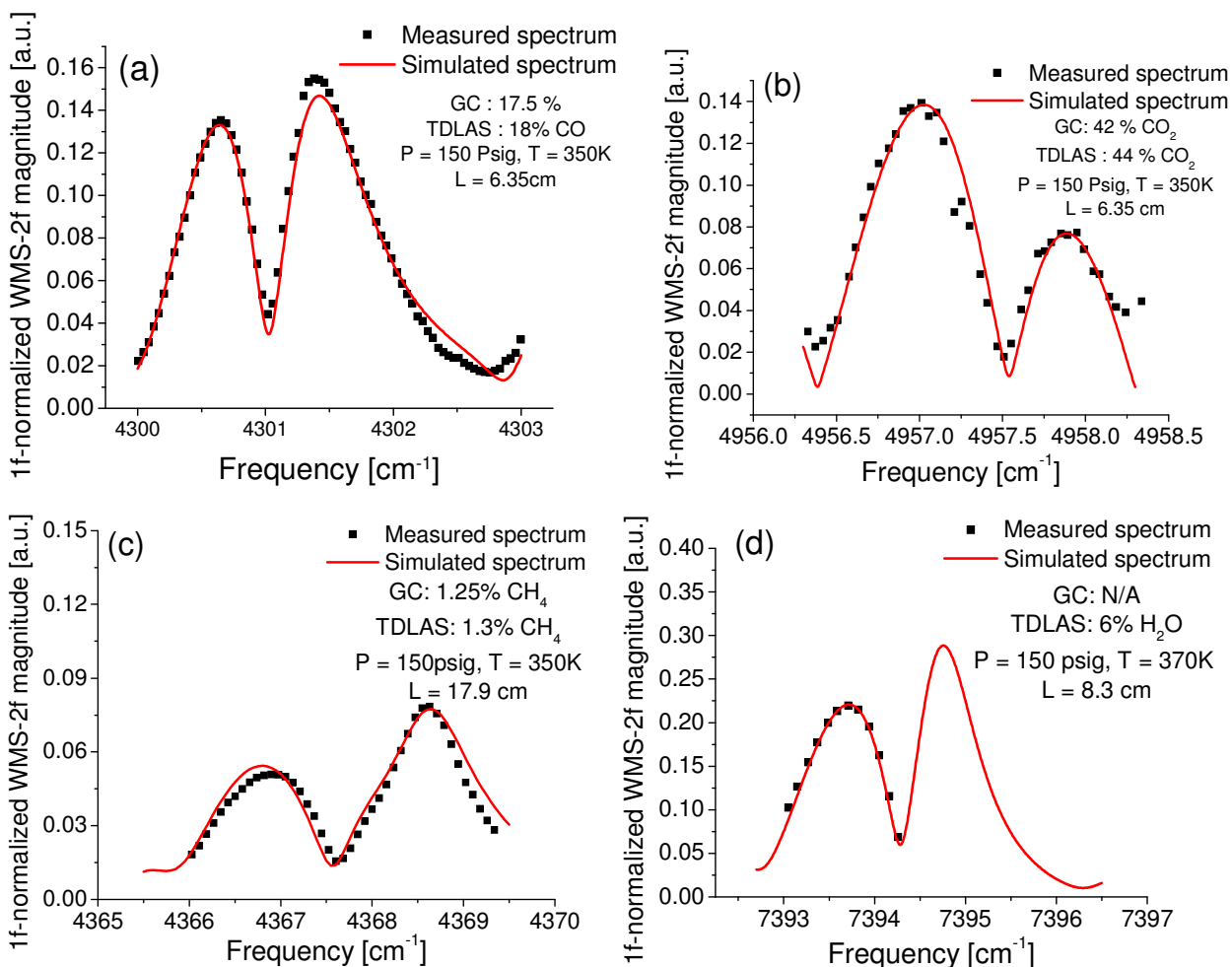
Fig. 6. Sample WMS spectra for (a) CO, (b) CO_2, (c) CH_4 and (d) H_2O measured in the gasifier at 150psig.

3.2. Simultaneous time resolved multi-species concentration measurements

After the verification of the sensor performorance, time-resolved multi-species concentrations were monitored over extended durations during a gasifier run. The time resolution of the measurements at section 3 was 0.33 Hz and at section 4 is 0.26 Hz.

The entrained flow gasifier (EFG) as operated at ICSE, Utah produced CH_4 at mole fractions less than 1% of the syngas. To test the CH_4 sensor over a wider dynamic range, controlled amounts of CH_4 were injected into the flow in order to validate the applicability of the CH_4 sensor in the field. The location of injection was sufficiently upstream of the measurement location to allow for uniform mixing with the incoming flow. The CH_4 was injected in discrete time-steps to facilitate understanding of the time response of each sensor location. The measured CH_4 mole fraction along with a comparison with a GC and a CAI NDIR gas analyzer is displayed in Fig. 7. The gas sampled for these analyzers was further downstream of the optical access location. The sampled gas was depressurized and dehumidified This resulted in a lag in response relative to the Stanford laser-based *in situ* sensors. As shown in Fig. 7, there is a time lag of 4.2 mins from section 3 and 75 secs from section 4. Such delays can range up to 30 minutes in commercial scale facilities. In addition, the time resolution of the gas sampling suppressed any rapid time variation in the syngas flow. After these experiments were complete, span-gas calibration of the CAI analyzer found the faulty sensor calibration led to high readings. Thus the utility of self-calibrating laser absorption sensing is illustrated in Fig. 7(a).
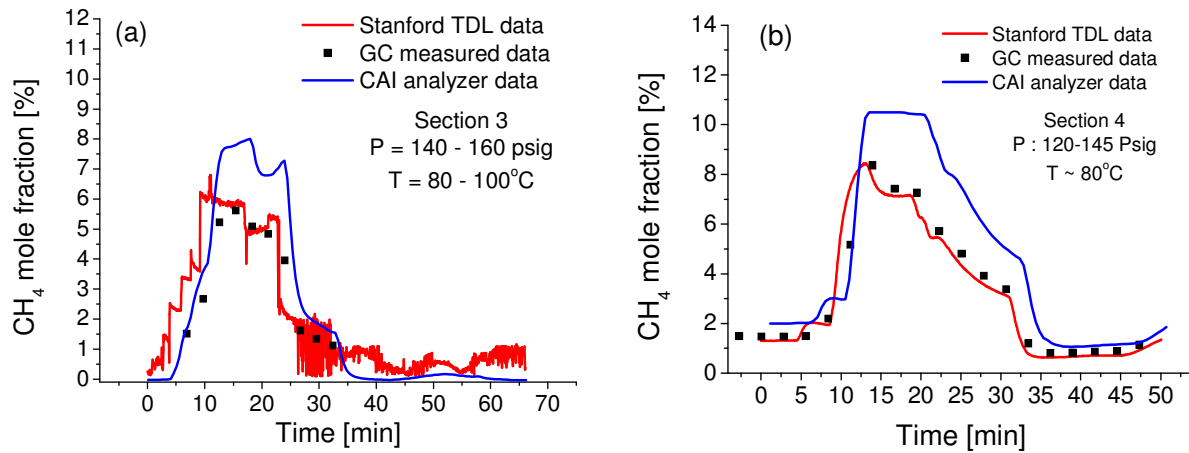
Fig.7. Time lag observed for traditional sensors vs. laser based in-situ sensors at (a) location 3 and (b) location 4.

At the same time, measurements were also taken for CO, CO_2 and H_2O as shown in Fig. 8. For a comparison with the GC measurements (which can only analyze dry gases), the water vapor mole fraction measured by using the TDLAS sensor was subtracted from the rest of the TDLAS based measurements to convert them into an equivalent dry basis. The measured data shows reasonable agreement with the GC measurements. Some nitrogen was also present in the flow as a result of the purges required by various other optical sensors upstream. But as expected, the N_2 in the flow was almost constant and the GC measurements were sufficient to capture any longer term changes. Thus with the knowledge of all other major species i.e. CO, CO_2, H_2O, CH_4 and N_2, the H_2 concentration can be found by balance. Consequently, the LHV of the syngas can be inferred.
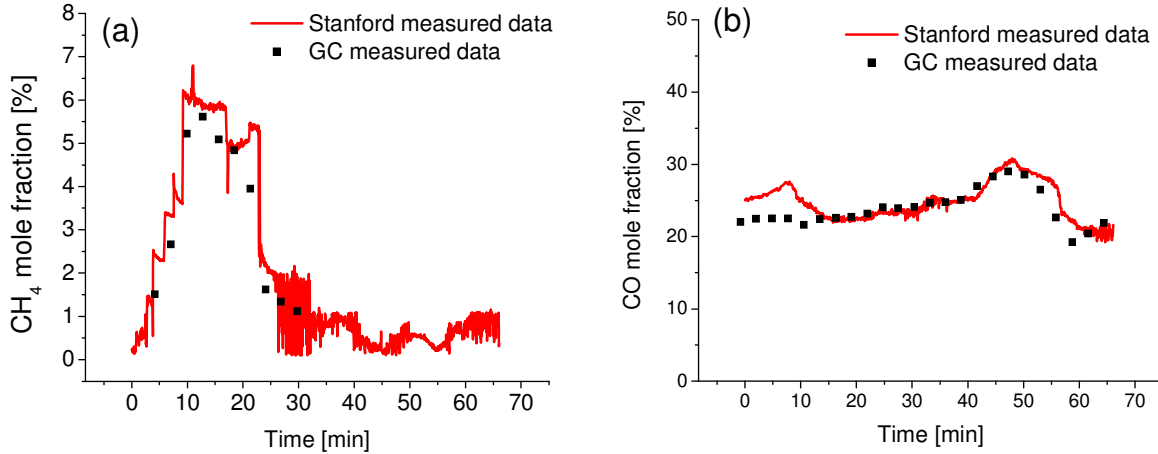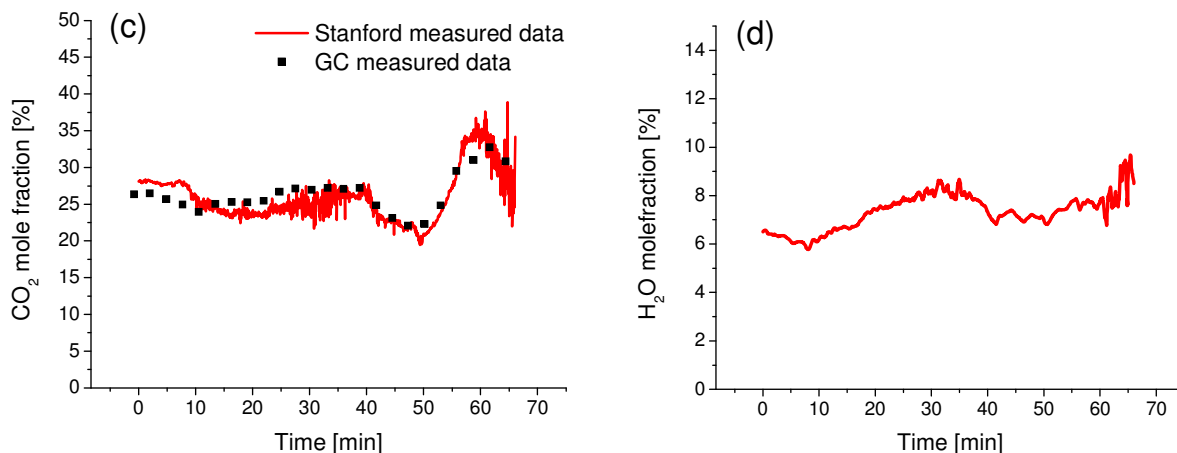
Fig. 8. Time-resolved (dry basis except H_2O) mole fractions of (a) CH_4, (b) CO, (c) CO_2 and (d) H_2O and comparison with GC measurements (except H_2O) in section 3 at 150 psig.

4. Conclusions

The prototype TDLAS-based gas mole-fraction sensors were first developed in the laboratory at Stanford. Simultaneous multi-species measurements of CO, CO_2, CH_4 and H_2O mole fractions were then conducted in the Utah gasifier at various operating conditions with a time resolution of ~3s. These sensors were shown to be free of interference from other species by the measurement of 1f-normalized WMS-2f lineshapes. Strategies to engineer a reliable setup for multi-wavelength infrared optical access within the gasifier were described. The major species composition of the syngas (for O_2-blown systems with significant but nearly constant amount of N_2) was determined from the measured CO, CO_2, H_2O, a separate monitor for N_2 (GC) and an assumption that the balance is H_2. To estimate the energy content of the syngas accurately to ± 5%, the important minor species CH_4 was also included in the sensor suite. The LHV and Wobbe Index determined in the wet syngas flow were in good agreement with dry values determined from gas sampling and GC analysis. Thus the prototype sensor demonstrated here has good promise for improved control of gasifier syngas quality, ushering in a new era of growth in IGCC based power generation.

References

1. T.F. Wall, *Proc. Comb. Inst.* **31**, 31 (2007).

2. S.J Clayton, G.J. Stiegel, J.G. Wimer, *US DoE report DOE/FE-0447* (2002).

3. J.B. Jeffries, A. Fahrland, W. Min, R.K. Hanson, D. Sweeney, D. Wagner and K. .J. Whitty, *Pittsburgh Coal Conference*, September, (2009).

4. H. Li, G.B. Rieker, X. Liu, J.B. Jeffries, R.K. Hanson*, Appl. Opt.* **45**, 1052 (2006).

5. G.B. Rieker, J.B. Jeffries, R.K. Hanson, Appl. Opt. **48**, 5546 (2009).

6. P. Kluczynski, J. Gustafsson, A. Lindberg, and O. Axner, Spectrochimica Acta Part B **56**, 1277 (2001).

7. H. Teichert, T. Fernholz, V. Ebert, *Appl. Opt.* **42**, 2043 (2003).

8. J. Wolfrum, *Proc. Comb. Inst.* **27**, 1 (1998).

9. R.K. Hanson, *Proc. Comb. Inst.* **33**, 1 (2011).

10. 8. X. Chao, J.B. Jeffries, R.K. Hanson, *Proc. Comb. Inst.* **33**, 725 (2011).

11. G.B. Rieker, J.B. Jeffries, R.K. Hanson, Appl. Opt. **48**, 5546 (2009).

12. H. Li, G.B. Rieker, X. Liu, J.B. Jeffries, R.K. Hanson*, Appl. Opt. **45**, 1052 (2006).

13. T. Fernholz, H. Teichert, and V. Ebert, Appl. Phys. B **75**, 229 (2002).

14. R. Sur, K. Sun, J. B. Jeffries and R. K. Hanson, Appl. Phys. B, *submitted* (2013).