Scanned-wavelength-modulation-spectroscopy sensor for CO, CO₂, CH₄ and H₂O in a high-pressure engineering-scale transport-reactor coal gasifier

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Keywords: *Transport-reactor gasifier; spectroscopy; high pressure; in-situ sensing; TDLAS*

Abstract

In-situ laser-absorption measurements of CO, CO₂, CH₄ and H₂O were demonstrated in the synthesis gas products of coal gasification (here called syngas) from an engineering-scale transport reactor. A wavelength-scanned, wavelength-modulation spectroscopy scheme was used to counter environmental challenges including severe loss in transmitted light intensity due to particulate scattering and beam steering in the synthesis gas stream. Separate lasers were used for each species (CO near 2326nm, CO₂ near 2017nm, CH₄ near 2290nm, and H₂O near 1352nm) and a novel fiber bundle was utilized to combine all four beams on a common optical path. Line-of-sight laser absorption utilized sapphire windows in the synthesis gas product pipe downstream of the gasifier reactor by approximately 5 seconds flow time. Time multiplexing enabled low-noise measurement of the transmitted light with a single detector. Successful measurements of the four species mole fractions were performed throughout the 54 day measurement campaign, including a significant period of unattended operation. The mole fractions of the

four target species were monitored versus time as the gasifier was transitioned from a cold startup to stabilization at the target 15 atm and 1260 K gasification condition, and after 35 days at relatively steady operating conditions, the campaign was terminated and the reactor shut down. The variations of time-resolved mole fractions of the four species were captured during the heating of the reactor with a propane/air flame, the continued combustion heating of the reactor as coal was added to the fuel, and the transition from combustion to gasification. The average values of CO, CO₂ and CH₄ measured by the laser absorption sensor were in good agreement with extractive gas chromatography; however, the extractive gas analysis was delayed by ~20 minutes and had a ~15 minute time response due to the transport and conditioning (filtering and drying) of the sampled gas. The laser absorption sensor provided essentially simultaneous species mole fractions with sub-second time resolution, which enabled identification of a wide range of dynamic behaviors. For example, small changes in the reactor conditions due to batch feeding of coal were observed by composition changes in the synthesis gas and were correlated with small temperature fluctuations in the reactor.

1 Introduction

Coal is one of the most abundant sources of energy in the world [1,2]. However, the use of coal is often shunned for environmental concerns due to production of pollutant and hazardous chemicals as well as large quantities of greenhouse gases. Coal gasifier technology offers the potential to provide an environmentally clean use of this natural energy resource. However, large-scale power generation driven by coal gasification remains a research and development concept. More than a decade ago, Clayton et al. [3] identified that process reproducibility was the most important barrier to gasifier commercialization. Key to reproducibility is a control scheme to account for changes in the heating value of the gasifier fuel and the variation of gasification conditions as the fuel is batch fed. In their report, Clayton et al. identify measurement and control of gasification as the number three research and development need for reliable and reproducible commercial-scale gasification for power production. The most typical monitoring of synthesis products of coal and biomass gasification uses gas chromatography (GC) of sampled gases, and this is quite effective for research on laboratory-scale gasification. However, industrial-scale processes

1 can have very long transit time from gas sampling to measurement (for the engineering-scale transport
2 gasifier measurements reported below this transit-time delay is of order twenty minutes). Because the
3 synthesis gas product stream (here called syngas) is quite humid and laden with particulate the sampled
4 gas also must be dehumidified, filtered, and cooled prior to GC analysis. These gas conditioning steps
5 can involve coolers and filters that degrade the time-resolution due to diffusion and that have large
6 volume due to maintenance concerns. (For the measurements reported below the observed rise time of the
7 GC measurement system is longer than 15 minutes.) Thus, faster syngas sensors are needed to capture
8 dynamic variation in large-scale gasification processes and understand the time-resolution needed for
9 effective process control.

10 *In situ* measurements with rapid time-resolution have long been reported using laser absorption
11 for a wide variety of chemically reactive gas flow applications including combustion [4–9], atmospheric
12 monitoring [10–12], aeroengine propulsion research [13], and even in the confined volumes of fuel cells
13 [14]. The references cited here are meant to provide a few examples of this vast literature and not a
14 comprehensive review of laser absorption in reactive gas flows. Laser absorption sensing infers species
15 mole fraction from the loss of transmitted light intensity when the laser wavelength is tuned to an
16 absorption feature in the target species. However, *in situ* monitoring of syngas is faced with significant
17 challenges. First, high efficiency coal gasifiers operate at elevated pressures (10-50 atm) and
18 temperatures (~2000K), which broadens and blends the absorption transitions and spreads the population
19 of any one absorbing state over a larger thermal distribution making on/off resonance wavelength
20 scanning difficult and decreasing the signal for a specific absorption transition. Second, the large water
21 vapor mole fraction in the hot syngas produces interference absorption for detection of other species,
22 which complicates the selection of absorption transitions that minimize this interference. Third, the
23 syngas product stream can be heavily laden with particulate, which can produce large non-absorption
24 transmission losses in the syngas due to light scattering. These challenges were overcome here by careful
25 selection of absorption transitions to minimize interference from other species and the detection of

absorption by a novel, wavelength-scanned, normalized wavelength modulation spectroscopy (WMS) strategy, which will be discussed below.

The laser-absorption sensor strategies used here were designed and validated with gas cell experiments in the laboratory [15], and optimized using the lessons learned during previous measurement campaigns using Stanford sensor technology at coal-gasifier facilities: (1) A 2011 campaign performed H₂O and temperature measurements in the syngas products from a pilot-scale (1 ton/day) oxygen-blown down-fired gasifier at the University of Utah [16]. (2) A 2012 campaign to Utah used a second-generation sensor for CO, CH₄, CO₂, and H₂O *in-situ* syngas measurements [17]. (3) A 2012/2013 campaign performed H₂O and temperature measurements in syngas from an engineering-scale fluidized bed transfer gasifier at the National Carbon Capture Center (NCCC) [18]. These H₂O measurements were the first-ever *in situ* laser-absorption measurements in the industrial-scale NCCC gasifier product stream. Here we build on this earlier work to report an *in situ* demonstration of time-resolved mole fraction measurements of CO, CO₂, CH₄, and H₂O in the syngas output of the NCCC gasifier during their R13 measurement campaign conducted February-April of 2014 (54 day campaign with 40 days of continuous gasifier operation and 35 days of steady-state operating conditions). Especially important for the success of this work were improvements in the optical engineering to enable measurements with four lasers spanning a wavelength range of 1.34-2.31 μm , including:

1. The use of scanned-wavelength normalized WMS, which made the long-term measurements insensitive to any drift in the laser wavelength or intensity during the 40 days of operation.
2. The use of time-division-multiplexing, enabling a single detector for measurement of four species with 0.2 s time resolution, which for the first time, captured sub-second dynamic changes in the syngas output (the facility GC analysis of sampled syngas had a 20 minute time delay and 15 minute rise time).
3. The use of a novel fiber bundle to combine light from four fiber-coupled lasers with a wide range of wavelength onto a single optical path.

- 1 4. An optical transmitter/receiver design with remote alignment capabilities that achieved the collection
2 of the transmitted laser intensity without the need for realignment throughout the 40 days of operation.
- 3 5. Remote detector gain adjustment to accommodate the large (300-fold) change in signal strength due to
4 non-absorption losses as the process is transitioned from pre-heating with combustion at 1 atm to full
5 gasification (5,000 lb/hr syngas) at 15 atm.

6 This paper is organized as follows: Section 2 (sensor design) of the paper discusses the
7 wavelength selection, scanned-wavelength normalized-WMS strategy, and wavelength multiplexing
8 scheme for the four color (four species) laser absorption sensor. Section 3 describes briefly the NCCC
9 gasifier to establish the context for the measurements. *In situ* laser absorption measurements require
10 optical access for laser transmission through the hot, pressurized, toxic, and explosive syngas. Section 4
11 (optical engineering) of the paper describes the challenges and the optical engineering solutions needed to
12 install and safely operate the four color sensor on the industrial-scale gasifier facility. Section 5, results,
13 presents the *in situ* measurements of CO, CO₂, CH₄ and H₂O mole fractions in the output syngas from the
14 NCCC gasifier. For the first time rapid changes in the syngas composition are monitored as the gasifier
15 conditions change (e.g., variations during the transition from combustion heating to gasification or
16 variations during gasification synchronous with the batch feeding of coal fuel). These measurements are
17 compared with gas-sampled GC monitoring, whose slower time resolution suppresses the rapid variations
18 in syngas composition. Section 6, conclusions, provides an overview of the most important results and
19 discusses the potential for laser absorption sensing as a control variable for optimization of gasifier
20 operation.

21 **2 Laser absorption sensor**

22 **2.1 Wavelength selection**

23 The design and laboratory validation testing of four-color laser-absorption for CO, CO₂, CH₄ and H₂O in
24 syngas was described in detail in Ref. 16. Crucial design features from that work are reviewed here to put
25 the optimization needed for the NCCC application into context. Assuming uniform gas composition and

temperature along the measurement line-of-sight (LOS), absorption measurements are interpreted using Beer's Law to compare the ratio of the transmitted intensity (I) to the incident intensity (I_0) of monochromatic laser light at frequency ν :

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

where α is the spectral absorbance for a pressure P , path length L , mole fraction of the i^{th} absorbing species x_i , transition linestrength $S_{i,j}$ and line shape function $\phi_{i,j}(\nu)$ of the j^{th} transition, as defined by the expression:

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

Fig. 1 shows the superposition of absorbance spectra for each of the target species in air versus near-infrared wavelength as simulated using the HITRAN database [19] assuming a mole fraction in the syngas of 10% CO, 10% CO₂, 1% CH₄, and 10% H₂O at 15 atm and 600 K, which are the temperature and pressure expected at the measurement location at NCCC. The wavelengths selected to maximize sensitivity to target species and minimize interference absorption are indicated by arrows in the figure and listed in Table 1. The HITRAN database near the selected wavelengths was validated in heated cell experiments with known concentrations of the target gas and the insensitivity to interference absorption was shown by similar experiments in gas mixtures to mimic those expected for syngas [15].

2.2 Absorption detection using wavelength modulation spectroscopy

There is a long (>30 year) history of WMS absorption measurements using injection-current-tuned diode lasers (TDL) [4,5,20–27], and an attempt to review the use of WMS for *in-situ* measurements in practical applications is beyond the scope of this paper. TDLs simultaneously vary laser intensity and output wavelength as the injection current is varied, and thus, when the injection current is used for the wavelength modulation, a simultaneous intensity modulation is produced. All of the nf components of the WMS signal are proportional to laser intensity, and at line center the WMS-1f term for injection-current tuned TDLs is dominated by the laser intensity contribution [24]. The simultaneous wavelength

1 and intensity modulation of injection-current-tuned TDLs enables the 1f-normalization of the WMS-2f
2 signal to avoid the need to scan on/off the transition for the zero absorption baseline used in the analysis
3 of wavelength-scanned direct absorption and accounting for non-absorption losses in laser power due to
4 scattering, window fouling or laser power drift. Quite early in the development of WMS using TDLs
5 [28], the line center WMS-1f signal was used to normalize the WMS-2f signal, which during the
6 measurements removed the need to scan the laser wavelength off the absorption transition to acquire a
7 non-absorption baseline. For harsh environments this normalization can account for non-absorption
8 variations of laser intensity, an approach which has been exploited by several authors for sensors in a
9 variety of harsh environments e.g., [27,29–32].

10 WMS analysis requires understanding of the collision- and Doppler-broadened line shape of the
11 absorption transition as the WMS-2f signal has contributions from both line shape and absorbance.
12 Traditionally, WMS measurements have relied on an *in situ* calibration to avoid knowing the line shape.
13 Alternatively if the line shape is known, this calibration measurement can be avoided (called “calibration
14 free” by Rieker et al. [32]). In addition to temperature and pressure, the line shape requires a reasonable
15 estimate of the respective mole fractions of the major components of the test gas and a database of the
16 pressure- and temperature-dependent coefficients for pressure broadening for each of the species in the
17 gas mixture. For a reactive mixture such as syngas, this model-based approach to the line shape is
18 problematic because the composition of the syngas is the primary target of the measurement. For
19 wavelength-scanned direct absorption, this line shape is determined from a fit to the measured absorption
20 feature, and a combination of direct absorption to determine line shape and WMS to determine absorption
21 has been successfully used in reactive flows [13]. In addition, because of laser wavelength drift, a
22 scanned-wavelength approach is superior to a fixed-wavelength strategy long term monitoring
23 applications. Rieker et al. [32] avoided this problem by scanning the center wavelength of the modulated
24 laser in a small range near line center at the cost of collecting useful data only for the time the laser
25 wavelength was near line center. Unfortunately, the simultaneous wavelength and intensity modulation

complicates the analysis of the complete WMS line shape [23], and until recently quantitative interpretation of full line shape of wavelength-scanned 1f-normalized WMS-2f was quite difficult.

In the past two years, a new paradigm for the acquisition and analysis of wavelength-scanned WMS has been developed [33,34]. This new method has been used previously for water vapor measurements in the syngas of the NCCC gasifier [18] and in a scramjet combustor [35] where the wavelength-scanned 1f-normalized WMS-2f signals are fit with only the line shape and the peak absorbance as free parameters. One of the key advantages of measuring these four species simultaneously is that the mixture composition becomes essentially known from such measurement. During gasification, N_2 broadening is the dominant component of the gas ($\sim 60\%$, obtained from GC measurements). During the transient changes, the concentration of H_2O , CO and CO_2 vary significantly over short periods of time. The fitting scheme utilizes an initial guess of gas composition based on the measured CO , CO_2 and H_2O (Contribution of CH_4 in broadening is ignored) from the previous time sample. This was very effective at reducing the fitting scheme iterations. The quality of fit was found to be quite similar ($<5\%$ of the peak 1f-normalized WMS 2f signal) for all the four species in the entire scan. The details of the analysis and fitting of this new wavelength-scanned WMS method [33,34] and the use of the method for practical absorption sensing [18,35] are well described in the literature, and will not be repeated here. The measurement for a single species was conducted by modulating the laser's injection current with a linear sum of a relatively fast sinusoidal modulation f (here 10 kHz) and a relatively slow sawtooth (or triangle wave, sine wave, etc.) (here a 200Hz linear ramp). The harmonics of the modulation (nf) of the laser transmission intensity were extracted with a series of lock-in amplifiers (use of a digital lock-in simplifies this approach), and signals were collected at the 1f and 2f harmonic. The slower scan leads to a time-varying center wavelength resulting in a wavelength scan of the WMS-1f and WMS-2f line shapes. Fig. 2 shows the 1f-normalized WMS-2f line shape for CO collected in the gasifier after gasification had begun while the pressure was being increased. The measured data is compared to a wavelength-scanned WMS fit following ref [34], and the uncertainty of the CO mole fraction from this single sweep measurement is estimated to be $\pm 4\%$. The laser parameters (center frequency, scan range and modulation

depth) are listed in Table 1. The accuracies of the measurements at 16 atm and 600 K are: CO : $\pm 4\%$,
CO₂ : $\pm 4\%$, CH₄ : $\pm 4\%$, H₂O : $\pm 3\%$. GC accuracy as specified by the manufacturer is $\pm 2\%$; however,
the GC is also subject to gas phase and gas surface chemistry in the long sampling flow path and large
volume gas conditioning (filter and drier).

2.3 Time-division multiplexing for four-species detection

Each of the four target species CO, CO₂, CH₄ and H₂O, is detected with a separate laser, tuned to scan
transitions near 2326, 2017, 2290 and 1352 nm, respectively. Each of the lasers is scanned in turn to
provide time-division multiplexing as illustrated in Fig. 3. Each scan takes 5ms and is repeated every
20ms. Thus, measurements on all four species with 1-second time resolution would each average 50
individual measurements of the wavelength-scanned, 1f-normalized WMS-2f line shapes. The injection
current is varied to turn on each laser for 5 ms and off for 15 ms (the injection current is zero during the
off periods). The laser reaches a steady state in temperature, and no significant drift was observed in the
peak location of the absorbance feature at a constant operating condition, indicating good thermal stability
of the laser. In addition, the use of the scanned-wavelength WMS technique ensured that the entire feature
was captured, leaving room for adjustment of laser drifts over the long duration runs.

3. Transport reactor gasifier at NCCC

The transport gasifier at NCCC is based on KBR's fluid catalytic cracking process [36,37] and is
illustrated in Fig. 4. The photograph in panel a) illustrates the scale of the facility and the schematic in
panel b) illustrates the sensor location in the process stream. Pulverized coal is added near the top of the
mixing zone where the target temperature is 1260 K and air and steam are added at the bottom. The bed
particles for this fluidized bed reactor are removed from the syngas in a pair of cyclones, the product
stream cooled to ~ 600 K and most of the remaining particulate from the coal gasification removed by a
proprietary particulate control device (PCD); the product syngas is specified to have 1 ppm solids by mass.
The laser absorption measurement station on the fifth floor of the gasifier structure was located
approximately 30 m further downstream, and the syngas conditions were approximately those listed in

Table 2. The temperature at the flow exiting the transport reactor loop was monitored by a thermocouple and referred to here as the gasifier exit temperature (see Fig. 4 b).

4. Optical engineering

The four-color, four-species laser absorption sensor used the optical access designed for the earlier H₂O measurements at NCCC [18]. The windows and the laser transmitter and receiver optics required for the line-of-sight absorption were mounted on opposing flanges on the syngas product duct as illustrated in Fig. 5. Redundant transmitter and receiver windows and shutoff ball valves provided isolation of the syngas flow in case of window failure. A pressure and temperature sensor mounted between each pair of windows would indicate fugitive syngas from a window leak, which was designed to trigger closure of the redundant ball valves to safely confine the syngas flow. The sapphire windows were 1” thick and were mounted onto 900lb ANSI flanges, which were pressure tested to 110 atm at 480 K by the manufacturer. Safety considerations limited the use of standard ac power to the instrumentation shelter, which was 30m from the measurement location. Like the earlier campaign [18], this shelter housed the computer, data acquisition and the laser current and temperature controllers. However, the lasers were relocated from the instrumentation shelter to near the measurement station, and the transmitter and receiver heads were completely redesigned to enable four-species sensing with lasers outside the telecommunications band.

The absorption transitions selected to optimize detection of CO, CO₂, and CH₄ are in the wavelength region 2-2.4 μm, which is beyond the useable range of telecommunications optical fiber. Thus, the lasers could not be located inside the instrumentation shelter and the light delivered to the transmitter head by fiber optics. Although a new, robust fiber is available for this wavelength region (Thorlabs SM-2000), this fiber exhibits large bend losses in the transmitted intensity at the CO wavelength of 2.326 μm. Thus, the fiber lengths were limited to short (<2 m) distances with a minimum of fiber bending. The lasers were located in an explosion-proof, nitrogen-purged NEMA container about

1 1.5 m away from the transmitter optics (see Fig. 5). The purge served two purposes: (1) isolation of the
2 electronics that may be considered an ignition hazard in case of fugitive syngas, and (2) heat transfer fluid
3 to remove heat from the laser thermoelectric temperature control. Standard diode laser current and
4 temperature controllers (ILX Lightwave LDC-3908) were located in the instrument shelter and connected
5 via 30m long shielded cables.

6 The four fiber-coupled lasers were multiplexed onto a single line-of-sight using a novel fiber
7 bundle (Neptec Optical Solutions). Three extended NIR fibers (Thorlabs SM-2000, NA=0.11) for the
8 CO, CO₂, and CH₄ lasers, and one telecommunications (Corning SMF-28+, NA=0.14) for the H₂O laser
9 were bundled into a cable. The center-to-center separation of the four fiber cores was approximately
10 125μm, and the large NA rapidly overlaps the beams as they emerge from the end of fiber bundle, as
11 illustrated in panel b) of Fig. 5. The output was nearly collimated with a 75mm focal length plano-convex
12 CaF₂ lens in the transmitter optics head and directed along the sensor LOS. The diameters of the four
13 beams were kept large to reduce the effect of beam steering. In the receiver optics head the four
14 overlapped beams were collected with a 50 mm plano-convex CaF₂ lens and focused onto the 2mm x
15 2mm active area of a TE-cooled extended InGaAs detector (Hamamatsu). All the collected data were
16 stored for subsequent analysis, although the experience gained here provides the confidence that near
17 real-time data analysis would be nearly as accurate.

18 The transmitter and receiver optics were mounted on a pitch-yaw mount, which was in turn
19 mounted on a manual x-y stage. After the initial installation and manual alignment on the cold process
20 pipe, the angular control of the transmitter/receiver optics was performed remotely with the
21 transmitter/receiver heads sealed and purged with nitrogen. Although remote angular adjustment could be
22 done at any time from the control computer in the instrumentation house, the sensor alignment remained
23 constant from optimization in the cold facility before their “leak-test cycle” until after gasifier shutdown,
24 a period of 40 days. The signal strength did vary more than two-orders-of-magnitude as a function of
25 reactor pressure and flow conditions as shown in Fig. 6. This transmission loss was also observed in the
26 first NCCC campaign [18], where the loss was only a function of reactor pressure and alignment

adjustment did not recover any of the loss. When the reactor was shut down and the pressure returned to near atmospheric, the signal loss was recovered. We speculate that the source of this loss was a combination of beam steering as the laser beam encountered the hot, rapid syngas flow and scattering from particulate (small particle fly ash) that escapes the PCD. Note the facility measurements show this particulate is ~ 1 ppm by mass. The laser beam is steered by density gradients in the turbulent core flow and at the interface between the hot core flow and the cold nitrogen purge flow. This increases the time-averaged laser beam diameter; adjustment of alignment in any particular direction did not improve the signal loss. The gain of the detector was increased as the pressure increased to avoid digital noise for the analog-to-digital conversion.

5. Results

During the 40 days of facility operation during the R13 campaign, time-resolved absorption data was collected for CO, CO₂, CH₄ and H₂O as the transport reactor transitioned through the following conditions:

1. Propane combustion to warm the internal ceramic liner of the gasifier
2. Pulsed-coal addition to the combustion in the second heating phase
3. Failed transitions from combustion to gasification
4. Successful transition to gasification
5. Pressure and temperature increase to target gasification conditions
6. Steady-state gasification
7. Reactor shut down at the end of the campaign

Laser absorption mole fraction measurements of CO, CO₂, and CH₄ were in good agreement with the facility gas chromatography (GC) analysis of sampled syngas. However, the fast time resolution of the laser absorption data revealed more dynamics in the syngas composition than could be seen with the GC analysis of the sampled gas, where a 15 minute time-constant was observed. Each of the sections below describes the results from one of these operating conditions.

5.1 Warming of the gasifier with propane combustion

After the optics setup and alignment, the transmitter and receiver optics heads were sealed and purged with nitrogen. On the reactor side of the windows, a steady nitrogen purge flow was added to the reactor product flow and was successful in avoiding all window fouling. After the gasifier was pressurized and leak checked, the facility and its ceramic lined piping were slowly heated by a propane/air flame. As soon as the burner was ignited (hour 55.5), the laser absorption sensors began to measure all four species in the combustion exhaust, as illustrated in panel a) of Fig. 7. For all of the data presented here, 100 wavelength scans of the laser absorption were averaged for each of the four time-multiplexed lasers producing a 2.4 second time resolution including the time needed for computer overhead and data recording. The exhaust contains significant CO_2 and H_2O , and transient peaks seen in panel a) occur in the measured CO and CH_4 each time the fuel flow is increased (hours 69.9, 74.7, and 75.1), and the corresponding fluctuations of the CO_2 and H_2O show that at each of these changes in fuel flow there is a short period of incomplete combustion. At hour 55.5 the gasifier and its plumbing are cold, and initially H_2O combustion product condenses on the inside of the flow path, but as wall temperature of the gasifier increases, the H_2O content of the exhaust gas increases, eventually stabilizing at the value expected for the propane combustion exhaust. GC measurements of CO_2 shown in panel a) Fig. 7 follow the trends of the laser absorption data, but the GC time resolution prevents it from capturing the transient behavior. The initial heating phase was accompanied by occasional addition of excess nitrogen into the flow resulting in flow dilution. The concentration of measured CO_2 is therefore lower than expected as recorded by the GC. We also suspect that gas-surface chemistry in the gas sampling system varied during the initial heating phase. Note the transit time of the gas sampling system also adds a 20 minute time delay to the GC data, which is shifted in all figures to allow direct comparison between GC and laser absorption.

5.2 Combustion heating with pulsed-coal

After the gasifier temperature stabilized at the target propane combustion pre-heat temperature, the fuel was transitioned from propane to pulsed-coal. These pulses provide an oscillating fuel/air equivalence

ratio in the reactor which is captured by the time-resolved absorption measurements, as shown in panel b) of Fig. 7. The ~2 minute period of these oscillations in combustion exhaust composition is too fast to be observed by the GC; however, the mean values of the GC CO₂ data agree with the laser absorption measurements to within 0.5% mole fraction (corresponding to ~ 10% difference for CO₂ at 5%). The hysteresis caused by the sampling system is primarily a result of mixing of the extracted gas in the large volume gas conditioning system (filter and drier). This mixing is not uniform in time, resulting in deviations in the extracted mixture composition for GC based measurements. At steady state, this difference is less than 3% for CO and CO₂ and less than 4% for CH₄. When the temperature in the reactor becomes hot enough to sustain coal oxidation, the propane flame is shut off, and reactor continues to heat from coal combustion.

5.3 Failed transition to gasification

A major advantage of the *in-situ* laser absorption sensing is the fast time response, which can capture transient events, as illustrated in panel c of Fig. 7. During the first (hour 92.43) and second (hour 92.74) attempts to transition from coal combustion to coal gasification by adjusting the fuel/air ratio were foiled by a malfunction in the coal feeding process, and the transition to gasification was unsuccessful. The laser sensor observes the sharp drop in CO₂ and H₂O levels and the corresponding steep rise in the CO and CH₄ mole fractions. A short time later (hour 92.58 and 92.83) the facility operators returned the facility to coal combustion. Note that the GC gas sampling did not have the time resolution to capture these events. The entire transition and failure occurred in less time than the time delay of the gas sampling. These data show that a laser absorption sensor has the potential to be a valuable guide for the operator to tune the transport coal gasifier.

5.4 Successful transition to gasification

Panel d) of Fig. 7 illustrates the laser absorption measurements of CO, CO₂, CH₄ and H₂O as the operation of the reactor was successfully transitioned to gasification at. Before hour 114.3 when gasification begins, the large fluctuations in CO₂ correlate with the pulsed feeding of coal, and although

the addition of steam in to the reactor reduces the corresponding fluctuations in H_2O , these oscillations are still observable. Note that in panel c of Fig. 7 when the coal feeder was malfunctioning and the transition to gasification was not successful, these large fluctuations were not observed. When gasification begins at hour 114.2, the CO_2 and H_2O mole fractions plotted in panel d) rapidly fall with a simultaneous increase in CO and CH_4 . This rapid increase in CO and CH_4 enables a precise determination of the GC time delay and time constant (delay equal to 20 minutes with a GC rise time of 15 minutes). The GC time delay of 20 minutes appeared to be consistent during the entire R13 measurement campaign. The transition to gasification occurred at a pressure of 8 atm and a gasifier exit temperature of 1160 K.

5.5 Temperature and pressure increase to gasification target

To reach the target gasification conditions of 15 atm and a mixing zone temperature of 1260 K (1600°F), the coal feed rate was increased, which leads to a stair-step-like rise in the CO and CH_4 mole fractions, as observed in panel a) Fig. 8. During this 100 minute period, the pressure increases from 9 to 12 atm and the gasifier exit temperature increases from 1160 K to 1200 K. The competition between the chemistry of water-gas shift and methanation in the mixing zone leads to a strong correlation between CO and CH_4 mole fractions. At about 115.5 hours, the pressure stabilizes at approximately 12 atm, but the gasifier exit temperature continued to rise with a corresponding increase in CO and CH_4 mole fraction.

5.6 Steady gasification conditions

At hour 121 of R13 the pressure had increased to 14 atm, the gasifier exit temperature to 1200 K, and the mixing zone temperature 1260 K. At this point an 840 hour (35 day) period of stable gasification was begun, and panel b) of Fig. 8 shows a 2+ hour segment of the laser absorption measurements of mole fractions of the four species at the beginning of this “steady-state” operation. First, we see rapid oscillation of the mole fractions of all the species, which is superimposed on a slower variation. These variations were periodic with a ~23 minute period and were anti-correlated with the temperature variation as might be expected on examination of the water gas shift and methanation chemistry. Later in the

operation, these slow oscillations cease and the data and the average mole fractions of all four species are remarkably constant and in excellent agreement with the GC as illustrated in panel c) of Fig. 8. The difference between the mean TDLAS and the mean GC measurements at steady state (3 hr average) was found to be about 3%, 2% and 2% for CH₄, CO₂ and CO, respectively, which are within the accuracies of the TDLAS and the GC measurements. The mole fractions of all of the species now show a pronounced oscillation with a period of approximately 13 minutes, which correlates with the oscillations in the gasifier exit temperature (also plotted). This correlation of the mole fractions with temperature show that small variations in the mixing zone conditions were not damped by diffusion after the ~5 second flow time to the laser absorption measurement station. Thus, the *in situ* measurements in the syngas flow offer the potential to track the reactor conditions, even though the measurement station was significantly downstream of the reactor exit.

5.7 Gasifier shutdown

Laser absorption and GC measurements are shown in panel d) of Fig. 8 for the last 80 hours of R13. The average laser absorption measurement of mole fraction is in excellent agreement with the GC values. The small rapid changes in gas composition observed in the laser data are not captured by the GC. Especially notable were the transients near 879 and 926 hours, which occurred due to blockage in the coal feed line, which were observed by both GC and laser absorption. Near 898 hours maintenance was performed on the GC to clear blockage in the gas sampling line, which was the only event in the entire 960 hour R13 campaign where the GC data significantly deviated from the laser absorption data, and this was due to failure of the gas sampling. A rapid transient was observed as expected when run R13 was shutdown.

6 Conclusions

Time-division-multiplexed, *in-situ* wavelength-scanned 1f-normalized WMS-2f laser absorption measurements of CO, CO₂, CH₄, and H₂O mole fractions were demonstrated for the first time in an engineering-scale transport reactor gasifier. Single-sweep laser scanning provided a 20 millisecond time resolution, although the data presented here averaged were averaged for one hundred wavelength scans of

each laser (combined with computer and data storage overhead the laser data had 2.4 second time resolution). The measurements identified for the first time dynamic changes in the syngas composition that correlate with the fluctuations of the mixing zone temperature from the batch feeding of coal into the reactor. Such rapid laser absorption measurements of species mole fraction have the potential to optimize the batch feeding system. The rapid identifications in transient changes to the syngas composition show that the laser absorption sensor has excellent potential to guide the gasifier operator from startup to gasification. Once the gasifier has reached steady state operation, the sensor has the potential to rapidly identify problems (e.g., issues in batch feed of fuel) or to identify changes in the heating value of the fuel that might require adjustment of the gasifier tuning (air and steam addition). Significant optical engineering was required for safe optical windows to enable *in situ* measurements of the high pressure and temperature syngas. The use of a fiber bundle to combine onto a single absorption LOS the light from multiple lasers whose wavelength span more than 1 μ m was especially novel.

7 Acknowledgements

The Stanford research was supported by the U.S Department of Energy NETL on grant DE-FE0001180 with Dr. Susan Maley and Mr. Charles Miller as technical monitors. The operation of the NCCC by Southern Company Services was supported by DoE. We thank Johannes Koeth and Lars Hildebrandt of NanoPlus for their help with custom laser wavelengths and Bryan Paolini of Neptec for his help designing a custom fiber bundle.

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Table 1 Operating conditions for the scanned WMS sensors

Species	Center frequency	Scan range (200 Hz)	Modulation depth (10 kHz)
CO	4300.7 cm ⁻¹	6.63 cm ⁻¹	0.717 cm ⁻¹
CO ₂	4957.1 cm ⁻¹	4.37 cm ⁻¹	0.376 cm ⁻¹
CH ₄	4367.0 cm ⁻¹	4.42 cm ⁻¹	0.907 cm ⁻¹
H ₂ O	7393.8 cm ⁻¹	6.77 cm ⁻¹	0.825 cm ⁻¹

Table 2 Typical conditions at the gasifier exhaust

Property	Value
Temperature	600 K
Pressure	15 atm
Path length (pipe diameter)	20 cm
H₂O mole fraction	0.06 - 0.12
CO mole fraction	0.08 - 0.12
CO₂ mole fraction	0.06 - 0.10
H₂ mole fraction	0.06 - 0.10
CH₄ mole fraction	0.005 - 0.010
Trace species mole fraction (H₂S, NH₃, etc)	< 0.01
N₂ mole fraction	balance
Flow rate	Up to 12,500 kg/hr
Flow velocity at measurement location	10 -15 m/s

Figure 1 Superposition of absorbance spectra in air for the target species (10% H_2O , 10% CO_2 , 10% CO and 1% CH_4) simulated using HITRAN [19] at 600 K and 15 atm.

Figure 2 Comparison of measurement and fit of the wavelength-scanned 1f-normalized WMS-2f line shape for 8% CO₂ at 8 atm and 580K during coal feed; note line shape is fit with only line width and peak absorbance as free parameters.

Figure 3 Illustration of the time division multiplexed multi-laser signal (not actual data).

Figure 4 a) Photograph of the gasifier facility at NCCC, which illustrates the scale with the laser sensor on the fifth floor of the gasifier structure (right side of the photo) and coal pulverizer (structure on left). b) Schematic of the transport gasifier illustrating the location of the laser sensor; safety considerations placed sensor electronics in a shelter 30m from the measurement port.

Figure 5 a) Schematic showing the optical window mounting, laser, and electronics locations. b) photo of the laser sensor installation with a schematic showing the use of a fiber bundle to multiplex the light from the four lasers onto a common path for collection on a single detector.

Figure 6 Variation of measured signal strength of transmitted laser intensity with gasifier operating pressure.

Figure 7 Simultaneous laser absorption (solid lines) and GC (dashed lines) measurements for four selected time segments during the gasifier heating and transition to gasification (time resolution of laser absorption 2.4 seconds and GC 15 minutes; note also the GC data is time-shifted by 20 minutes to account for transit time in the gas sampling system. a) Heating with propane burner at 5 atm; note burner ignition at 55.5 hrs and peaks in the CO and CH_4 observed at 69.9, 74.7, and 75.1 hrs when the fuel flow is increased. b) Pulsed fluctuations in CO , CO_2 and H_2O levels as the coal fuel is pulsed. c) Failed attempts to transition from coal combustion to gasification; gas conditions at sensor 9.3 atm and 600K. d) Successful transition to gasification near 114.3 hrs; note large fluctuations in the CO_2 that are captured by laser absorption (steam addition suppresses similar fluctuations in H_2O) that indicate successful pulsing of coal batch feeder. Lack of fluctuations near 92 hrs in panel c) are indicative of fuel feed problems.

Figure 8 Simultaneous laser absorption (solid lines) and GC (dashed lines) measurements for four selected time segments during the gasification (similar to Fig 7 laser absorption time resolution is 2.4 seconds and GC 15 minutes with a 20 minute shift). a) CO and CH₄ mole fraction increases with pressure and temperature as gasifier conditions are adjusted from start up toward target conditions. b) Rapid oscillations in mole fractions track the coal batch feed pulsing, and slower oscillations in CO and CH₄ illustrate the stabilization of the reactor conditions. c) Mole fraction oscillation of CH₄, CO₂, and CO observed by laser sensor follow slow changes in gasifier exit temperature (and reflect reactor changes with batch feeding of coal). GC data do not capture these oscillations although the GC value is in good agreement with the average value of the laser absorption measurement. d) Final 80 hours of run R13 (16 atm and 630 K at the laser sensor location). Note fast change in the GC reading near 898 hrs due to maintenance of gas sampling. Near 879 and 928 hrs coal feed interruption resulted in sharp changes in all the species concentrations, which illustrates the ability of the laser absorption to monitor the gasifier conditions (and potentially be a control sensor).