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(54) **METHOD FOR CONTINUOUSLY MONITORING CHEMICAL SPECIES AND TEMPERATURE IN HOT PROCESS GASES**

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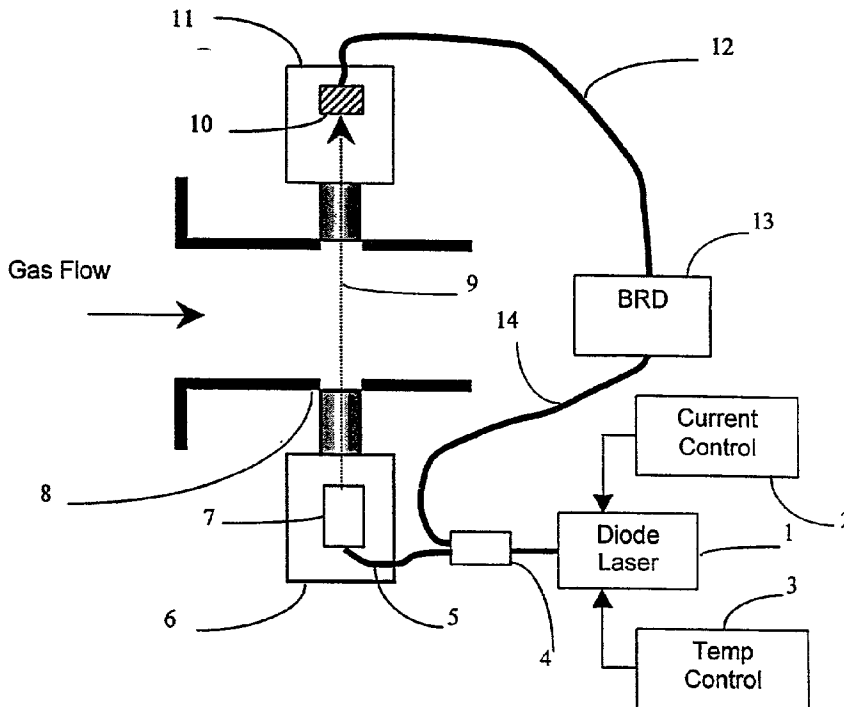
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(57) **ABSTRACT**

Methods and apparatus are presented using tunable diode lasers for monitoring and/or controlling a high temperature process using an oxidizer containing O₂ and organic fuel. Real-time monitoring of key species such as O², CO, and H₂O allow determination of the global or local stoichiometry, gas temperature, particulate concentration, and air entrainment levels into the process. Coupling the measured information with a control system provides a means for optimizing and controlling the process.



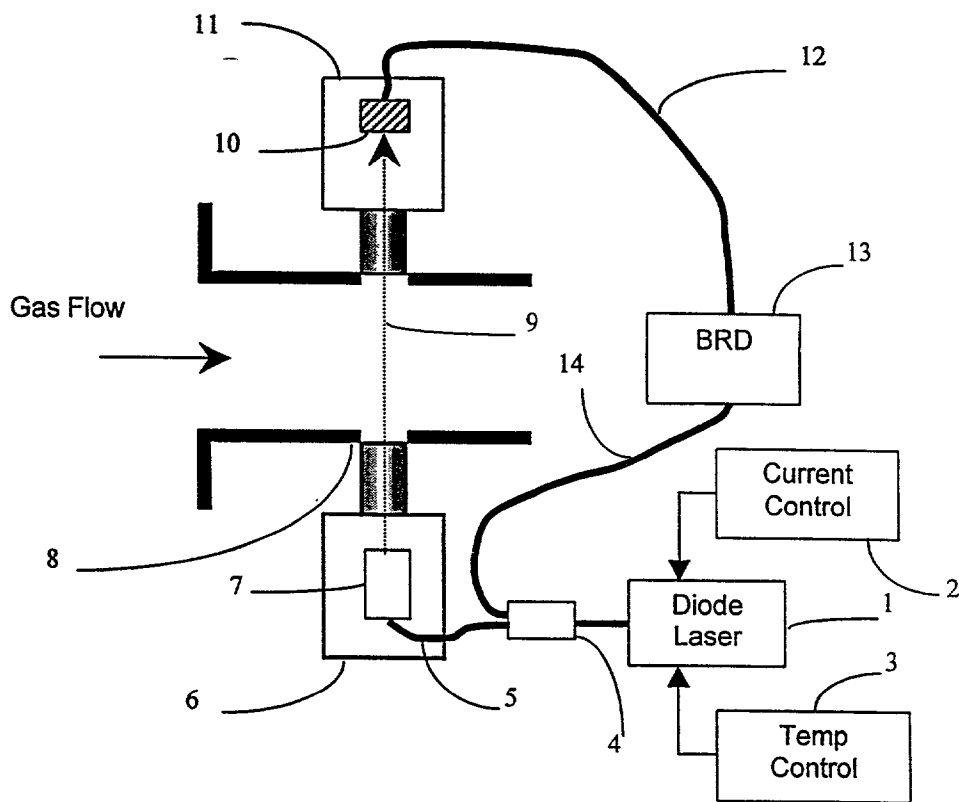


FIG. 1

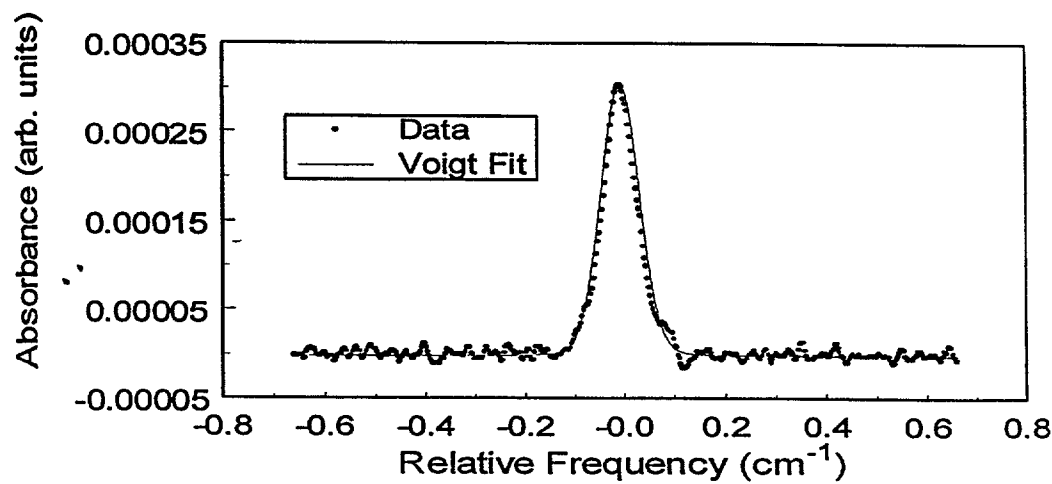


FIG. 2

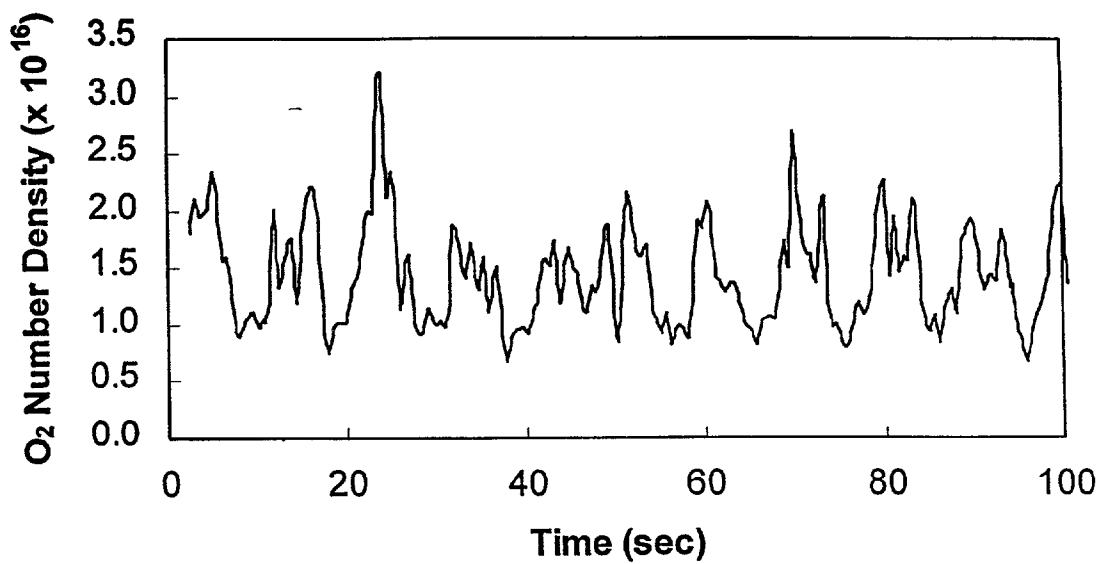


FIG. 3

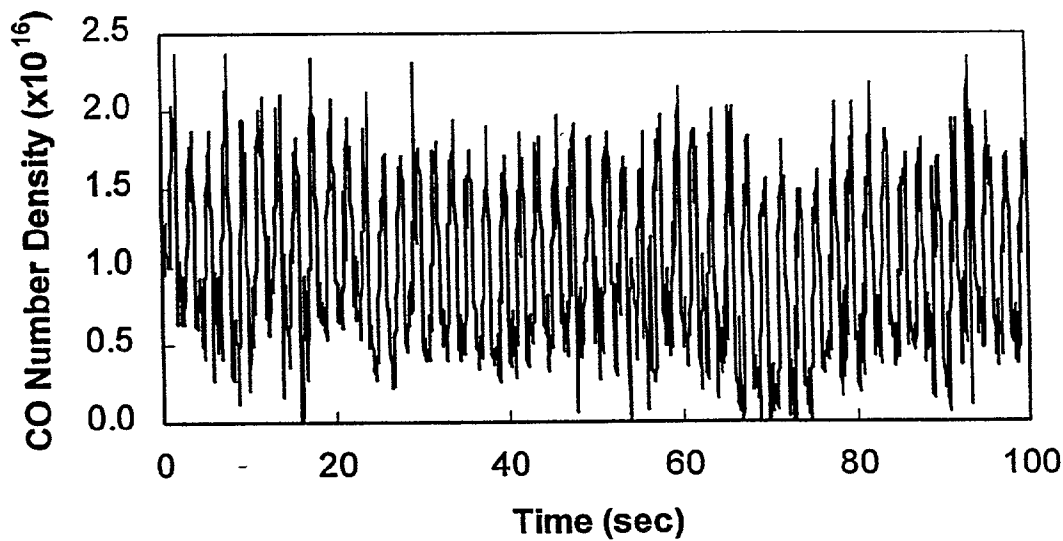


FIG. 4

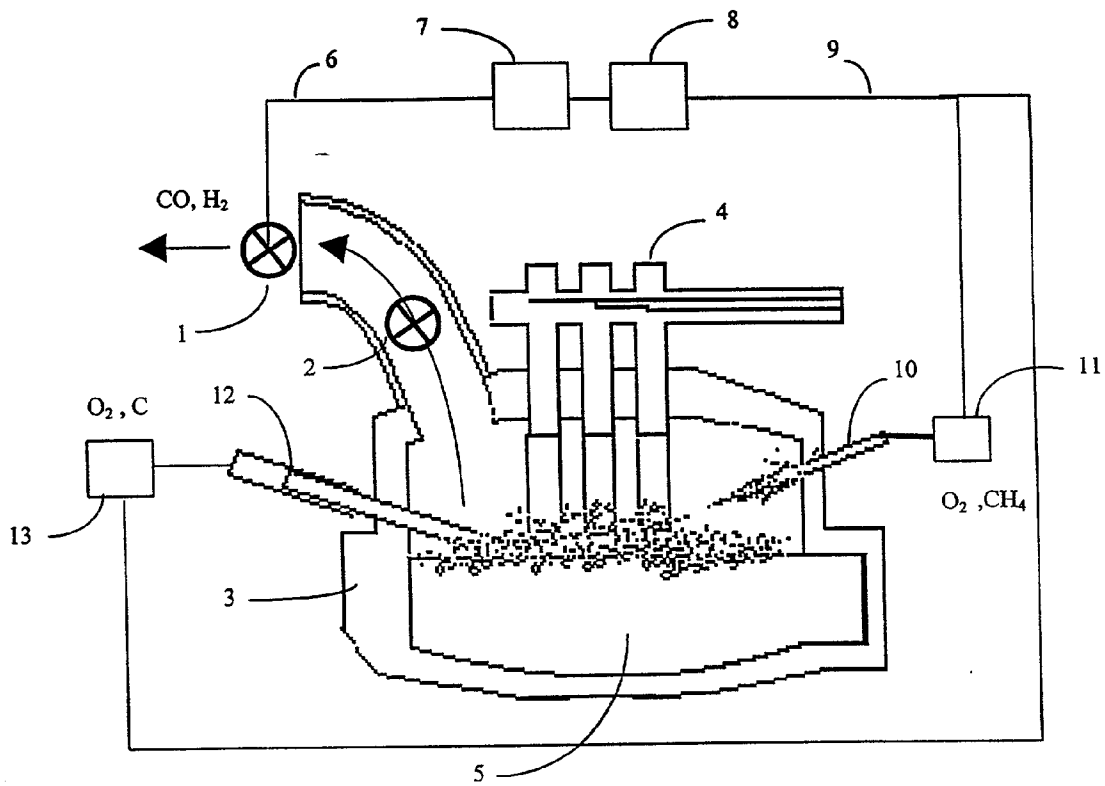


FIG. 5

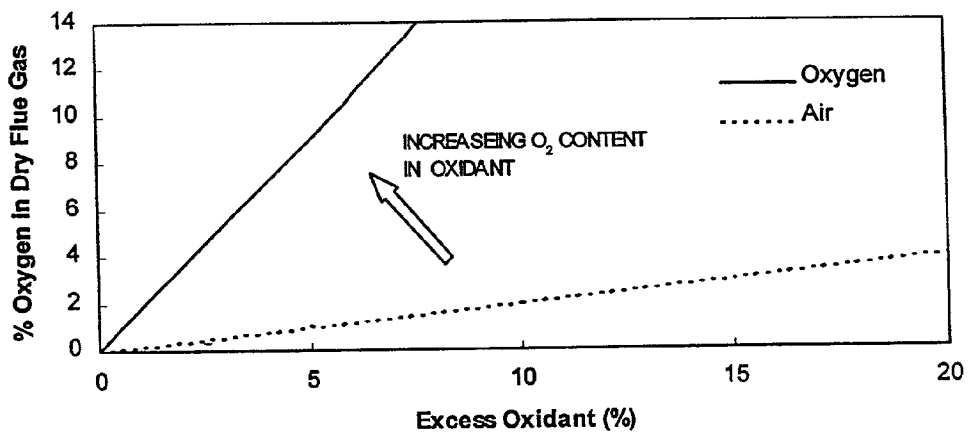


FIG. 6

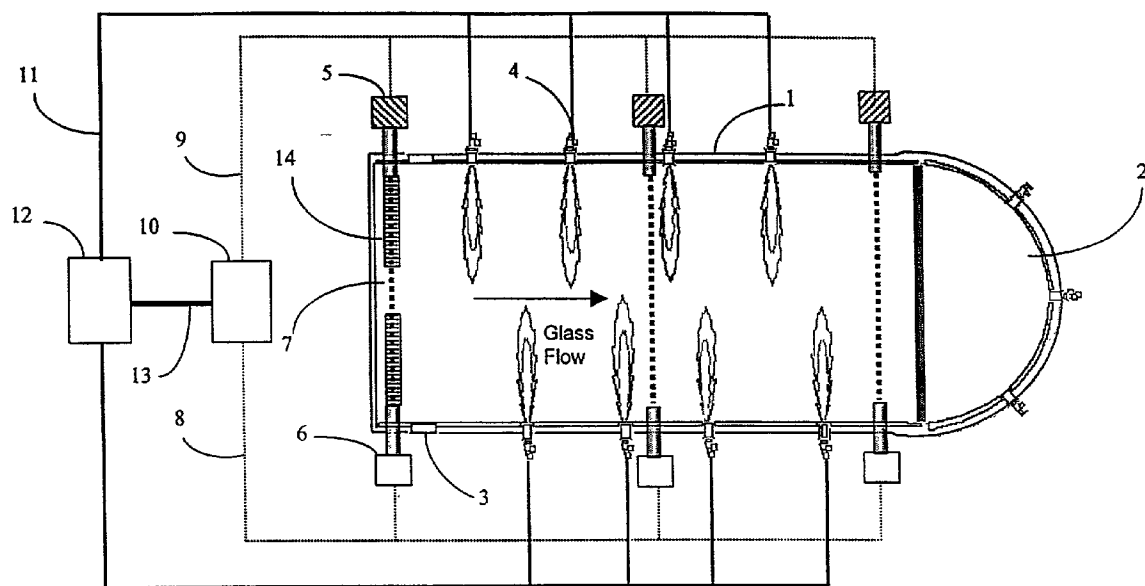


FIG. 7

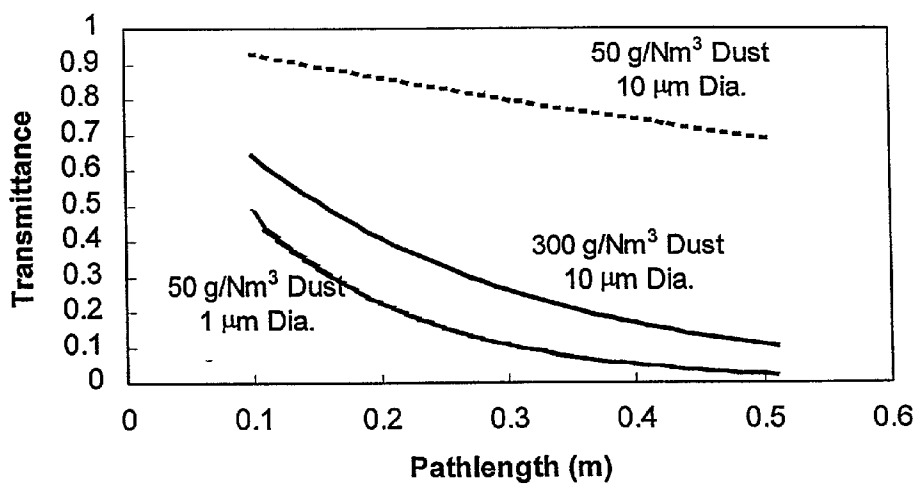


FIG. 8

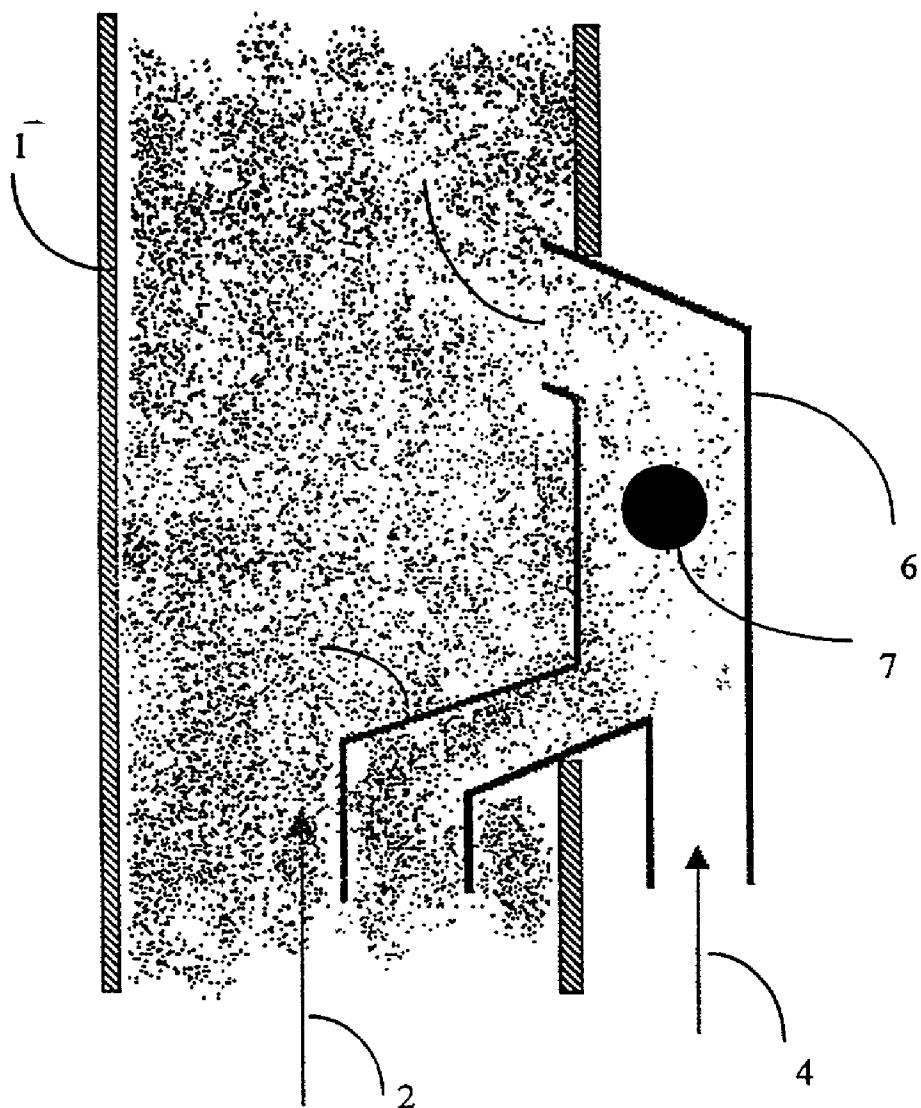


FIG. 9

METHOD FOR CONTINUOUSLY MONITORING CHEMICAL SPECIES AND TEMPERATURE IN HOT PROCESS GASES

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to the field of combustion. In particular, the invention relates to continuously monitoring the concentration of reactants, intermediates, or products from or in high temperature combustion processes. In addition, measurements on the process gas temperature, particulate concentration level and air entrainment rates can be obtained.

[0003] 2. Related Art

[0004] Numerous instrumentation choices are available for gas composition monitoring on industrial combustion processes operating at high temperatures ($T > 500^\circ \text{C}$). In particular, diagnostic instrumentation is useful for analysis of key combustion species such as O_2 , CO_2 , CO , NO_x , etc. and using the measurement information for optimizing and controlling the process to improve energy efficiency, product quality, and minimize pollutants. However, high temperature and high particulate densities typically found in industrial processes limits the available monitoring methods to extractive sampling techniques. In special cases as will be discussed, in-situ techniques are available for limited operating conditions and a specific set of chemical species.

[0005] Conventional extractive sampling methods for gas composition analysis is performed using a temperature resistant probe, e.g., water-cooled, a water removal system, a particle filter, and a suction pump to withdraw the sample from the process. These components are assembled before the analyzers to ensure the sample is cooled and free of water and particulate matter. Since many industrial environments are not suitable for sensitive instrumentation, sampling lines from the process to the analyzer can be 10's to 100's of feet in length. The use of long sample lines introduce a delay that can be 10's to 100's of seconds before reaching the analyzer. The choice of analysis instrumentation is dependent on the chemical species of interest. For example, to monitor the O_2 concentration in the process or stack a paramagnetic resonance technique or electrochemical cell is often used. To monitor CO , CO_2 or NO nondispersive infrared detectors can be used. All of these commercially available analyzers also exhibit a characteristic response time that will add to the measurement delay.

[0006] Other instruments that can be used with extractive sampling systems are gas chromatographs (GC), mass spectrometers (MS) or the combination GC/MS. GC instruments have an advantage of monitoring an array of chemical species such as, O_2 , N_2 , CO_2 , CO , and H_2 that are important in combustion processes. However, these instruments sample the gas in a batch mode with a slow response time ranging from approximately 30 seconds to several minutes depending on the GC operating conditions. Discrete sampling and slow instrument response time hinders the ability to use the acquired information in a process control loop, particularly for processes with dynamic behavior. Continuous gas sampling with an MS instrument can be conducted with a fast response time $< 1\text{-sec}$. However, the resulting mass spectra obtained are difficult to interpret due to over-

lapping fragments of ionized molecules having the same atomic mass. In addition, MS instruments need to operate under vacuum conditions. Variations in the sampling flow rate, e.g., due to plugging or pressure fluctuations in the process itself, will change the response of the detector resulting in a measurement error.

[0007] In-situ zirconium oxide (ZrO_2) probes developed in the late 1960s by NASA have been used on many industrial applications for O_2 monitoring. The sensor uses a sealed ZrO_2 tube which when heated becomes an electrolytic conductor because of the mobility of O_2 ions which requires a minimum operating temperature of $\sim 600^\circ \text{C}$. for permeation of the ions. The sensor can operate at moderate to very high temperatures $> 1600^\circ \text{C}$. with response times reported to be approximately seconds. These devices work well in relatively clean environments where low levels (few percent) of excess O_2 are present such as steel slab reheating furnaces. However, in high particulate processes or in reducing environments plugging of the probe surface results in measurement degradation. In addition, on processes that can have large thermal cycles as experienced in batch processes thermal shock of the ceramic probe can occur resulting in permanent damage.

[0008] To overcome the delay time issues associated with extractive sampling techniques and limited versatility of ZrO_2 probes optical measurement techniques, viz., absorption, provide a means for conducting in-situ measurements on combustion processes. Since optical measurements are non-intrusive, measurements can be conducted on the harshest of environments containing high particle density atmospheres that can be either reducing or oxidizing. Temperature limits are not a concern since the measurements are optical and conducted in-situ. Additionally, optical measurements in corrosive atmospheres that are acidic or basic are handled without the difficulties typically experienced with extractive sampling.

[0009] For monitoring and control of a combustion processes the products, reactants, or intermediates can be detected. In the case of hydrocarbon based fuels, the major products of complete combustion consist of N_2 (introduced with the fuel or oxidizer), CO_2 , and H_2O . Operating under O_2 lean conditions CO and H_2 will also be present and for O_2 rich conditions, excess O_2 is observed in the process exhaust. Therefore, monitoring CO and O_2 are key species in defining the local or global process stoichiometry.

[0010] Optical measurement techniques provide a means for conducting in-situ measurements on harsh process environments that avoid issues such as long delay times, thermal cycling, and atmosphere effects such as reducing or oxidizing. For monitoring and controlling the combustion space stoichiometry O_2 and CO can be simultaneously monitored by a number of optical techniques using lasers such as Raman, REMPI (resonance enhanced multiphoton ionization), or absorption in the UV region. However, these techniques suffer due to the complexity of the optical equipment needed and to date have been restricted to well controlled environments. With the advancement of solid state diode lasers, the devices offer the simplicity necessary for conducting absorption measurements in industrial harsh environments. Solid state lasers are compact robust devices that provide a spectrally pure narrow line width tunable source of radiation (typically 1 MHz) with wavelength accessibility ranging from 600 nm to 25 μm .

[0011] In particular diode lasers operating in the near infrared spectral region (600-2000 nm) offer a tunable source of radiation from a device that operates near room temperature and is compatible with standard optical fiber components, where standard refers to common materials used in the telecommunication industry, e.g., silica. Diode lasers operating at longer wavelengths (greater than 2.0 μm) require special cooling. Mid-infrared diode lasers (2.5-25 μm) require cryogenic cooling and are not easily coupled to fiber optic components, making the devices cumbersome for industrial applications. On the other hand, the transitions observed in the near infrared are not from the fundamental bands, but rather overtones or combination band systems. Thus, observed signals are orders of magnitude less compared with mid-infrared lasers probing the fundamental bands. Nevertheless, numerous publications have been presented demonstrating high sensitivity detection (ppm level) of many gaseous species, including those of interest in combustion. The combination of room temperature operation and compatibility with commercially available fiber optic systems makes the near-infrared diode lasers a preferred choice for industrial monitoring applications. Compatibility with fiber optic components provides a means of transporting the laser radiation to the process measurement point and provides a means to network multiple sensors together.

SUMMARY OF THE INVENTION

[0012] The methods presented herein provide means for conducting in-situ real-time measurements on important combustion process parameters such as product, intermediate or reactant species concentrations, gas temperature, and particulate loading density using diode laser light source to conduct absorption measurements. This information can then be related to the global or zone process stoichiometry, air entrainment rates, particulate density levels, and gas temperature. Use of the measured values in process control strategies can lead to improvements in energy efficiency, product quality, and pollutant reduction. Since the methods use a line-of-sight optical measurement, no gas extraction is required. This reduces the system cost and associated maintenance issues due to probe plugging. A unique feature of the methods is the fast-time response that allows real-time monitoring of the combustion atmosphere. In addition, effects from thermal shock or extreme changes in the combustion atmosphere, e.g., highly reducing or oxidizing, will not be detrimental to the sensor. The proposed inventive methods also offer additional benefits by monitoring the real gas temperature along with the particle density and air entrainment. All of this information is obtainable at one line-of-sight location on the process. Multiple line-of-sight measurements can also be conducted by having a plurality of diode laser systems mounted on the process location points of interest.

[0013] A primary objective of the present invention is to provide a method to monitor and, preferably, control the performance of an industrial combustion space, where performance may refer to global stoichiometry, or zone stoichiometry of the process, gas temperature, particulate density, or air entrainment level. One or more of the performance criteria can be monitored simultaneously.

[0014] A first aspect of the invention is a method of monitoring or controlling the global or local stoichiometry

of a process (preferably an oxy-fuel combustion process) operating at lean conditions, i.e., excess O_2 present, the method comprising the steps of:

[0015] a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the process; (For O_2 , monitoring a selected rotational line near the B-X (0,0) band of O_2 is preferred. This corresponds to a wavelength near 763 nm, which can be accessed using commercially available AlGaAs diode lasers that are fiber optically compatible.)

[0016] b) Substantially opposite the launch position the transmitted radiation is collected and transported to a photo detector having a filter element; (The detector is preferably a silicon photo-diode, photo-multiplier tube, or similar photo detector with sensitivity in the O_2 spectral region. The filter element is preferably be either a narrow band reflector or transmitting optic and/or a dispersing element for use in suppressing background radiation.)

[0017] c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of O_2 ; (The integrated area of the absorption line is directly proportional to the O_2 number density for a given temperature.) and

[0018] d) producing an electrical signal based on the O_2 number density for use in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

[0019] The electrical signal produced preferably alerts an operator of the process operating condition, allowing manual adjustment of the process by adjusting oxidant, fuel or process pressure or any combination of these three variables. One preferred method is to use the electrical signal to control the operation of one or more actuators, which in turn allows manipulation of one or more of the process variables. For example, if the process is a furnace, the furnace pressure may be increased by reducing the stack area thereby decreasing air infiltration, which will decrease the measured O_2 concentration. Alternatively, the oxidant input flow rate which preferably comprises air, oxygen enriched air or oxygen, can be adjusted to reach the desired amount for the process. Similarly, the input fuel flow rate can be adjusted, however, this will also influence the energy input to the process.

[0020] A second aspect of the invention is a method of monitoring or controlling the global or local stoichiometry of a process (preferably an oxy-fuel combustion process) operating at fuel rich conditions, i.e., excess CO present, (processes that produce a reducing atmosphere of CO), the method comprising the steps of:

[0021] a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the process; (For CO, monitoring a selected rotational line is preferably used from the CO overtone band near 1.56 μm , which can be accessed using commercially available InGaAsP/InP diode lasers that can be fiber optically coupled.)

[0022] b) opposite the launch position the transmitted radiation is collected and transported to photo detector having a filter element; (The detector is preferably InGaAs photo-diode, photomultiplier tube, or similar photo detector with sensitivity in the CO spectral region. The filter element is preferably either a narrow band reflector or transmitting optic and/or a dispersing element for use in suppressing background radiation from hot walls and/or particles.)

[0023] c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of CO; (The integrated area of the absorption line divided by the line strength and pathlength is directly proportional to the CO number density for a given temperature.) and

[0024] d) producing an electrical signal based on the CO number density for use in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

[0025] The electrical signal produced preferably alerts an operator of the process operating condition, allowing manual adjustment of the process by adjusting oxidant, fuel or process pressure or any combination of these three variables. One preferred method is to use the electrical signal to control the operation of one or more actuators, which in turn allows manipulation of one or more of the process variables. For example, if the process is a furnace, the furnace pressure may be decreased by increasing the stack damper area thereby increasing air infiltration, which will decrease the measured CO concentration due to combustion with air. Alternatively, the oxidant input flow rate which preferably comprises air, oxygen enriched air or oxygen can be adjusted to reach the desired CO concentration for the process. Similarly, the input fuel flow rate can be adjusted.

[0026] A third and preferred aspect of the invention is a method for monitoring both CO and O₂ number density simultaneous or nearly simultaneous at a specified location on a process, preferably an oxy-fuel combustion process. A preferred method is adaptable to a range of process operating conditions with CO and O₂ ranging from 100% to 0.01%, the method comprising the steps of:

[0027] a) launching a plurality of collimated beams of radiation emitted by a plurality of tunable diode lasers along a line-of-sight path through the process; (The collimated beam comprising a plurality of wavelengths, e.g., 763 nm and 1.5 μ m radiation for O₂ and CO monitoring respectively.)

[0028] b) simultaneously launching a plurality of tunable beams by spatially introducing the radiation through a fiber optic network; (Alternatively, near simultaneous beam introduction by temporally separating the multiple input beams, i.e., tune the lasers at different times.)

[0029] c) simultaneous transmission of multiple frequencies separated using dispersion elements and/or narrowband filters and detector combination allowing discrimination between the different wavelengths; (In the case of temporal separation a single

detector can be used to demodulate the input signal thereby resolving all wavelengths tuned.)

[0030] d) processing the optical signal by observing the amount of attenuation observed from a plurality of signals tuned over a resonance absorption line for a specific species; (The integrated area of the absorption line is directly proportional to the number density for a given temperature.) and

[0031] e) producing an electrical signal based on the O₂ number density for use in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

[0032] A fourth aspect of the invention is a method for monitoring temperature of gas phase of a process, preferably an oxy-fuel combustion process, comprising the steps of:

[0033] a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the combustion process;

[0034] b) tuning the diode laser over two or more rotational lines of the selected species; (CO and or O₂ can be used for temperature monitoring however the preferred species is H₂O or another detectable process gas that may be present, e.g., HCl. Which-ever species is chosen it is preferred that the dependence on process stoichiometry is minimal. For near infrared monitoring of H₂O (numerous absorption transitions exist in the 1.4, 1.5 and 2.0 μ m spectral region that is accessible by near infrared diode lasers) from hydrocarbon fueled combustion processes, both CO and O₂ concentrations are strongly dependent on the process operating conditions, and one may encounter cases where no detectable levels of either species is observed, i.e., concentration too low for temperature determination. For this reason, and the fact the H₂O is present in the vast majority of combustion processes makes it an ideal candidate for temperature monitoring oxy-fuel combustion process and others where H₂O is known to be present.)

[0035] c) opposite the launch position the transmitted radiation is collected and transported to a photo detector (sensitive at the wavelength of interest) having a filter element; (The filter element is preferably either a narrow band reflector or transmitting optic and/or a dispersing element for use in suppressing background radiation from hot walls and/or particles.)

[0036] d) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over two or more resonance absorption lines; (The temperature is obtained by applying the following expression

$$R = \left(\frac{S_1}{S_2} \right)_{T_o} \times \exp \left[\frac{-hc\Delta E}{k} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right]$$

[0037] where R is the ratio of the integrated absorbance of each transition at the unknown temperature T. The right hand side of the expression is composed of all known parameters

except T . $(S_1/S_2)_{T_0}$ is the ratio of the linestrength values at some reference temperature, T_0 , ΔE is the energy separation of the absorbing states, h is Planck's constant, k is Boltzmann's constant and c is the speed of light.) and

[0038] e) producing an electrical signal based on the temperature of gas phase for use in regulation of one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

[0039] Measurement of gas phase temperature provides additional information that is preferably used in process mass and energy balances, provide information on linestrengths used in determining the number density from absorption measurements, useful in unit conversion, and beneficial for process optimization. For unit conversion, temperature is used to convert number density values obtained from absorption measurements to the more industrial acceptable percent concentration values typically used in industrial plant environments. Process optimization is preferably practiced for temperature measurements at defined process locations. For example, one objective of a reheat furnace is to achieve a uniform temperature of a billet and hold the temperature for a predetermined time. Measurement of the gas phase temperature near the surface of the billet provides feedback information on the temperature level and stability, providing a means to control an undesired temperature or fluctuations in temperature.

[0040] A fifth aspect of the invention is a method for monitoring particulate concentration level in a monitored gas phase region of a process comprising the steps of:

[0041] a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the gas phase;

[0042] b) opposite the launch position the transmitted radiation is collected and transported to photo detector (sensitive at the wavelength of interest) having a filter element; (The filter element can be either a narrow band reflector or transmitting optic and/or a dispersing element for use in suppressing background radiation.)

[0043] c) tuning the laser off any resonance absorbing species and monitor the attenuated radiation detected;

[0044] d) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned away from all resonance absorption lines; (The observed attenuation is related to the particle density along the line-of-sight optical path by the following expression

$$\frac{I}{I_0} = e^{-\alpha_{\text{ext}} l}$$

[0045] where I_0 is the beam initial intensity and I is the measured intensity after the beam propagates a distance l through the process. In the presence of particles, the measured attenuation can be related to the particle number density if the extinction coefficient, α_{ext} , is known.) and

[0046] e) producing an electrical signal based on the particle number density. (The electrical signal is

preferably used in regulation of one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate. In addition, adjustment of burner momentum and position is preferably varied with real-time feedback on the impact of these adjustments with respect to particulate entrainment.)

[0047] A sixth aspect of the invention is a method for monitoring the rate of air entrainment into a combustion process comprising the steps of:

[0048] a) measuring the concentration of the major combustion product species such as CO_2 or H_2O by launching a collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the combustion process;

[0049] b) opposite the launch position the transmitted radiation is collected and transported to a photo detector (sensitive at the wavelength of interest) with a filtering element; (The filter element can be either a narrow band reflector or transmitting optic and/or a dispersing element for use in suppressing background radiation from hot walls and/or particles.)

[0050] c) processing the optical signal by observing the amount of attenuation observed as the laser is tuned over a resonance absorption line; (The integrated area of the absorption line divided by the line strength and pathlength is directly proportional to the number density for a given temperature.)

[0051] d) estimating the air entrainment rate into the process using the fuel and oxidizer inlet composition and flow rates along with the ambient air composition, and using a difference between the theoretical value for complete combustion and the measured species concentration; and

[0052] e) producing an electrical signal based on the air entrainment rate for use in regulating one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

[0053] A seventh aspect of the invention is an indirect means of monitoring H_2 (which has no infrared absorption transitions) and/or combustible hydrocarbons in a high temperature $>1000^\circ \text{C}$. gas phase comprising of the steps:

[0054] a) measuring the concentration of H_2O by launching an initial collimated beam of radiation by a tunable diode laser along a line-of-sight path through a gaseous phase (preferably flue gas of a combustion process) in the spectral region where H_2O absorption transitions are found.

[0055] b) opposite the launch position the transmitted radiation is collected and transported to a photo detector with a filter element; (The filter element preferably comprises a narrow band reflector, narrow bandpass filter, and/or a dispersing element for use in suppressing background radiation.)

[0056] c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of H_2O ; (The integrated area of the absorption line is directly proportional to the H_2O number density for a given temperature.)

[0057] d) a second measurement point is used either within the gas phase region or in a diverted stream of gas; (The measurement of H_2O is conducted in a similar manner as described above but here O_2 is introduced and allowed to mix with the heated gas. The O_2 gas will react with unburned H_2 and/or hydrocarbons that may be present thereby forming H_2O as a product.)

[0058] e) measuring the difference between H_2O downstream and H_2O upstream of the O_2 gas introduction to back calculate the amount of H_2 and/or unburned hydrocarbons in the gaseous phase; and

[0059] f) producing an electrical signal based on the amount of unburned H_2 and/or hydrocarbons. (This signal is preferably used in controlling one or more of the following variables: fuel inlet flow rate and/or oxidant inlet flow rate, and process pressure.)

[0060] For the introduction of O_2 into the gas stream, the O_2 content can range from air to pure O_2 . However, to insure complete reaction of the gases and minimizing dilution effects O_2 purity >90% is preferred. In addition, the same strategy can be applied to CO monitoring. Here, CO in a high temperature gas such as combustion flue gas reacts with injected O_2 forming CO_2 . The CO_2 can then be monitored using a near infrared laser in the $1.5 \mu m$ spectral region. Comparison between the CO_2 observed before O_2 injection and after O_2 injection provides an indirect means for measuring CO.

[0061] A further aspect of the invention is a means to monitor pollutant X where X is a pollutant of specific interest to a process. For example, X can be NO or SO in exhaust of a process flue or at a specified location in the process. The method for monitoring comprising the steps:

[0062] a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the combustion process; (For monitoring species X, the preferred method consists of monitoring one of the absorption transitions in the near infrared that is free of interfering background species such as H_2O .)

[0063] b) opposite the launch position the transmitted radiation is collected and transported to a photo detector having a filter element; (The detector is preferably a silicon photo-diode, photomultiplier tube, or similar photo detector with sensitivity in the spectral region of species X. The filter element can be either a narrow band reflector or transmitting optic and/or a dispersing element for use in suppressing background radiation.)

[0064] c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of species X; (The integrated area of the absorption line is directly proportional to the number density for a given temperature.) and

[0065] d) producing an electrical signal based on the number density of species X. The electrical signal may be useful in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

[0066] The inclusion of additional combustion species such as NO and/or SO with the main monitoring species set namely O_2 , CO, and H_2O provides a means to fully characterize the exhaust gas and/or zone of a combustion process. Since diode lasers cover a broad wavelength range the limitations for detecting a specific species is dictated by the physics of the absorption process. For example, some species are not infrared active such as N_2 . While other species that are infrared active have limited use due to weak absorption transitions and/or interference by other species in the measurement volume.

[0067] The generality of this invention provides unique methods for monitoring operating conditions on high temperature large-scale industrial processes. The fast-time response provides a means for monitoring the process conditions in a real-time mode allowing the identification of processes changes, e.g., global or local stoichiometry and applying regulation to correct and adjust the process to the desired operating condition. These and other aspects of the invention will become apparent from review of the following descriptions and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0068] The figures are not to scale and are only representative of actual embodiments.

[0069] FIG. 1 represents a schematic block diagram illustrating the configuration for industrial monitoring and control;

[0070] FIG. 2 is a graph showing measured O_2 absorbance compared with theoretical Voigt fit;

[0071] FIG. 3 is graph showing the variation of measured O_2 number density with time for a dynamic combustion process;

[0072] FIG. 4 is graph showing the variation of measured CO number density with time for a dynamic combustion process;

[0073] FIG. 5 represents a schematic block diagram illustrating a conceptual application using the diode laser monitoring method on an electric arc furnace;

[0074] FIG. 6 is a graph showing the relationship for increasing O_2 concentration in the oxidant between excess oxidant introduced in the combustion process and percent O_2 observed in the dry flue gas;

[0075] FIG. 7 represents a schematic block diagram illustrating a conceptual application using the diode laser monitoring method on a glass melting furnace;

[0076] FIG. 8 is a graph showing the relationship between the observed transmittance through a medium containing particles of specific sizes; and

[0077] FIG. 9 represents a schematic block diagram illustrating a conceptual method for conducting absorption measurements under high particle loading.

[0078] DESCRIPTION OF PREFERRED EMBODIMENTS

[0079] Methods for monitoring important species in-situ in the gas phase with fast response times and high accuracy provides a means to regulate many industrial processes for maintaining optimum performance, where performance

means global or local stoichiometry, gas temperature, particle density, and air entrainment estimates. Measuring and controlling these quantities provides a means for production quality control, pollutant reduction, and improved energy efficiency.

[0080] Implementation of the preferred monitoring method on a combustion process includes the following basic elements illustrated in **FIG. 1**. A single or multiple diode laser **1** is used in this embodiment. In the case of O₂ monitoring the diode laser model 760DFB supplied by Sarnoff Corp. Princeton, N.J. is suitable. Each laser has a current controller **2** and temperature controller **3** for stability and wavelength tuning (such as available from Melles Griot, Carlsbad, Calif., model 56DL403). The output of diode laser **1** is fiber optically coupled (by a Gould Electronic, Millesville, Md., model 22-10676040-4687) and transported to coupler **4** that splits the input energy in half. If multiple lasers are used then the divider would be $n \times 2$, where n is the number of inputs with 2 outputs. The output of the coupler is transported by single mode fiber **5** (OZ Optics, Ontario, Canada), core with FC/APC connector/collimator ends which can be hundreds of meters in length, allowing the sensitive laser and associated electronics to be placed in a secure, well controlled environment away from the harsh environment typically found near industrial combustion processes. Beam launch module **6** is mounted at the monitoring point of interest **8** on the process using water or gas cooled pipes **16**. The beam exits fiber optic **5** and propagates through shaping and collimating optics **7** (for example OZ Optics anti-reflection coated with a 2 mm waist at 1 mm). Here the beam is shaped to the desired diameter and divergences. For industrial processes where particulate matter is present, a typical beam diameter ranging from 1-9 centimeters (cm) is preferred. The expanded beam diameter provides a spatial averaging effect that improves the signal-to-noise for particle laden flows and reduces the angular divergence, which reduces beam steering due to temperature gradients. Beam **9** propagates through the cooled pipe **16** on the launch side and traverses across the process where it is received by the detector module **11** mounted opposite beam launch module **6**. Both the beam launch module **6** and detector module **11** are purged with a gas **15**. Any gas can be used provided it does not contain the gaseous species being monitored. For example, N₂ or air can be used if only CO monitoring is being conducted. The process gas itself can even be used provided it is cleaned (free of particulate matter) and dry (moisture removed) and does not contain any absorbing gaseous species. In addition, the process gas must be cooled to an acceptable temperature dictated by the components used in the module. Detector module **11** receives the beam and directs it to detector **10**, which comprises one or more of the following elements: a narrowband pass filter, dispersing elements or narrowband reflectors to selectively direct the laser radiation to the photo detector (e.g., EG&G Optoelectronic, Salem Mass. Model UV-245BQ). The filters are used to suppress any background radiation from the high temperature process. The output of the photo detector **12** is sent to a balanced radiometric detector (BRD) **13** along with the split portion of the beam **14** from the coupler **4**, which is used as a reference. The BRD **14** is a noise canceling electronic circuitry. The output from the BRD gives the log ratio measured intensity from the detector **12** and the reference

intensity **14**. The output from **14** is processed in computer **17** where number density of the measured species can be obtained.

[0081] The apparatus illustrated in **FIG. 1** is an example of a preferred apparatus for conducting absorption measurements on industrial combustion processes. A beam is generated by a diode laser and propagated across the gas region of the process and the absorbance measured. The differences between known approaches and methods and apparatus of the present invention lie in how one measures the absorbance signal. Since diode lasers are inherently "noisy" devices and the vibrational overtone and combination band transitions accessible in the near infrared region generally have weak absorbances, noise reduction is necessary. Direct absorption monitoring can be performed in some cases under the following conditions: the absorption transition is strong, the monitored species concentration is high, or the path length is sufficiently long. However, for combustion applications, where a large dynamic range is needed and pathlengths need to be short due to beam steering and particulate matter in the gas, direct absorption has limited use, requiring implementing a noise suppression technique.

[0082] Numerous diode laser-monitoring applications have been demonstrated using a technique that modulates the diode laser at high frequency(f) and detects the absorbance with a lock-in amplifier at $2f$ (second derivative). This method commonly referred to as frequency modulation (FM spectroscopy) detects the 2nd derivative of the resonance absorbance lineshape. Though this technique can be used, the preferred method is the one publicized by Physical Sciences, Inc., which uses balanced radiometric detection electronics first developed by Hobbs et. al. U.S. Pat. No. 5,134,276. See P.C.B. Hobbs, "Shot noise-limited optical measurements at baseband with noisy lasers, "Lasers Noise", 1376, Society of Photo-Optical Instrumentation Engineers, pp. 216-221 (1990), incorporated by reference herein. This technique has the advantage of measuring the true lineshape and eliminates the need for high frequency generators and lock-in amplifiers. A discussion of high frequency generators may be had by reviewing K. L. Haller and P. C. B. Hobbs, "Double Beam Laser Absorption Spectroscopy: Shot Noise-Limited Performance at Baseband with a Novel Electronic Noise Canceller", Optical Methods for Ultrasensitive Detection and Analysis: Techniques and Applications", 1435, Society of Photo-Optical Instrumentation Engineers, p. 298 (1991), incorporated herein by reference.

[0083] By tuning the laser over a narrow wavelength range across a resonance absorption transition of a target species isolates the absorption of the target species from effects due to window fouling, presence of particles along the beam path and other molecular species. Using a plurality of lasers and/or multiple wavelength regions from a single laser with broad tuning capability such as that presented by Upschulte et.al. for "Measurement of CO, CO₂, OH and H₂O in Room Temperature and Combustion Gases By Use of a Broadly Current-Tuned Multi-Section Diode Laser" in Applied Optics 38 (9), 1999, near simultaneous detection of multiple target species can be performed. Continuous bandwidths of 100 Hz (measurement time of 0.01 second) provide superior time response and in special cases bandwidths of 1000 Hz are achievable. The fast-time response allows monitoring of dynamic process conditions with the capability of resolving

subtle changes such as CO bursts or variations in air infiltration that can impact the overall performance of the process.

[0084] In the following example, real-time monitoring of O₂ was conducted using the configuration illustrated in **FIG. 1** installed on a pilot furnace operating at 1.5 MMBtu/hr with a natural gas oxygen flame. For O₂ monitoring an AlGaAs diode laser was tuned across the P₂(25) rotational line of a weak transition of the forbidden electronic system for O₂ near 763 nm. In this case, the process gas temperature was 1363 K with an excess O₂ concentration of 5.2%. Tuning the laser across the transition provides a means for obtaining the full lineshape as illustrated in **FIG. 2**. Also, shown in **FIG. 2** is the Voigt lineshape function that shows an excellent comparison between the measured and theoretical lineshape. The concentration is obtained by applying Beer's law

$$I = I_0 e^{-S(T)g(v)NL}$$

[0085] where I₀ is the incident laser intensity, I is the measured laser intensity after propagating a distance I through the process, S(T) is the temperature dependent absorption line strength, g(v) is the frequency dependent lineshape, and N is the absorber number density. Note that the log (I/I₀) is directly recorded from the BRD circuit used in the system illustrated in **FIG. 1**. Since S(T) is a function of temperature, knowledge of the temperature is needed, or else an absorption line can be selected that is relatively insensitive to temperature within the range of interest. The number density, which can be converted to concentration by applying an equation of state, can be obtained by integrating the signal across the absorption lineshape as follows

$$N = \frac{1}{S(T)L} \int \ln \left(\frac{I_{vo}}{I_v} \right) dv$$

[0086] where S(T) is the line strength, I is the pathlength, I_{vo} is the reference beam intensity, and I_v is the measured intensity through the process.

[0087] A demonstration of the real-time monitoring is illustrated in **FIG. 3** for measuring the change in the O₂ number density. Here the stoichiometry is dynamically changing by implementing a square wave (0.1 Hz) variation in the fuel (natural gas) flow rate for an average firing rate of 1.5 MMBtu/hr oxygen-fuel flame conducted in the flue of a 4 m×1 m×1 m furnace. Variations in the fuel flow rate cause a dynamic change in the combustion stoichiometry that oscillates between fuel-lean and fuel-rich conditions. Similarly, measurements conducted on CO using an InGaAs/InP diode laser near 1.56 μm are shown in **FIG. 4** for varying the fuel flow at a frequency of 0.5 Hz. This mode of operation produces a flue gas composition that also oscillates between excess CO and O₂ concentration during the fuel-rich and fuel-lean cycles respectively. The time dependent measured number densities demonstrate the unique capability of the diode laser absorption scheme for capturing the cyclic time behavior of the process. Conventional extractive and solid state analysis methods for O₂ and CO, as described previously, can not resolve such time-dependent variations.

[0088] Monitoring real-time dynamic process changes provides a means for coupling the sensor to a regulation

system that can be used to optimize the process. For example, processes such as electric arc furnaces for processing secondary steel or rotary kilns for secondary aluminum or iron melting operate in a batch mode. The scrap and/or raw material are first loaded into the process and melting begins with the input of electrical and/or chemical energy. Processes of this type produce large quantities of CO that represents an energy loss and an environmental hazard. Improvement in the energy efficiency is obtained by monitoring the flue gas composition and injecting O₂ containing gas with a concentration range of (20%-100). The excess O₂ oxidizes the CO to recover the thermal energy. However, the release of CO from these processes can be transient in nature. Conventional extractive sampling systems applied to these types of processes suffer from the slow response time and maintenance issues associated with plugging due to high particulate loading, as discussed previously. Implementing near simultaneous real-time monitoring of CO and O₂ with a diode laser system on the process exhibiting dynamic behavior and high particle loading avoids the problems encountered with traditional off-gas analysis. By monitoring the concentration of key target species a regulation system using this information can optimize the processes energy utilization, product quality, and minimize pollutants.

[0089] An example illustrating diode laser monitoring on a dynamic process is shown in **FIG. 5** for an electric arc furnace (EAF). In this case, the sensor beam launch and detector modules as previously discussed are mounted near the flue region at location 1 or 2 on **FIG. 5**. Location 1 is between the EAF furnace exhaust and water cooled duct. At this position air is entrained and mixed with the flue gas. Therefore monitoring at this location requires setting the optical pathlength between the beam launch and receiver modules such that surrounding air entrainment does not influence the measurement. Location 2 fixes the sensor system on the lid 14 of the process. Since the process operates in batch mode lid 14 is removed to load the raw material 5 in to tank 3. Lid 14 is then replaced along with electrodes 4. Off-gas monitoring at either location 1 or 2 sends the transmittance signal 6 for CO, O₂ and H₂O to processor 7 which converts the signal to concentration. This information is then transferred to control system 8, e.g., programmable logic controller (PLC), which sends a signal 9 to flow control valves 11 and 13. Based on the off-gas analysis the control valve for the auxiliary burner 10 can be adjusted to increase or decrease the O₂ flow rate. Similarly, the O₂ flow rate can be adjusted on the O₂ lance 12. Though this example illustrates the use on an EAF any dynamic combustion processes can be adapted with an integrated diode laser control system.

[0090] Incorporating a second monitoring location upstream of locations 1 or 2 shown in **FIG. 5** that is either conducted on the process or in a diverted stream of the flue gas provides a means to indirectly monitor the H₂ content in the gas. For the EAF example, besides CO representing an energy loss in the off-gas, H₂ can also be present in high concentrations. Injection of O₂ at the second location into the hot process gas will react with H₂ off-gas and any unburned hydrocarbon, with H₂O being the product species. The O₂ injection can be ambient or heated using a heat exchanger utilizing thermal energy from the flue itself or another means such as, secondary burner or electrical, etc. By measuring the H₂O concentration at the 2 different

locations the change in H_2O content can be attributed to the amount of H_2 and/or unburned hydrocarbons.

[0091] Dynamic processes such as the EAF can experience rapid changes in the off-gas composition on a 10's of seconds time scale. The response time of conventional industrial flow control valves can be the rate-limiting step in this scheme, since adjustment of these valves can take many 10's of seconds. The preferred system uses the fast-time response of the diode laser sensor with a regulation system and a solid state proportioning control valve such as described and claimed in U.S. Pat. No. 5,222,713, incorporated by reference herein. In this case, high volume gas flows can be rapidly controlled thus fully using the fast-time response of the diode laser sensor with the delay being limited to the process residence time. In this application, the diode lasers measure the exhaust gas composition. Based on the CO and O_2 content in the exhaust the controller would change the amplitude of the proportional valve to the desired value to either decrease or increase the O_2 flow rate. The proportional valve response is on the order of milliseconds which can be considered essentially instantaneous. This control valve can also be pulsed which will improve process gas mixing further reducing the residence time. In addition, the diode laser measurement location is preferably located at the point of interest in the process, thus further reducing delay times, since measurement delays on very large volume processes can still be an issue.

[0092] In the next set of examples, applications using diode laser sensor methods of the invention with full monitoring capabilities comprising T, CO, O_2 , particle concentration, and air entrainment rates are discussed. Each of these parameters provides important information on the process that can be used in optimization and control. For example, control of industrial processes using an oxidizer fluid consisting of oxygen enriched air up to pure oxygen imposes a higher tolerance for controllability as compared with air. As shown in FIG. 6 small changes in the oxidant inlet result in a large change in the oxidant outlet for processes using pure O_2 . The excess O_2 in the exhaust will enhance NOx formation. For O_2 enriched air the sensitivity lies between the air curve and pure O_2 curve on FIG. 6 with the slope increasing as the O_2 content in the oxidizer increases. The tolerance for excess O_2 is process dependent and can impact the production operation in terms of quality, capacity, thermal efficiency, in addition to environmental effects related to NOx formation. Air entrainment into the process increases the oxidant level along with introducing additional N_2 contributing to energy losses and/or increased NOx formation. Similarly, the presence of CO indicates a reducing atmosphere that can affect the process quality, production, and can be a safety hazard due to the toxicity and combustibility of CO.

[0093] The first example presented, a diode laser sensing method of the invention is applied to a glass melting tank 1 as illustrated in FIG. 7. The raw material enters melting tank 1 at the left side and flows to the right into refining zone 2 where it is then distributed for fiber or container manufacturing. The furnace exhaust 3 is located in the same area as the raw material inlet. The furnace can operate with O_2 -fuel or O_2 enriched air fuel burners 4. Beam launch modules 6 and detector modules 5 are mounted at selected locations on furnace 1. For illustration purposes, three monitoring locations are shown in FIG. 7. In principle N monitoring points

can be selected. The laser system 10 is located away from the process and delivers N selected wavelengths by fiber optic 8 to the beam launch module 6. Beam 7 consisting of N wavelengths temporally separated propagates along line-of-sight path through the process to detector module 5. The resulting transmittance signal 9 is sent back to laser system 10 for processing the information into physical quantities, e.g., temperature and concentration. Measured results are sent to the furnace supervisory system 12 by connection 13. Based on the measured results supervisory system 12 using a regulation algorithm will send signal 11 to the appropriate flow control valves. Regenerative or recuperative furnaces are also suitable for the monitoring and control method. In addition, hybrid furnaces consisting of regenerative or recuperative type using O_2 lances and/or auxiliary burners are also adaptable for the method.

[0094] Monitoring at three locations as illustrated in FIG. 7 provides information at different zones in the process. At location A the measured values are near the exhaust of the furnace and can provide global information on the O_2 , CO, air entrainment, and particulate carry over. In addition, the path length observed may be adjusted to localize the measured region since the monitoring technique is line-of-sight path integration. The pathlength control is shown by extending the cooled pipes (as discussed in FIG. 1) 14 thus shorting the path. Shorter pathlength is desirable for high particulate loading that can result in significant beam attenuation over longer path distances due to extinction. Zones B and C can monitor the average stoichiometry and Temperature observed in this region. In addition, variations in particulate density can be observed by changing operating conditions such burner momentum.

[0095] Measurements conducted in the exhaust provide global process stoichiometry monitoring by following the O_2 and CO concentration. Using these measurements in combination with the air entrainment rates estimated from the H_2O measurements provide a means for tuning the burner oxidizer input and furnace pressure. In addition, the air entrainment preferably alerts operators of possible furnace leaks from refractory damage. The level of particulate matter in the exhaust is measured by tuning at least one of the lasers off an absorption transition. Here this information is preferably used as feedback regarding the burner placement within the glass tank, burner momentum, and angle of the flame with respect to the glass bath. It is known that variation in these parameters can influence the volatilization that leads to higher levels of particulate matter (ref) in the flue exhaust. In addition, any large variation or sudden changes in the particulate level can alert furnace operators of potential problems, e.g., flame impingement due to deflection toward the crown or refractory damage near the burner exit. Measurements of the temperature from at least two rotational allows determination of the linestrength value needed for determining the concentration of all species measured. This allows the measured value to be converted in to a percentage reading, instead of number density, which is accepted more favorably by furnace operators.

[0096] Process monitoring can also be conducted at a selected location within the process, as illustrated in FIG. 7. Because the measurement is optical, no disturbances are introduced to the process as in the case of sampling probe measurements. In this case, the measurement is conducted along the pathlength providing an integrated average across

the line-of-sight path. Thus, the spatial location of high or low levels of O_2 detected along the path is not known. In addition, the observed absorption signals can be weighted toward higher or lower temperatures depending on the transition being monitored. The preferred method would be to select an absorption transition that has a weak temperature dependence over a given temperature range of the process. This application allows local stoichiometry control for a particular zone in the process. A control loop integrating the sensor and flow control provides a means for optimizing the desired stoichiometry. In the case of glass, melting furnaces operating with reducing atmospheres will cause instabilities in glass color.

[0097] The basic principles outlined above for application in a glass melting tank can be similarly applied to steel reheat furnaces. In this case, the stoichiometry is a critical control parameter to minimize scale formation on the billets. Here desirable sensor locations can be positioned such that the beam propagates near the billet surface to regulate O_2 concentration and temperature uniformity. Though the process is different from glass melting the method and integration with a regulation system is the same. However, the key parameters in optimizing and controlling the process can be different.

[0098] Other applications using the diode laser sensor methods of the invention can be found in the chemical industry on processes that can be highly corrosive. The non-intrusive nature of the methods of the invention are ideal for applications on such processes. As one such example, sulfur recovery units are used to recycle sulfur used in the production of MMA (methyl methacrylate) for the Plexiglas industry. Improvements on this process have been demonstrated by using pure O_2 as a replacement for a fraction of air which leads to increased capacity, overall pollutant reduction (SO_x and NO_x), improved fuel efficiency and reduction in CO_2 emission. In this case, the sensor is positioned on the first stage of the process. Monitoring real-time O_2 , CO and T, the process O_2 inlet flow rate is adjusted through a regulation system to minimize NO_x . In addition, organic compounds are present in the spent acid, which need to be burned. Here CO monitoring is used to insure complete combustion of all organic entering the process with appropriate regulation to adjust oxidant inlet conditions.

[0099] A variation of the monitoring method can be considered for industrial processes where the particulate loading is extremely high causing severe attenuation of the beam energy. The effect of particulate concentration and pathlength is shown in FIG. 8. At high particulate densities and small diameter particles, the attenuation of the laser intensity can be completely absorbed. Shortening the pathlength is the preferred solution but in some cases, a shorter pathlength may not be sufficient. In this case, a dilution method shown in FIG. 9 can be applied. Here a dirty process gas is flowing through a duct 1 in the direction shown by 2. A portion of the flow is diverted into 3 where a dilution gas 4 is used to mix and dilute the particulate density. The flows through external chamber 6 and exits at location back into the main process stream. Mounted on the external chamber is the diode laser monitoring system 7. The preferred dilution gas would be any gas that does not contain the target species monitored by the diode laser. To convert back to the process gas concentration the flow rate of the dilution gas must be

known. The amount of dilution gas can be high since the sensitivity of the diode laser monitoring method is high.

[0100] Having described the present invention, it will be readily apparent to the artisan that many changes and modifications may be made to the above-described embodiments without departing from the scope of the present invention.

What is claimed is:

1. A method of monitoring or controlling the global or local stoichiometry of a process operating at lean conditions, the method comprising the steps of:

- a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the process, and, for O_2 , monitoring a selected rotational line near the B-X (0,0) band of O_2 , corresponding to a wavelength near 763 nm, which can be accessed using commercially available AlGaAs diode lasers that are fiber optically compatible;
- b) collecting and transporting the transmitted radiation at a site substantially opposite the launch position to a photo detector having a filter element, the photo detector having sensitivity in the O_2 spectral region;
- c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of O_2 the integrated area of the absorption line being directly proportional to the O_2 number density for a given temperature; and
- d) producing an electrical signal based on the O_2 number density for use in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

2. Method in accordance with claim 1 wherein the electrical signal produced alerts an operator of the process operating condition, allowing manual adjustment of the process by adjusting oxidant, fuel or process pressure or any combination of these three process variables.

3. Method in accordance with claim 2 wherein the electrical signal is used to control the operation of one or more actuators, which in turn allows manipulation of one or more of the process variables.

4. A method of monitoring or controlling the global or local stoichiometry of a process operating at fuel rich conditions, the method comprising the steps of:

- a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the process, and, for CO, monitoring a selected rotational line is used from the CO overtone band near $1.56 \mu m$, which can be accessed using commercially available InGaAsP/InP diode lasers that can be fiber optically coupled;
- b) collecting and transporting the transmitted radiation at a site substantially opposite the launch position to a photo detector with a filter element, the photo detector having sensitivity in the CO spectral region;
- c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of CO, the integrated area of the absorption line divided by the

line strength and pathlength being directly proportional to the CO number density for a given temperature; and

- d) producing an electrical signal based on the CO number density for use in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

5. Method in accordance with claim 4 wherein the electrical signal produced alerts an operator of the process operating condition, allowing manual adjustment of the process by adjusting oxidant, fuel or process pressure or any combination of these three variables.

6. Method in accordance with claim 5 wherein the electrical signal to control the operation of one or more actuators, which in turn allows manipulation of one or more process variables.

7. Method in accordance with claim 6 wherein the process pressure may be decreased by increasing the stack damper area thereby increasing air infiltration, which will decrease the measured CO concentration due to combustion with air.

8. Method in accordance with claim 6 wherein the oxidant input flow rate which can consist of air, oxygen enriched air or oxygen can be adjusted to reach the desired CO concentration for the process.

9. A method for monitoring both CO and O₂ number density simultaneous or nearly simultaneous at a specified location on a process, the method comprising the steps of:

- a) launching a plurality of collimated beams of radiation emitted by a plurality of tunable diode lasers along a line-of-sight path through the process, the collimated beams containing a plurality of wavelengths, e.g., 763 nm and 1.5 μm radiation for O₂ and CO monitoring respectively;

- b) simultaneously launching a plurality of tunable beams by spatially introducing the radiation through a fiber optic network, or alternatively, nearly simultaneously introducing beams by temporally separating the multiple input beams, i.e., tune the lasers at different times;

- c) simultaneous transmission of multiple frequencies separated using dispersion elements and/or narrowband filters and detector combination allowing discrimination between the different wavelengths, and in the case of temporal separation, a single detector to demodulate the input signal thereby resolving all wavelengths tuned;

- d) processing the optical signal by observing the amount of attenuation observed from a plurality of signals tuned over a resonance absorption line for a specific species, the integrated area of the absorption line being directly proportional to the number density for a given temperature; and

- e) producing an electrical signal based on the O₂ number density for use in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

10. A method for monitoring temperature of gas phase of a process comprising the steps of:

- a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the gas phase of the process;

- b) tuning the diode laser over two or more rotational lines of the selected species selected from the group consisting of CO, O₂, H₂O or another detectable process gas, such as HCl, that is not strongly dependent on the process stoichiometry;

- c) collecting and transporting the transmitted radiation at a site substantially opposite the launch position to a photo detector (sensitive at the wavelength of interest) having a filter element, the photo detector having sensitivity in the spectral region of interest, to produce an optical signal;

- d) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over two or more resonance absorption lines, the temperature being obtained by applying the following expression

$$R = \left(\frac{S_1}{S_2} \right)_{T_o} \times \exp \left[\frac{-hc\Delta E}{k} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right]$$

where R is the ratio of the integrated absorbance of each transition at the unknown temperature T, (S₁/S₂)_{T_o} is the ratio of the line strength values at some reference temperature, T_o, ΔE is the energy separation of the absorbing states, h is Planck's constant, k is Boltzmann's constant and c is the speed of light; and

- e) producing an electrical signal based on the for use in regulation of one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

11. A method for monitoring particulate concentration level in a monitored gas phase region of a process comprising the steps of:

- a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the gas phase;

- b) opposite the launch position the transmitted radiation is collected and transported to a photo detector (sensitive at the wavelength of interest) having a filter element;

- c) tuning the laser off any resonance absorbing species and monitor the attenuated radiation detected;

- d) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned away from all resonance absorption lines, the observed attenuation being related to the particle density along the line-of-sight optical path by the following expression

$$\frac{I}{I_o} = e^{-\alpha_{ext}l}$$

where I_o is the beam initial irradiance and I is the measured irradiance after the beam propagates a distance l through the process, and, in the presence of particles, the measured attenuation can be related to the particle number density if the extinction coefficient, α_{ext}, is known; and

- e) producing an electrical signal based on the particle number density that can be used in regulation of one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

12. A method for monitoring the rate of air entrainment into a combustion process comprising the steps of:

- a) measuring the concentration of the major combustion product species such as CO_2 or H_2O by launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the combustion process;
- b) opposite the launch position the transmitted radiation is collected and transported to a photo detector (sensitive at the wavelength of interest) with a filter element;
- c) processing the optical signal by observing the amount of attenuation observed as the laser is tuned over a resonance absorption line, the integrated area of the absorption line divided by the line strength and path-length is directly proportional to the number density for a given temperature;
- d) estimating the air entrainment rate into the process using the fuel and oxidizer inlet composition and flow rates along with the ambient air composition, and using a difference between the theoretical value for complete combustion and the measured species concentration; and
- e) producing an electrical signal based on the estimated air entrainment rate for use in regulating one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

13. A method for indirectly monitoring H_2 concentration and/or hydrocarbons in a high temperature gas phase comprising the steps of:

- a) measuring the concentration of H_2O by launching an initial collimated beam of radiation by a tunable diode laser along a line-of-sight path through a gaseous phase (preferably flue gas of a combustion process) in the spectral region where H_2O absorption transitions are found.
- b) opposite the launch position the transmitted radiation is collected and transported to a photo detector with a filter element;
- c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of H_2O ;
- d) a second measurement point is used either within the gas phase region or in a diverted stream of gas;
- e) measuring the difference between H_2O downstream and H_2O upstream of the O_2 gas introduction to back calculate the amount of H_2 and/or unburned hydrocarbons in the gaseous phase; and
- f) producing an electrical signal based on the amount of unburned H_2 and/or hydrocarbons.

14. A method to monitor pollutant X in gas phase where X is a pollutant of specific interest to a process, the method for monitoring comprising the steps:

- a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through a gas phase of the process;

- b) opposite the launch position the transmitted radiation is collected and transported to a photo detector having a filter element, the detector having sensitivity in the spectral region of species X;

- c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of species X; and

- d) producing an electrical signal based on the number density of species X.

15. A method of monitoring or controlling the global or local stoichiometry of an oxy-fuel combustion process operating at lean conditions, the method comprising the steps of:

- a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through combustion products of the process, and, for O_2 monitoring a selected rotational line near the B-X ($0,0$) band of O_2 , corresponding to a wavelength near 763 nm, which can be accessed using commercially available AlGaAs diode lasers that are fiber optically compatible;

- b) collecting and transporting the transmitted radiation at a site substantially opposite the launch position to a photo detector having a filter element, the photo detector having sensitivity in the O_2 spectral region;

- c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of O_2 , the integrated area of the absorption line being directly proportional to the O_2 number density for a given temperature; and

- d) producing an electrical signal based on the O_2 number density for use in controlling one or more of the following variables of the oxy-fuel combustion process: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

16. Method in accordance with claim 15 wherein the electrical signal produced alerts an operator of the process operating condition, allowing manual adjustment of the process by adjusting oxidant, fuel or process pressure or any combination of these three process variables.

17. Method in accordance with claim 16 wherein the electrical signal is used to control the operation of one or more actuators, which in turn allows manipulation of one or more of the process variables.

18. A method of monitoring or controlling the global or local stoichiometry of an oxy-fuel combustion process operating at fuel rich conditions, the method comprising the steps of:

- a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through combustion products of the process, and, for CO, monitoring a selected rotational line is used from the CO overtone band near 1.56 μm , which can be accessed using commercially available InGaAsP/InP diode lasers that can be fiber optically coupled;

- b) collecting and transporting the transmitted radiation at a site substantially opposite the launch position to a photo detector with a filter element, the photo detector having sensitivity in the CO spectral region;

c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of CO, the integrated area of the absorption line divided by the line strength and pathlength being directly proportional to the CO number density for a given temperature; and

d) producing an electrical signal based on the CO number density for use in controlling one or more of the following variables of the oxy-fuel combustion process: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

19. Method in accordance with claim 18 wherein the electrical signal produced alerts an operator of the process operating condition, allowing manual adjustment of the process by adjusting oxidant, fuel or process pressure or any combination of these three variables.

20. Method in accordance with claim 20 wherein the electrical signal to control the operation of one or more actuators, which in turn allows manipulation of one or more process variables.

21. Method in accordance with claim 20 wherein the process pressure may be decreased by increasing stack damper area thereby increasing air infiltration, which will decrease the measured CO concentration due to combustion with air.

22. Method in accordance with claim 20 wherein the oxidant input flow rate which is selected from the group consisting of oxygen enriched air or oxygen can be adjusted to reach the desired CO concentration for the process.

23. A method for monitoring both CO and O₂ number density simultaneous or nearly simultaneous at a specified location on an oxy-fuel combustion process, the method comprising the steps of:

a) launching a plurality of collimated beams of radiation emitted by a plurality of tunable diode lasers along a line-of-sight path through combustion products of the process, the collimated beams containing a plurality of wavelengths, e.g., 763 nm and 1.5 μ m radiation for O₂ and CO monitoring respectively;

b) simultaneously launching a plurality of tunable beams by spatially introducing the radiation through a fiber optic network, or alternatively, nearly simultaneously introducing beams by temporally separating the multiple input beams, i.e., tune the lasers at different times;

c) simultaneous transmission of multiple frequencies separated using dispersion elements and/or narrowband filters and detector combination allowing discrimination between the different wavelengths, and in the case of temporal separation, a single detector to demodulate the input signal thereby resolving all wavelengths tuned;

d) processing the optical signal by observing the amount of attenuation observed from the plurality of tunable beams tuned over a resonance absorption line for a specific species, the integrated area of the absorption line being directly proportional to the number density of a species for a given temperature; and

e) producing an electrical signal based on the number density of a species for use in controlling one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

24. A method for monitoring temperature of gas phase of oxy-fuel combustion process comprising the steps of:

a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through combustion products of the combustion process;

b) tuning the diode laser over two or more rotational lines of the selected species selected from the group consisting of CO, O₂, H₂O or another detectable process gas, such as HCl, that is not strongly dependent on the process stoichiometry;

c) collecting and transporting the transmitted radiation at a site substantially opposite the launch position to a photo detector (sensitive at the wavelength of interest) having a filter element, the photo detector having sensitivity in the spectral region of interest, to produce an optical signal;

d) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over two or more resonance absorption lines, the temperature being obtained by applying the following expression

$$R = \left(\frac{S_1}{S_2} \right)_{T_o} \times \exp \left[\frac{-hc\Delta E}{k} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right]$$

where R is the ratio of the integrated absorbance of each transition at the unknown temperature T, (S₁/S₂)_{T_o} is the ratio of the linestrength values at some reference temperature, T_o, ΔE is the energy separation of the absorbing states, h is Planck's constant, k is Boltzmann's constant and c is the speed of light; and

e) producing an electrical signal based on the for use in regulation of one or more of the following variables of the oxy-fuel combustion process: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

25. A method for monitoring particulate concentration level in a monitored gas phase region of an oxy-fuel combustion process comprising the steps of:

a) launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the gas phase combustion products of the process;

b) opposite the launch position the transmitted radiation is collected and transported to a photo detector (sensitive at the wavelength of interest) having a filter element;

c) tuning the laser off any resonance absorbing species and monitor the attenuated radiation detected;

d) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned away from all resonance absorption lines, the observed attenuation being related to the particle density along the line-of-sight optical path by the following expression

$$\frac{I}{I_0} = e^{-\alpha_{\text{ext}} l}$$

where I_0 is the beam initial irradiance and I is the measured irradiance after the beam propagates a distance l through the process, and, in the presence of particles, the measured attenuation can be related to the particle number density if the extinction coefficient, α_{ext} , is known; and

- e) producing an electrical signal based on the particle number density that can be used in regulation of one or more of the following variables of the oxy-fuel combustion process: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

26. A method for monitoring the rate of air entrainment into an oxy-fuel combustion process comprising the steps of:

- a) measuring the concentration of the major combustion product species such as CO_2 or H_2O by launching an initial collimated beam of radiation emitted by tunable diode laser along a line-of-sight path through the oxy-fuel combustion process;
- b) opposite the launch position the transmitted radiation is collected and transported to a photo detector (sensitive at the wavelength of interest) with a filter element;
- c) processing the optical signal by observing the amount of attenuation observed as the laser is tuned over a resonance absorption line, the integrated area of the absorption line divided by the line strength and path-length is directly proportional to the number density for a given temperature;
- d) estimating the air entrainment rate into the process using the fuel and oxidizer inlet composition and flow rates along with the ambient air composition, and using a difference between the theoretical value for complete combustion and the measured species concentration; and
- e) producing an electrical signal based on the estimated air entrainment rate for use in regulating one or more of the following variables: process pressure, fuel inlet flow rate, and oxidant inlet flow rate.

27. A method for indirectly monitoring H_2 concentration and/or hydrocarbons in a high temperature gas stream of an oxy-fuel combustion process comprising the steps of:

- a) measuring the concentration of H_2O by launching an initial collimated beam of radiation by a tunable diode laser along a line-of-sight path through a gaseous phase region of the process (preferably flue gas of the combustion process) in the spectral region where H_2O absorption transitions are found.

- b) opposite the launch position the transmitted radiation is collected and transported to a photo detector with a filter element;

- c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of H_2O ;

- d) a second measurement point is used either within the gas phase region or in a diverted stream of gas;

- e) measuring the difference between H_2O downstream and H_2O upstream of the O_2 gas introduction to back calculate the amount of H_2 and/or unburned hydrocarbons in the process stream; and

- f) producing an electrical signal based on the amount of unburned H_2 and/or hydrocarbons.

28. A method to monitor species X where X is a species of specific interest to an oxy-fuel combustion process, the method for monitoring comprising the steps:

- a) launching an initial collimated beam of radiation emitted by a tunable diode laser along a line-of-sight path through combustion products of the combustion process;

- b) opposite the launch position the transmitted radiation is collected and transported to a photo detector having a filter element;

- c) processing the optical signal by observing the amount of attenuation observed from the initial beam as the laser is tuned over a resonance absorption line of species X ; and

- d) producing an electrical signal based on the number density of species X .

29. An apparatus for monitoring a species X where X is a species of specific interest to a process, the apparatus comprising:

- a) a tunable diode laser for launching an initial collimated beam of radiation along a line-of-sight path through a gas phase of a process;

- b) a collector to collect the launched radiation, the collection positioned substantially opposite the tunable diode laser, the collector capable of transporting the collected radiation to a photo detector, the photo detector having a filter element;

- c) an optical processor for observing attenuation of the initial beam as it is tuned over a resonance absorption line of species X ; and

- d) means for producing an electrical signal based on the number density of species X .

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