IN-SITU LASER SPECTROSCOPY OF CO, CH_4, AND H_2O IN A PARTICLE LADEN LABORATORY-SCALE FLUIDIZED BED COMBUSTOR

by

Maximilian LACKNER, Gerhard TOTSCHNIG, Gerhard LOEFFLER, Hermann HOFBAUER, and Franz WINTER

Original scientific paper
UDC: 662.6/.9:544.45–912
BIBLID: 0354–9836, *6* (2002), 2, 13–27

The pyrolysis, devolatilization and char combustion of bituminous coal and biomass (beechwood, firwood) were investigated in a laboratory-scale fluidized bed combustor by tunable diode laser spectroscopy.
Individual fuel particles were suspended in the freeboard of the unit. The bed temperature was 800 °C, the oxygen partial pressure 0 to 20 kPa (0-10 vol.%).
Two Fabry Perot type tunable near infrared diode lasers were deployed for quantitative in-situ species concentration measurements.
CH_4 and CO were measured simultaneously during devolatilization and char combustion in-situ 10 mm above the surface of the fuel particles as well as H_2O using laser spectroscopy.
Sand particles were passing the probing laser beam path. Besides the resonant absorption of the laser light by CO, CH_4 and H_2O, severe and strongly transient non-resonant attenuation by partial blocking of the beam and beam steering effects occurred. By wavelength tuning the two laser sources, species concentrations could be determined. The measured absorbances had to be corrected for the real temperature measured at the position of the probing laser beam. In addition, CO, CO_2 and O_2 were determined ex-situ by conventional methods.
A spatial profile inside the FBC of major species (CH_4, CO, CO_2, O, H, OH) was calculated using a chemical kinetics program for a single fuel particle in a plug flow reactor geometry. The results were compared to the experimental findings. Good agreement was found.
Tunable diode laser spectroscopy was found to be an apt method of determining quantitative species concentrations of multiple gases in a high temperature multi phase environment.

Key words: *coal, biomass, in-situ laser spectroscopy, tunable diode laser, concentration measurements, devolatilization, pyrolysis, char combustion, carbon monoxide, methane, water, modeling*

Introduction

Combustion of coal and, to a lesser extent, biomass, contributes strongly to the production of thermal and electrical power, a status which is not likely to change in the near future. Among the array of methods for advanced (coal) combustion, that is low-cost at the least environmental impact, gasification 1 and fluidized bed combustion (FBC) 2 are two leading techniques.

This paper focuses on the latter.

The fluidized bed technology has gained wide acceptance in many fields of applications, *e. g*. catalytic cracking or mineral processing.

The appropriation of a nearly isothermal environment with high heat transfer efficiency to submerged objects and the fluid-like behavior which facilitates the mixing and handling of solids can also be exploited for combustion applications. A detailed assessment of criteria for and against fluidized bed firing is given in 3 .

A fluidized bed combustor (FBC), pressurized or circulating, represents a multi-phase, hostile environment. Elevated pressures, high temperatures and soot, ash and bed material particles present in the gas flow all pose severe problems for experimental investigations. Yet it is interesting to gather process parameters either for optimizing the performance or for controlling the process online 4 . Conventional techniques often use intrusive suction probes for species concentration determinations.

In this publication, the authors deploy *in-situ* tunable diode laser spectroscopy to measure species concentrations directly in a laboratory fluidized bed combustor.

Two lasers are used to quantitatively determine the concentrations of carbon monoxide (CO), methane (CH_4) and water (H_2O) formed during pyrolysis, devolatilization and char combustion of a single fuel particle suspended in a laboratory-scale fluidized bed combustor.

Theory

Absorption spectroscopy is an established technique that is used to obtain information on species concentrations right at the spot. The major advantages of *in-situ* measurements are their supreme timeliness and the fact that sampling errors that are likely with conventional methods are avoided. Optical methods like absorption spectroscopy are intrinsically non-intrusive, which means that they do not influence the system under investigation. This is especially relevant for instable species such as radicals.

Absorption spectroscopy is based on Lambert Beer's law. Essentially, it states that the number density (concentration times path length) of an absorbing species can be related to the attenuation of a light beam sent through the sample volume. The absorbance A is defined as $A = \ln(I_0/I)$ with I_0 being the initial light intensity (before passing the sample volume) and I the transmitted (attenuated) light intensity, the ratio I/I_0 is also known as the transmittance T.

Absorption spectroscopy delivers path averaged results, which is not necessarily a disadvantage, since one is often interested in the overall performance of a combustor device.

For a fixed wavelength, Lambert Beer's law works as long as there are no interferences.

Imagine now solid particles passing the beam path as in an FBC. Part of the light attenuation comes from resonant absorption by the investigated species, however, another part of the initial light intensity is blocked or scattered by the solid particles. The two effects cannot be discerned, and if the latter is neglected, too high an absorbance and hence too high a concentration of the absorber will be assumed.

This obstacle can be overcome by using a tunable light source, for instance a tunable diode laser.

The implications of a measurement deloying a tunable light source is schematically depicted in Fig. 1.

The absorbance is not only determined at the center wavelength resulting from a transition, that is where the absorption coefficient is strongest, but also in the wings of the absorption feature. Usually, the absorbance is determined for the whole absorption feature well into the left and right adjacent areas of the absorption peak where no absorption occurs.

By doing so, resonant absorption can be discerned from non-resonant effects.

As for diode lasers, the wavelength can be tuned by changing the injection current. As the injection current is raised, the wavelength shifts to higher values, too. Since the output power also increases with injection current, the baseline will be tilted upwards. In Fig. 1(a), one can see the baseline I and the transmitted signal I_0 (the curve with the absorption ”dip” or peak) for the undisturbed case (grey lines). Undisturbed means that only the laser light hits the photodetector with its full energy.

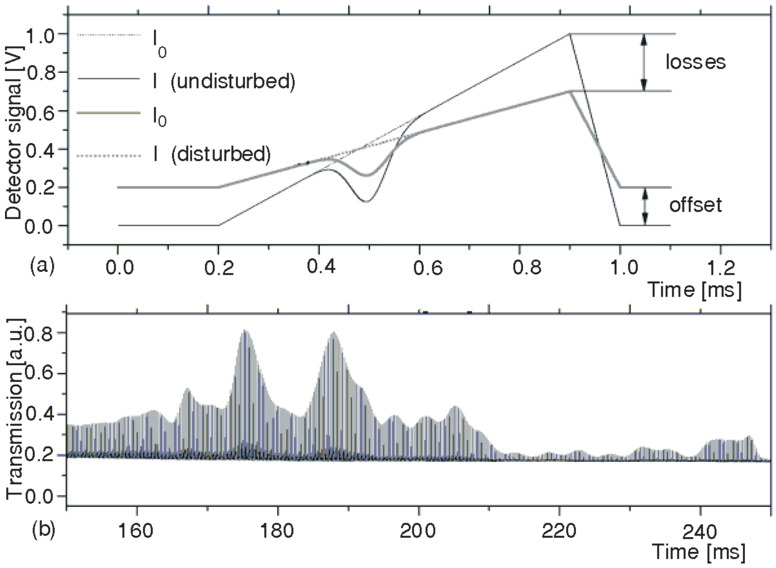

Figure 1. Theory of tunable diode laser absorption spectroscopy (TDLAS) applied to hostile (combustion) systems. (a) schematically shows how interferences can be dealt with by tuning the wavelength. (b) illustrates how the transmission of a laser beam through a flame fluctuates with time

The black lines depict the same baseline I_0 and transmitted signal I for a disturbed case.

First, as one can see, the whole signal has got an offset now. This offset might result from emissions of a flame also falling onto the detector system. Second, the height of the curves has receded. This decline in transmission might result from partial blocking of the beam (solid particles passing the beam path) or beam steering effects. Refractive index gradients caused, for instance, by flames in the sample volume will act as a lens and hence deflect the laser beam off the detector system. Since one deals with transient processes, the offset and the transmission will show a strong and uncorrelated dependence on time.

In Fig. 1(b), the transmission of the laser beam through a 100 mm long flame (stoichiometric, premixed methane/air mixture at 200 °C and 30 bar) is shown. The absorbance could be determined with as little as 3% total transmission.

Let us return to Fig. 1(a). When the absorbance A is determined as $A = \ln(I_0/I)$ for the disturbed and the undisturbed case, the same value will be obtained in this example. I_0 and I experience the same effects (non-resonant attenuation and offset by light, *e. g.* a flame), hence the effects is compensated (calculation of the ratio I_0/I). Compared to the absorption by a target species which occurs at a specific wavelength, the effects of non-resonant attenuation and offset do not show a marked dependence on the wavelength, at least not within the narrow tuning range of a diode laser.

In a first approximation, the new baseline (that is for the disturbed case) can be determined mathematically by linear transformation $y = kx + d$ (k for beam steering and beam blocking, d for the offset, with y being $I_{0,\text{ disturbed}}$ and x being $I_{0,\text{ undisturbed}}$).

When the laser wavelength is tuned over the absorption peak of the target species faster than the time scale on that the experimental noise occurs, the investigated system seemingly comes to a standstill and can be probed by this method, which is also known as tunable diode laser absorption spectroscopy (TDLAS). Details on rapid tuning to probe (combustion) systems with strongly transient behavior can be found in [5].

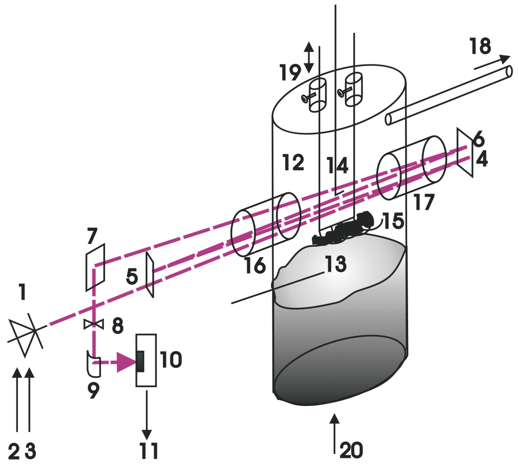

Figure 2. Experimental setup
1 – tunable diode laser (2.3 μm for CO, CH_4; 2.55 μm for H_2O), 2 – laser driver, 3 – temperature controller, 4, 5, and 7 – mirrors, 6 – 2nd reflection, 8 – slit, 9 – focusing mirror, 10 – photodetector, 11 – to amplifier and data acquisition, 12 – laboratory-scale fluidized bed combustor, 13 – thermocouple in particulate phase, 14 – thermocouple near beam path, 15 – basket suspending the fuel particles, 16 and 17 – optical access ports (wedged windows), 18 – to exhaust gas analysis (CO, CO_2, O_2), 19 – suspension of the basket, 20 – air inlet from mass flow controllers

Experimental

Laboratory-scale fluidized bed combustor (FBC)

In this study, carbon conversion of biomass and coal was investigated by *in-situ* laser spectroscopy of major species (CO, CH_4 and H_2O) in a laboratory-scale fluidized bed combustor (see [6] for details on the unit).

Figure 2 schematically shows the FBC and the experimental setup around it.

Korean bituminous coal was used alongside beech wood (a typical hard wood) and fir wood (a typical softwood representative) in the test runs (see Table 1 for analysis of the composition).

Table 1. Proximate and ultimate analysis of the fuels

	Beech wood	Fir wood	Bituminous coal
Proximate analysis			
Volatile matter [wt.%]	80.7	80.8	30.6
Moisture [wt.%]	6.8	6.8	1.6
Ash content [wt.%]	0.4	0.2	15.2
Fixed carbon [wt.%]	12.1	12.1	52.6
Ultimate analysis (water, ash free)			
Carbon [wt.%]	46.4	45.7	66.0
Hydrogen [wt.%]	6.3	6.3	4.1
Nitrogen [wt.%]	0.0	0.0	1.3
Oxygen [wt.%] by diff.	47.3	48.0	28.6

The FBC essentially consists of an upright tube made of refractory steel (68 mm inner diameter, 380 mm height) sealed by a lid on the top. The unit can be electrically heated from room temperature to approximately 1100 °C. The bed material was quartz sand (315-400 μm). The gas coming from two mass flow controllers, one for air, the other for nitrogen, entered the FBC from the bottom through a porous frit. The flow rate was 20.0 l/min. (STP), which results in a superficial velocity of 331 mm/s at 800 °C (uncertainty 0.2 mm /s). The superficial velocity is defined as the velocity of the gases in the FBC and was obtained by dividing the flow by the diameter of the reactor. The exhaust gas exists laterally 75 mm below the lid. The lid contains two rods that protrude inwards towards the bottom of the FBC. A basket made of wire to hold fuel particles is attached to the two rods. It can be adjusted in its height. The lid, the two rods and the basket are firmly attached to each other and can be taken off the FBC easily. The basket is placed in the freeboard section of the FBC in the middle of the steel tube approximately 110 mm from the top lid. Since the experiments were conducted in the freeboard, the bed height is not relevant and was thus not determined. Basically, a simple tube with a heated gas stream could also have been used to provide a homogeneous temperature environment (decoupling of temperature and combustion). At the height of this basket, the unit has got two windows. A thin NiCrNi thermocouple (type K) is attached to the basket above the position of the particle. Another, thicker NiCrNi thermocouple (type K) is placed in the particulate phase of the FBC to regulate the temperature. The time response of the upper thermocouple was determined as 2-3 s. The heat-up of the particles themselves was delayed by 19 s (at 800 °C) because of cooling effects by the metallic parts holding the particle.

The laser beam of the probing laser is sent through the two windows into the FBC 10 mm above the particle under investigation lying in the basket. The distance was measured from the surface of the fuel particles to the laser beam. Altogether, the probing laser beam passes the sample volume four times (total path length $4 \cdot 68$ mm ~ ~280 mm).

The four beams were aligned horizontally with the least lateral distance possible. The maximum beam diameter was determined to be approximately 3 mm. Since the aperture of the detector was smaller than the beam diameter and since a tight iris was used in order to prevent the photodetector from being saturated by the infrared emission of the flame and the heated FBC walls, the probed volume was smaller than it would result from the beam diameter.

The swelling behavior of the samples and the fact that the fuel regresses with time were considered to be of minor importance here so that a constant distance of the laser beam to the surface could be assumed.

The lasers are used to determine the concentrations of CO, CH_4 and H_2O above the fuel particles during pyrolysis, devolatilization and char combustion. The temperature above the particle is also recorded. CO, CO_2, and O_2 are determined *ex-situ* by conventional techniques (non-dispersive infrared analyzer and a paramagnetic method, respectively).

For each experiment, a fuel sample (1.0 g of coal, approximately 4 chucks, aligned in a row, and 0.5 g of biomass in the shape of a cylindrical stick, respectively) was placed on the basket outside the FBC and attached by a thin wire. The length of the fuel particles was approximately 55 mm. Then the basket was inserted into the FBC to start the measurement. The alignment of the fuel particle was parallel to the probing laser beam. An InSb semiconductor detector was used in conjunction with a homemade amplifier and a focusing mirror. An iris was used to reduce the emissions from the flame (leading to saturation of the detector). The detector signal was digitized on a personal computer using a 12 bit 125 MS/s data acquisition board.

A LabView™ program was written for data acquisition and processing. The absorbances for CO, CH_4 and H_2O were calculated online and converted into concentrations.

Laser measurement system

Two room temperature continuous wave InGaAsSb/AlGaAsSb quantum well ridge diode lasers were used. One of the lasers was 500 μm long and emitted at 2.55 μm

(H_2O), the other one measured 250 μm in length and emitted at 2.3 μm (CO and CH_4). The device is described in detail elsewhere (7, 8).

Diode lasers can be wavelength tuned in a narrow range by either varying their temperature (at constant current) or by varying their injection current (at constant laser heat sink temperature). Temperature tuning permits to access a broader wavelength range, but is comparatively slow. Current tuning, on the other hand, is fast, but tuning cannot be achieved very far. Therefore, the center wavelength of the laser is usually matched to the position of a suitable absorption line belonging to the absorbing species by choosing an appropriate temperature of the laser, and wavelength tuning is achieved by current tuning.

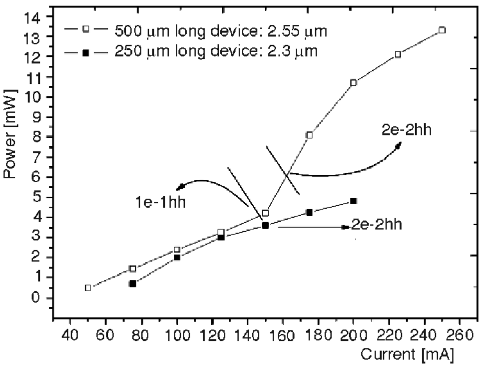

Figure 3. Output power of the diode laser emitting at 2.3-2.35 μm to measure CO and CH_4 and 2.55 μm for H_2O as a function of injection current. The wavelength increases with increasing injection current

This laser was operated at 16.0 °C. The current was tuned from 0-160 mA by a linearly increasing current ramp at 300 Hz. As the current was linearly ramped, the laser wavelength shifted, in an approximation, linearly too.

Figure 3 shows the characteristic curve of the laser. The output power has been plotted as a function of injection current. The first laser in this study is 250 μm long and emits at 2.3-2.35 μm. The second laser is longer (500 μm) and starts lasing at 2.55 μm and switches to 2.3 μm at higher injection currents.

1e-1hh is the notation for the recombination first electron to heavy hole transition in the quantum well, 2e-2hh is the notation for another quantum state transition.

Within the tuning range of the 2.3 μm diode laser, several absorption lines of CO and CH_4 could be observed. Therefore, it was possible to monitor two species simultaneously by using only one diode laser.

In Fig. 4 the two peaks that were chosen for CO and CH4 are shown.

Figure 5 shows the peak for the determination of H_2O using the 2.55 μm diode laser. One can see the transition of 1e-1hh lasing action to 2e-2hh at about 140 mA (compare Fig. 3). In fact, a double

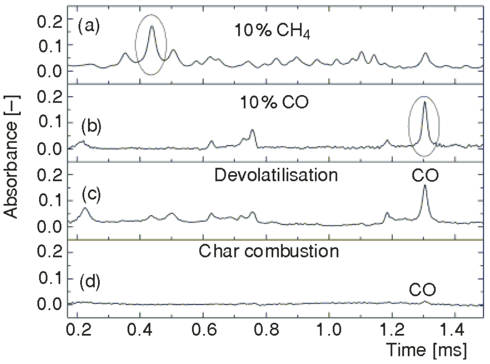

Figure 4. Absorption peaks of CO and CH_4 that were chosen for quantitative species concentration measurements. The laser wavelength was scanned around 2.3 to 2.35 μm

peak was used – Fig. 5(a). The spectrum was recorded with 2.3% water vapor (background air humid- ity of 75% at 26.1 °C) over a path length of 440 mm at 300 °C. The laser was ramped from 0 to 170 mA. The insert (b) shows a fit (Voigt line shape function) for the two peaks. (c) gives the residual.

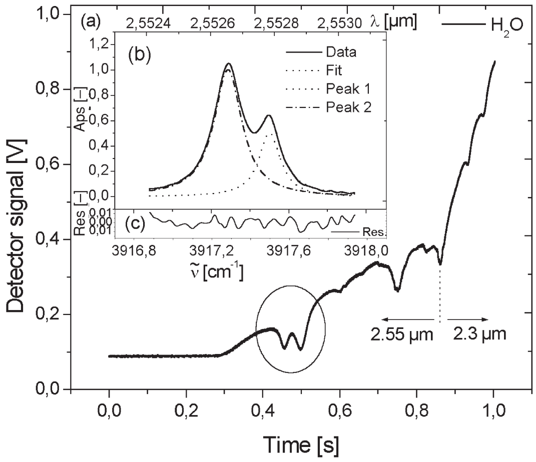

Figure 5. (a) shows the double peak of H_2O that was used in the test runs for quantitative evaluation. One can see where the laser switches. The insert (b) shows a fit (Lorentz) of the peak with the residual being given in (c)

For the selection of a suitable absorption peaks the following aspects have to be considered:

No mode hops of the diode laser at the wavelength of the transition,

Suitable strength of the absorption line,

No interference by other species, and

- Suitable and known temperature dependence of the absorption peak.

These requirements have to be matched with the availability of diode lasers.

It is therefore not possible to always use two or three standard wavelengths for each species. The monitored transition depends on the problem and has to be chosen properly. Only one laser was used at a time. By combing the two laser beams, the simultaneous detection of all three species would have been possible. For sake of simplicity, however, this was not done within the scope of these measurements.

The absorbance A is proportional to the number density of the target molecule: $A(\lambda) = k(\lambda) \cdot l \cdot c$ with λ being the wavelength, $k(\lambda)$ the absorption coefficient, l the path length and c the concentration of the absorber.

The absorption coefficient is not a constant, but depends strongly on the temperature. This dependence was determined experimentally for CO and CH_4 by measuring the absorbance at a fixed concentration (10%) of the gas inside the FBC at different temperatures ranging from 25 to 1100 °C. For the calibration of the H_2O signal with temperature, a heated quartz cell was sued.

The laser beam was sent through the FBC 10 mm above the coal. During devolatilization and char combustion, the temperature of the air along the beam path above the coal will not equal the bed temperature. It was found to exceed the ambient bed temperature by up to 200 °C. Therefore, the temperature at the position of the laser beam had to be determined and the measured absorbances corrected for the temperature.

The two opposing windows through which the laser beam passed the FBC were made of wedged fused silica. Wedged windows were preferred to plane parallel ones because they prevent the unwanted appearance of fringes due to optical interferences. These fringes, known as the etalon effect, are caused by multiple inadvertent reflections between parallel surfaces. They disturb sensitive absorption spectroscopic measurements 9 . In the exhaust duct, approximately 300 mm from the exit of the FBC, gas samples were continuously taken and analysed online for carbon monoxide (CO), carbon dioxide (CO_2) and oxygen (O_2). These *ex-situ* determinations were carried out in addition to the *in-situ* measurements of H_2O, CO and methane (CH_4) by the laser. A paramagnetic method was used for O_2 (range 0-20 vol.%, absolute accuracy 0.1%), CO (range 0-6000 ppm, absolute accuracy 5 ppm), and CO_2 (range 0-20 vol.%, absolute accuracy 0.1%), were determined by a non-dispersive infrared technique. The delay introduced by the 7.5 m long plastic tube was 12 s. This delay was considered by shifting and superimposing the timescales of the *in-situ* and *ex-situ* measurements correspondingly.

Results and discussion

Measurements inside the fluidized bed combustor were repeated at least three times to check for the reproducibility of the results. The temperature profile over the fluidized bed combustor was studied prior to the experiments and found to be homogeneous. Tunable diode laser absorption spectroscopy is based on line-of-sight absorption of targeted rovibrational transitions. The measurements present an average of the concentration profile over the entire pathway. This fact does not constitute a problem here, though, since homogeneous conditions along the laser beam path were ensured. The row of coal particles (four to five pieces) was approximately 55 mm long and 10 mm wide. The sticks of beech wood (3 mm diameter) and fir wood (cross section 3 times 5 mm^2) were also 55 mm long. With an inner diameter of the fluidized bed combustor of 68 mm and the zone of volatile release being approximately 10 times 55 mm in cross section, the dilution of the species can be estimated to be 1:7.

In Fig. 6(a), the temperature above the coal particles at the height of the traversing laser beam (*i. e.* 10 mm above the coal) is shown.

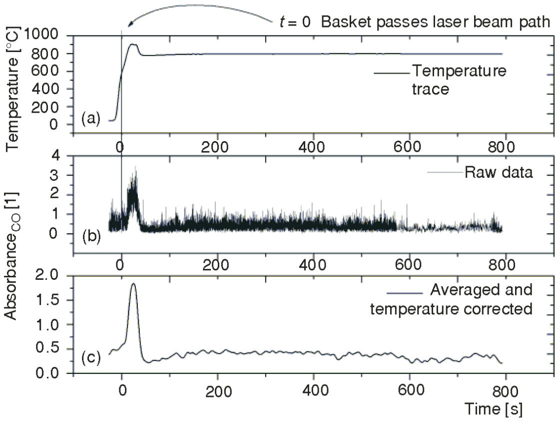

Figure 6. Determination of the concentration from the raw absorbance data, depicted for CO. (a) shows the temperature 10 mm above the burning particle at the position of the laser beam. (b) gives the raw data in terms of the absorbance. In (c) the concentration of CO is shown

The relatively slow rise of the temperature curve is due to cooling by the basket and the two supporting metallic rods. One can see that the flame temperature exceeds the bed temperature by approximately 100 °C.

Figure 6 shows the data processing of a test run. In Fig. 6(a), the temperature above the particle is shown. In Fig. 6(b), the measured absorbance of CO has been plotted as a function of time.

The insertion process (which itself takes 1-2 s) provides a comfortable means of determining the start of the experiment. As the basket with the fuel sample traverses the laser beam path shortly before reaching its final position, the absorbance goes up sharply (no transmission). Note the sharp ”peak” at $t = 0$. One can see that the absorbance is very noisy.

Besides the resonant absorption of laser light at the wavelengths of the molecular transitions, the transmission through the FBC fluctuates strongly over time. The hot interior of the FBC produces blackbody radiation. According to Planck’s law, the peak intensity location at 800 °C is at 2.70 μm with the total intensity being approximately 24 kW/m^2. The response curve of the detector ranges from 1 to 10 μm. The fraction of radiation contained in this domain is approximately 0.93. The fraction of radiation in the visible wavelength range (0.4 to 0.7 μm) is less 10^{-5}. So a constant offset by the background radiation will be observed.

In addition, the emissions from the flame in the infrared region also fall onto the detector.

These preceding two effects increase the light intensity.

Several effects also reduce the transmission. Beam steering is the effect that (temperature gradients that translate into) refractive index gradients act as a lens for the probing laser beam and make it change its position. As a result, the laser light intensity hitting the detector will fluctuate. Also, solid particles passing the beam path will partly obstruct the laser and reduce the transmission. Sand particles that reach the freeboard region of the FBC where the experiments were conducted hence also cause fluctuations of the transmission.

It was observed that during combustion, especially under reduced oxygen partial pressures, that soot caused blocking of the windows. This layer of soot brought the transmission several times close to zero. The minimum in transmission coincides with the maximum devolatilization rate. Subsequently, the slow burning of the soot in the hot gas stream reconstituted the full transmission of the windows.

All these effects are non-correlated and cause the laser light intensity falling onto the detector to vary vigorously.

As pointed out in the section on the theoretical background, the laser has to tune over an entire absorption feature faster than the timescale on which experimental noise (flickering of the flame, sand particles passing the beam) occurs.

The reason why this approach works is that all major non-resonant effects described here do not show a strong dependence on the wavelength, but the absorption peaks do.

At scan rates of 300 Hz as set in these experiments, this requirement is simply not fulfilled. Therefore, as the beam gets deflected from the detector or partially blocked, an absorption value that is too high is obtained. However, by averaging the raw data – Fig. 6(b), one gets a smooth curve – Fig. 6(c). In order to directly obtain quantitative results without the need for averaging, it is necessary to tune over the selected absorption feature(s) faster than the time scale of the fluctuations. In Fig. 2(b), the shortest spikes in the transmission are on the order of 1 ms.

They stem from beam steering effects and solid particles passing the beam path. By scanning the laser wavelength over the absorption line with repetition rates faster than 1000 Hz, the system seemingly comes to a standstill. All non-resonant effects only manifest themselves by a constant attenuation of the laser light plus an offset. Both can easily be subtracted as shown above. A special type of tunable diode lasers, so-called vertical-cavity surface emitting lasers (VCSELs), possesses the ability of extremely fast wavelength modulation. Modulation frequencies of up to 5 MHz and the application of these lasers to spectroscopy have been demonstrated 5 . Therefore, these devices are apt for probing extremely transient environments, for instance particle laden gas flows as encountered in this publication.

The concentration history of CO measured *in-situ* closely above the coal as depicted in Fig. 6(c) has also been temperature corrected to display correct values.

Before devolatilization ended, flame extinction was observed. The lower detection limit at 800 °C was determined to be 0.2 vol.% (approximately 500 ppm·m) for CO and CH_4. It could have been improved by using a sensitive detection technique instead of simple absorption spectroscopy, the most common ones being wavelength modulation spectroscopy (WMS) and frequency modulation spectroscopy (FMS) 10 . At lower temperatures approaching room temperature, the detection limit improves due to the fact that the intensity of the selected absorption lines rises.

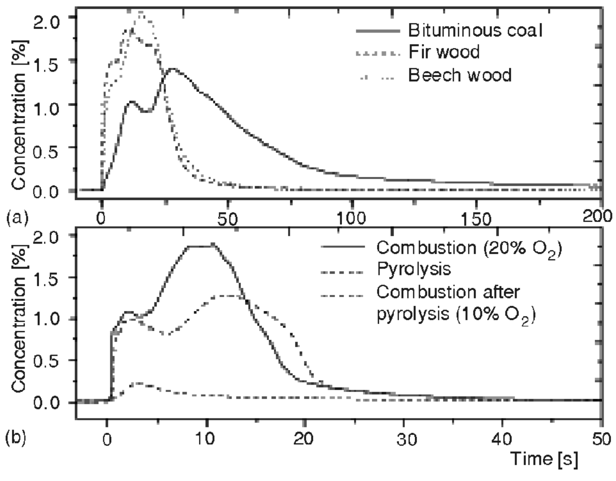

Figure 7. Experimental data of a typical test run with the 2.55 μm H_2O laser (bed temperature 800 °C, oxygen partial pressure 10 kPa (10 vol.%), distance 10 mm. (a) shows the H_2O concentration histories of the different fuels. The double peak might stem from drying and subsequent water generation. (b) shows a fuel sample that was burned at once (solid curve) and pyrolized and subsequently burned in oxygen (lowest curve, no double peak)

Experimental findings

In Fig. 7(a) the concentration history of water vapor 10 mm above the fuel particles (measured at 2.55 μm) is shown for all three fuels. In Fig. 7(b) tests with beech wood (a 55 mm long cylindrical particle, 3 mm diameter, mass 0.25 g) was used. The gas flow was 20.0 l/min at room temperature or 72.5 l/min at 800 °C inside the reactor. For the combustion test, pure air was used, the oxygen partial pressure being 20 kPa. For the pyrolyis test, an identical sample was exposed to a pure nitrogen gas flow. After 90 s, the gas flow was changed to 10% oxygen (also 20 l/min). This subsequent combustion is shown by the third curve. There is no double peak observable. It can therefore be assumed that the first peak in the combustion test stems from drying, whereas the second results from chemical reaction forming water. In 11 the effect of drying, devola- tilization and char combustion was investigated by intra-particle temperatures.

The lower detection limit at 800 °C was 0.02% for a path length of 0.28 m. This corresponds to 50 ppm·m. Since the absorbance of the selected peak also decreases from room temperature to 800 °C, the detection limit at ambient conditions would also be higher.

Figure 8 shows concentration histories of CO (measured with the 2.3 μm diode laser) for all fuels 10 mm above the particles. The bed temperature was 800 °C, the oxygen partial pressure 10 kPa, the gas flow 20.0 l/min. at room temperature. In contrast to the water vapor histories shown in Fig. 7(a), it is now easily possible to discern devolatilization (the first, steep peak) from the subsequent char combustion phase. Since char combustion lasts much longer for the coal (750 s in contrast to less than 150 s for the biomass fuels), an insert is shown for coal.

Turbulence was not considered in the evaluation of the experimental data, though the experiments were carried out in the wake region of the particles in the gas flow. Mixing effects lead to dilution and concentration peak broadening, but these facts were considered to be of minor importance here.

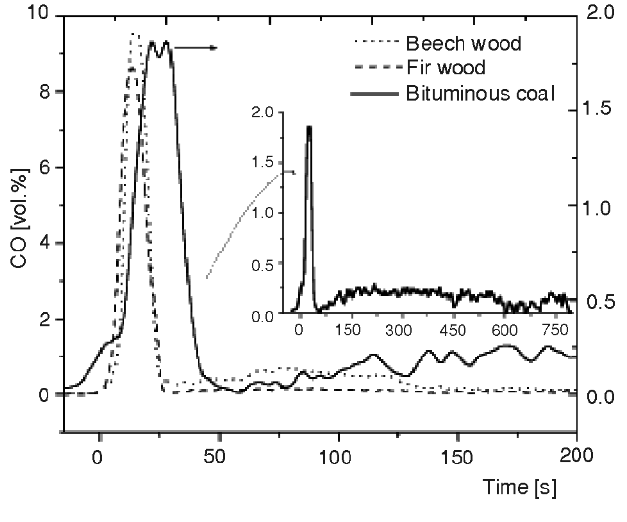

Figure 8. Experimental data of a typical test run with the 2.3 μm CH$_4$ and CO laser (bed temperature 800 °C, oxygen partial pressure 10 kPa (10 vol.%), distance 10 mm

Comparison of the laser measurements with calculations

In Fig. 9, the experimental results are compared with calculated values.

For the calculations a modified version of a model for a single fuel particle burning in a laboratory-scale fluidised bed 12 is used. Due to the easy implementation the model of van den Bleek *et al.* 13 was modified. In this work only the reactions ongoing in the freeboard downstream the fuel particle are considered.

The freeboard is considered to be a plug flow reactor. The temperature profile within the freeboard is taken from measurements and given as input to the calculations.

During devolatilization and char combustion respectively the measured release rates of carbon were applied for the model. All species were assumed to be released proportional to the carbon.

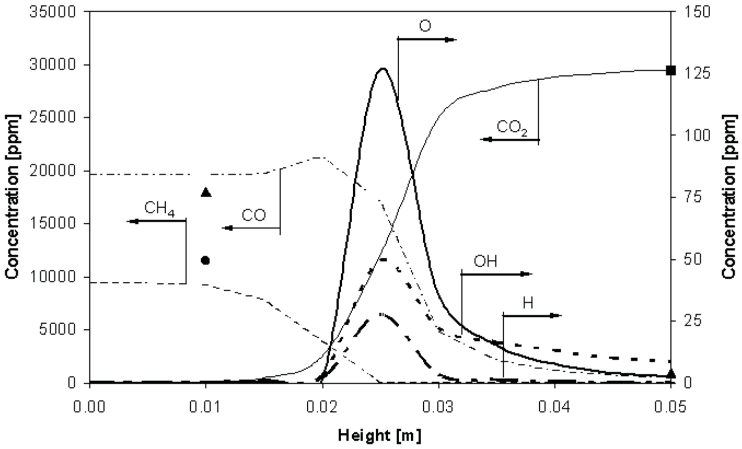

Figure 9. Comparison of experimental data on CO and CH_4 with modeling. The calculation of the spatial species distribution was performed for $t = 10$ s after the insertion of the particle. Experimental parameters: bed temperature 800 °C, oxygen partial pressure 10 kPa (10 vol.%), distance 10 mm

During char combustion it was assumed that the primary products are CO and H_2O. Assuming an H/C ratio of 1 in the char, H_2O was released proportional to the carbon. This ratio was varied within a reasonable range of 0.5 to 2 without any significant effect on the predicted emissions.

A limitation of the model is that it only works one-dimensionally. Gas flow that passes the fuel particles at the borders cannot be considered. Due to the chosen dimensions, however, this can be neglected here.

Details on the modelling are given elsewhere 14 .

A concentration profile has been calculated for all major species, that is CO, CH_4, O, CO_2, H, and OH. For data points, two for the CO, one for CH_4, and one for CO_2, are shown. Figure 9 depicts the situation 10.0 s after the start of the experiment.

The experimental parameters were the following: 10 kPa oxygen, 800 °C bed temperature, 1.0 g bituminous coal. The distance of the laser beam to the particles was 10 mm.

The datapoints at 10 mm height for CO and CH_4 were determined *in-situ* by the laser spectroscopic technique. Those at 50 mm height were taken from the *ex-situ* analysis of CO and CO_2. Good agreement between measured and calculated results was observed.

Conclusion

In this work, carbon conversion (pyrolysis, devolatilization and char combustion) of Korean bituminous coal and two biomass fuels (beech wood, fir wood) was investigated experimentally by tunable diode laser absorption spectroscopy in the 2.3 to 2.55 μm wavelength range.

Sand particles were passing the probing laser beam path. Besides the resonant absorption of the laser light by CO, CH_4, and H_2O, severe and strongly transient non-resonant attenuation by partial blocking of the beam and beam steering effects occurred. By wavelength tuning the two laser sources, species concentrations could be determined. The measured absorbances had to be corrected for the real temperature measured at the position of the probing laser beam.The lower detection limit at 800 °C was determined to be 0.2 vol.% (500 ppm·m) for CO and CH_4. For H_2O, it was determined as (50 ppm·m).

A spatial profile inside the FBC of major species (CH_4, CO, CO_2, O, H, OH) was calculated and compared to the experimental findings. Good agreement was found.

Tunable diode laser spectroscopy was found to be an apt method of determining quantitative species concentrations of multiple gases in a high temperature multi phase environment.

References

[1] Huang, J., Watkinson, A. P., Coal Gasification in a Stirred Bed Reactor, *Fuel and Energy Abstracts*, *38* (1997), 3, p. 152

[2] Chen, H., Experimental Research on Combustion Characteristics of Pulverized-Coal Fluidized Bed, *Fuel and Energy Abstracts*, 3 (1997), 6, p. 422

[3] Jacobs, J. P., The Future of Fluidized-Bed Combustion, *Chemical Engineering Science*, *54* (1999), pp. 5559-5563

[4] Furlong, E. R., Mihalcea, R. M., Webber, M. E., Baer, D. S., Hanson, R. K., Diode Laser Sensor System for Closed-Loop Control of a 50 kW Incinerator, 33rd Joint Propulsion Conference, Seattle, USA, July 7-9, 1997, paper AIAA-97-2833

[5] Totschnig, G., Development of Diode Laser Systems for *in-situ* Combustion Diagnostics and Trace-Gas Sensing, Ph. D. thesis, Vienna University of Technology, Vienna, Austria, 2002

[6] Lackner, M., Totschnig, G., Winter, F., Maiorov, M. A., Garbuzov, D. Z., Connolly, J. C., *In situ* Laser Measurements of CO and CH_4 Close to the Surface of a Burning Single Fuel Particle, *Meas. Sci. Technol*. 13 (2002), pp. 1545-1551

[7] Garbuzov, D., Menna, R., Maiorov, M., Lee, H., Khalfin, V., DiMarco, L., Capewell, D., Martinelli, R., Gelenky, G., Connolly; J., 2.3-2.7 μm Room Temperature CW-Operation of InGaAsSb/AlGaAsSb Broad-Contact and Single-Mode Ridge-Waveguide SCH-QW Diode Lasers, *Proceedings of SPIE* (Society of Photo-Optical Instrumentation Engineers), 1999, Vol. 3628, pp. 124-129

[8] Donetsky, D. V., Westerfeld, D., Belenky, G. L., Martinelli, R. U., Garbuzov, D. Z., Connolly, J. C., Extraordinarily Wide Optical Gain Spectrum in 2.2-2.5 μm In(Al)GaAsSb/GaSb Quantum-Well Ridge-Waveguide Lasers, *Journal of Applied Physics*, *90* (2001), 8, pp. 4281-4283

[9] Wang, J., Maiorov, M., Jeffries, J. B., Garbuzov, D. Z., Connolly, J. C., Hanson, R. K., Remote Sensing of CO in Vehicle Exhausts Using 2.3 μm Diode Lasers, *Measurement Science and Technology*, *11* (2000), pp. 1576-1584

[10] Pavone, F. S., Inguscio, M., Simultaneous Detection of CO and CO_2 Using a Semiconductor DFB Diode Laser at 1578 μm, *Appl. Phys. B*, *56* (1993), pp.118–122

[11] Winter, F., Prah, M. E., Hofbauer, H., Intra-Particle Temperatures under Fluidized Bed Combustor Conditions: the Effect of Drying, Devolatilization and Char Combustion, *Combust. Flame*, *108* (1997), pp. 302-314

[12] Löffler, G., Wartha, C., Winter, F., Hofbauer, H., NO_x and N_2O Formation Mechanisms – A Detailed Chemical Kinetic Modeling Study on a Single Fuel Particle in a Laboratory-Scale Fluidized Bed, *J. Energy Res. Techn*., *23* (2001), 3, pp. 228-235

[13] van den Bleek, C. M., Brem, G., Grubor, B., Johnsson, J. E., Jones, R. F., Langer, V., Verweyen, N., Documentation of the IEA-AFBC Model, Version 1.1, (Ed. G. Brem), TNO Apelddorn, The Netherlands, 1990

[14] Lackner, M., Loeffler, G., Totschnig, G., Winter, F., Hofbauer, H., Carbon Conversion of Solid Fuels in the Freeboard of a Laboratory-Scale Fluidized Bed Combustor (FBC) – Application of in-situ Laser Spectroscopy, for submission in *Fuel*, 2002

Authors' address:

M. Lackner, G. Totschnig, G. Loeffler,
H. Hofbauer, F. Winter
Institute of Chemical Engineering
Vienna University of Technology
Getreidemarkt 9/166
A-1060 Wien, Austria

Corresponding author (M. Lackner):
Phone: +43-1-58801-159-48
Fax: +43-1-58801-159-99
E-mail: lackner@mail.zserv.tuwien.ac.at

Paper submited: September 15, 2002
Paper revised: November 11, 2002
Paper accepted: November 15, 2002