

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



WIPO | PCT

(10) International Publication Number

WO 2013/170039 A2

**(43) International Publication Date
14 November 2013 (14.11.2013)**

(51) International Patent Classification:
G01N 21/61 (2006.01)

(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(21) International Application Number: PCT/US2013/040361

(22) International Filing Date: 9 May 2013 (09.05.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 61/645,330 10 May 2012 (10.05.2012) US

(71) Applicant: FUEL TECH, INC. [US/US]; 27601 Bellaire

Vista Parkway, Warrenville, IL 60555 (US).

(71) **Applicants** : CARMIGNANI, Paul, G. [US/US]; 908 Brocks End Court, Naperville, IL 60540 (US). BOYLE, John, M. [US/US]; 1047 North Lombard Avenue, Oak Park, IL 60302 (US). MAYHEW, Scott, M. [US/US]; 507 Dogwood Court, North Aurora, IL 60542 (US).

(74) Agent: **CARVIS, Thaddius, J.**; 102 North King Street, Leesburg, VA 20176 (US).

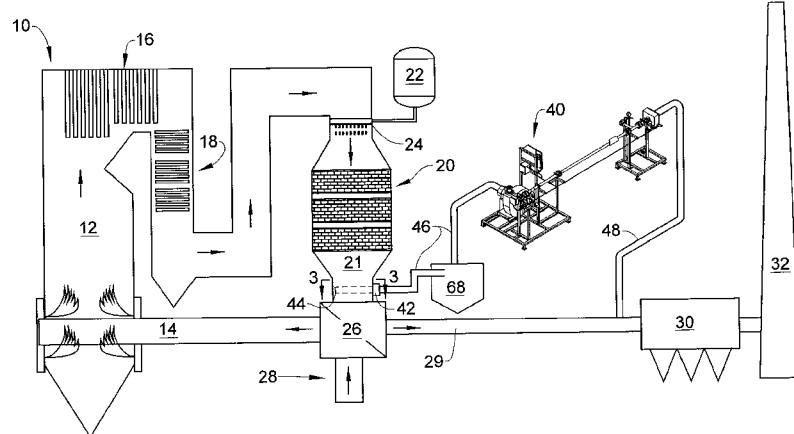
(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: EXTRACTIVE CONTINUOUS AMMONIA MONITORING SYSTEM

FIG. 1



(57) Abstract: Disclosed are methods and apparatus for treating and analyzing a gas stream to determine the ammonia concentration. A gas stream is continuously monitored to determine the ammonia concentration by extracting gas samples from one or more locations and sending it to a tunable diode laser absorption spectroscopy instrument for analysis. By proper placement of sampling probes within a duct, depending on the particular flow patterns that have been determined by suitable modeling, e.g., computational fluid dynamics or cold flow modeling, the valves can be operated manually or by a controller to take samples at predetermined locations within the duct. This will enable taking samples from particular locations, samples representative of the entire cross section, or samples that are an average of a particular cross section. It will be possible by judicious placement of the probes and operation of the valves to map the concentrations of ammonia at a plurality of load settings and will permit continuous control.

WO 2013/170039 A2

UNITED STATES PATENT APPLICATION

EXTRACTIVE CONTINUOUS AMMONIA MONITORING SYSTEM

Cross Reference and Priority Claim

[000] This application claims priority to U. S. Provisional Patent Application No. 61/645,330, filed May 10, 2012, the disclosure of which is incorporated herein by reference in its entirety.

Field of the Invention

[001] The invention relates generally to continuously monitoring a gas stream to determine the ammonia concentration by extracting gas samples from one or more locations of an apparatus and analyzing the samples by tunable diode laser absorption spectroscopy.

Background of the Invention

[002] To assess the performance of a number of processes in which urea or ammonia are employed, it is often necessary to have the ability to determine how much ammonia is in a process or effluent stream. Traditionally, samples have been extracted and analyzed by chemiluminescent techniques, resulting in extended lag times between sample acquisition and analysis. These methods also lacked a desired precision at low concentrations because they relied upon assumptions to make the necessary calculations.

[003] Recently, interest has turned to tunable diode laser (TDL) absorption spectroscopy. In a typical TDL installation, the transmitter and receiver are mounted directly to the ductwork. Since ammonia can convert to other compounds or be absorbed in ash at temperatures less than 500°F, the ideal installation location for a TDL is upstream of the air heater. Installations of this type are difficult for a variety of reasons. Access is frequently difficult due to limited space existing between the economizer or catalyst outlet and the air heater inlet. Walkways are frequently absent. TDL's rely upon the line of sight between the transmitter and receiver, with a longer distance aiding accuracy at low concentrations. However, as the distance increases, the required alignment of the device becomes more

difficult. Thermal cycles can also affect this alignment. Ash loading degrades the signal and in high ash environments, a longer TDL path length may not be possible. Maintenance is frequently difficult due to the instruments installed, location and the challenges with access.

[004] TDL's measure the ammonia concentration on a line of sight path between a transmitter and a receiver. If the gas flow is stratified and the ductwork is large, this ammonia concentration may not be indicative of the actual, overall ammonia concentration. For this reason, on larger units or units with multiple ducts, a typical TDL installation may require more than one transmitting and receiving unit.

[005] Many commercial processes use extractive techniques to obtain samples of off-gas from the exhaust. The extracted gas is typically cooled and then analyzed using mass spectrometry or non-dispersive infrared absorption methods or chemical cells. However, the steps required to obtain a sample of the off-gas from extractive techniques can result in time delays in acquiring the data. By contrast, a process using real time sensors could obtain selective measurements of the off-gas constituents and provide adjustment of the inputs to a furnace on a continuous feedback loop. In one example of a continuous extractive analysis, WO 97/499979 to Frish, *et al.*, describes a TDL system to monitor trace concentrations (e.g., on the order of one part per million) of ammonia in gases extracted from coal-fired utility boilers. The system includes a filter to remove particulates and a heater and temperature sensors that maintain the temperature of extracted gases. The device illustrated employs a Herriot cell to magnify TDL sensitivity in a small foot print, but this is not an ideal arrangement for use in obtaining accurate readings from a utility boiler where gas (and particulate) component compositions can vary across any given cross section.

[006] Both selective noncatalytic NO_x reduction (SNCR) and selective catalytic NO_x reduction (SCR) processes used for controlling nitrogen oxides release from power plants and other combustors, employ ammonia either directly or indirectly as a NO_x -reducing reagent. It must be fed at the right concentrations and temperatures with regard to the NO_x concentration to assure effective NO_x control without excessive ammonia slip. There is always a delicate balance, and control systems must have accurate information to assure

effective operation to comply with all regulations and guarantees as well as to avoid the practical problems of ammonium bisulfate production.

[007] What is needed is a system designed to solve the difficulties of a typical TDL installation. A useful system would be capable of sampling gases over a broad array of locations through probes designed and operated to assure that extracted gas samples can be taken that are representative of actual operation conditions.

[008] There is a present need for a process, apparatus and system that will enable the real-time analysis of ammonia concentration in a process or effluent stream.

Summary of the Invention

[009] The present invention provides processes, apparatus and systems for measurement of ammonia in a process or effluent stream.

[010] In one aspect, a process is provided for continuously monitoring ammonia (or other gas species) in an apparatus utilizing flowing gas streams containing ammonia, comprising: providing at least one (preferably a plurality) of hollow sampling probe(s), each comprising a hollow tube having an internal passage defined by a tube wall having at least one opening through the tube wall and means for connecting the internal passage to an intake line; locating a plurality of said probes within the flowing gas stream positioned to permit communication between the internal passage in the tubes with the gas in the flowing gas stream; providing at least one valve for each hollow probe (in the case of a plurality) to control gas flow through a probe; creating a negative pressure differential between each internal passage of each probe and the flowing gas stream; directing flow of gases from the flowing gas stream through a sample path positioned between a transmitter and a receiver for a tunable diode laser; maintaining the temperature of the gases in the sample path at a predetermined value; directing a beam of light, tuned to a selected wave length (e.g., a narrow band), from the transmitter through the gas stream in the sample path to the receiver and generating a signal representative of the received signal; based on the signal calculating the concentration of ammonia in the gas stream; and, preferably, utilizing the concentration of ammonia as calculated to control one or more operational parameters.

[011] In a preferred aspect the sample stream is redirected from the sample path to recombine with the flowing gas stream.

[012] In another aspect, an apparatus is provided, comprising: at least one (preferably a plurality) of hollow sampling probe(s), each comprising a hollow tube having an internal passage defined by a tube wall having at least one opening through the tube wall and means for connecting the internal passage to an intake line; means for locating a plurality of said probes within the flowing gas stream positioned to permit communication between the internal passage in the tubes with the gas in the flowing gas stream; at least one valve for each hollow probe (in the case of a plurality) to control gas flow through a probe; means for creating a negative pressure differential between each internal passage of each probe and the flowing gas stream; means for directing flow of gases from the flowing gas stream through a sample path positioned between a transmitter and a receiver for a tunable diode laser; means for maintaining the temperature of the gases in the sample path at a predetermined value; means for directing a beam of light, tuned to a selected wave length, from the transmitter through the gas stream in the sample path to the receiver and generating a signal representative of the received signal; means for, based on the signal, calculating the concentration of ammonia in the gas stream; and, preferably, means for utilizing the concentration of ammonia as calculated to control one or more operational parameters.

[013] In a further aspect, the invention provides a system employing the process and apparatus as disclosed.

[014] Other and preferred aspects of the invention are described below.

Description of the Drawings

[015] The accompanying drawings, which are incorporated in and constitute a part of this description, illustrate presently preferred embodiments of the invention, and together with the detailed description of the preferred embodiments given below, serve to explain the principles of the invention. As shown throughout the drawings, like reference numerals designate like or corresponding parts.

[016] **Fig. 1** is a schematic diagram of a combustion installation that takes advantage of the present invention employing a preferred embodiment of the process and system of the invention.

[017] **Fig. 2** is a schematic diagram showing greater detail of aspects of a system of the invention of the type shown in **Fig. 1**.

[018] **Fig. 3** is a cross section taken along line 3-3 in **Fig. 1**, showing a possible arrangement of sampling probes within a conduit containing a flowing gas stream of gases to be analyzed.

[019] **Fig. 4** is a cross section of a sampling probe taken along line 4-4 in **Fig. 3**.

Detailed Description of the Invention

[020] In describing the present invention, reference is made to the drawings, wherein a simplified, preferred embodiment is shown schematically. The drawings and the process and apparatus they represent will be described briefly below.

[021] As noted above, a gas stream from a combustor has not been easily susceptible to continuous, accurate analysis for target species like ammonia by available equipment. The invention addresses this concern and provides a simple, reliable, low-cost solution.

[022] **Fig. 1** is a schematic diagram of a combustion installation that takes advantage of the present invention to analyze a combustion effluent for ammonia slip, *i.e.*, the ammonia that is left after SNCR or SCR treatment of exhaust gases by either injecting ammonia itself or another chemical used to provide active NO_x reduction species.

[023] The combustion installation includes a combustor **10** having burners that provide thermal heat in combustion zone **12** by burning fuel from a source not shown with air supplied by duct work **14**. Hot combustion gases will pass through the furnace **10** in the direction indicated by the arrows, and the heat from combustion is transferred to heat exchangers **16** and **18** prior to passing into a selective catalytic reduction (SCR) reactor **20** wherein NO_x created during combustion can be treated with a NO_x-reducing agent such as ammonia or gasified urea (including ammonia and HNCO) to convert the NO_x to nitrogen and water. The NO_x-reducing agent is supplied, for example, by means of reagent storage tank **22** and injection grid **24**. Alternatively, many installations will benefit from selective non catalytic reduction (SNCR) using urea alone or other NO_x-reducing agent at higher

temperatures, *e.g.*, as taught by Epperly, *et al.*, in U. S. Patent No. 5,057,293, without requiring the reactor **20**.

[024] Following SCR reactor **20**, the combustion gases will flow through an air-to-air heat exchanger **26**, which is used to preheat outside air supplied via duct **28** for delivery to the combustion zone **12** via line **14**. The combustion gases leaving the heat exchanger **26** are cooled significantly by the time they are passed through duct work **29** to electrostatic precipitator (ESP) **30** wherein particulates are collected prior to passing the gases up stack **32**. This is a highly-simplified version of actual industrial or utility combustors and effluent treatment processes, but illustrates a workable scheme.

[025] A tunable diode laser gas analyzer apparatus of the invention **40** is shown generally in **Fig. 1** to include a support structure **42** for holding a plurality of hollow probes **44** (see **Fig. 3** for a schematic arrangement). An intake line **46** is provided to direct a flow of gases to analyzer apparatus **40** from the flowing gas stream following the SCR reactor **20** to the probes **44**.

[026] Each of the probes **44** comprises a hollow tube having an internal passage **47** defined by a tube wall **45** having at least one opening **49** through the tube wall and means for connecting the internal passage to noted intake line **46**. Once analyzed by passing through apparatus **40**, the gases are returned via line **48** to the stream of exit gases, preferably just downstream of the sampling point (not shown), but can be later say in duct **29** (as illustrated). Lines **46** and **48** are shown schematically only and are preferably stainless steel pipe, which tends to be rigid. If suitable flexible tubing is available, it can be used.

[027] The invention enables simplified and real-time analysis of the stream for ammonia taken from a stream of gases flowing from the SCR unit **20** in duct **21**, via intake line **46** to a suitable connection, such as intake flange **46'** on apparatus **40**, as best seen in **Fig. 2**. As will be apparent from the discussion of **Fig. 3**, the probes **44** can be fitted with valves and adjusted with the duct **21** to enable taking samples from particular locations, representative of the entire cross section, or an average of a particular cross section. A fan **50** is provided to pull the gases through apparatus **40** and return them to a suitable duct, say **29**, via line **48** attached by means of a suitable connection, such as flange **48'**. The gases to be analyzed are drawn into sample path **52**, typically a stainless steel tube, by a negative pressure

differential between each internal passage of each probe **44** and the flowing gas stream in duct **21**. The sample path **52** is insulated, *e.g.*, as shown partially at **54**, to maintain the gas temperature and to avoid injury to operators. A preferred length of the sample path **52** is twelve feet but this may vary as requirements dictate, *e.g.*, from about 3 to about 20 feet.

[028] The sample path **52** has sight glasses **56** and **56'** located on opposite ends, with **56** being at the transmitter end and **56'** being at the receiver end to protect the transmitter **60** and the receiver **62** for a tunable diode laser from any contamination by the hot gases being directed through the sample path. The sight glasses physically separate the transmitter **60** and the receiver **62** from the interior of the sample path **52** while still permitting the transmitter **60** to direct a beam of light, tuned to a selected wave length, and for the receiver **62** to receive it for analysis by logic and computation unit **64**. Electrical power to the transmitter and control signals to and from the logic and computation unit **64** can be supplied via electrical lines shown generally as **66**. A supply of cooling air, not shown, is preferably provided to each of the transmitter **60** and the receiver **62** units to maintain a safe operating temperature.

[029] The temperature of the gases in the sample path **52** is easily maintained at a predetermined value, *e.g.*, at least about 450°F, and preferably within the range of from 500° to 600° F, without any additional heat by maintaining a suitably high flow rate through the path **52**. The sample path can be heated by heaters, not shown, that can be embedded in insulation **54**, if necessary. It is an advantage of the invention is that the high flow rate of hot gases makes heating unnecessary except in anomalous situations. In the exemplary situation of a two inch diameter sample chamber path **52**, which is twelve feet long, a flow rate of 120 scfm (*e.g.*, from 20 to 300 scfm) provides a complete exchange of gases about eight times per second. The entire system residence time will typically be less than a second. This assures the gases will not cool substantially. In a target system residence time will be between 0.2 and 5 seconds, *e.g.*, about 1 second, preferably and that the target measurement volume residence time is within this range where temperatures can be maintained and extractive effectiveness retained, and preferably between 0.05 and 0.5 seconds. The high flow rate also can eliminate the need for a filter to remove ash in embodiments where the ash is never given the opportunity to collect. In others, the use of a

cyclone **68**, receiving gas from line **46** and discharging it to the analyzer apparatus **40**, can effectively handle significant ash loadings.

[030] The details of the wavelengths of light, electrical and temperature requirements for the particular tunable diode laser selected, will all be available from the manufacturer. We presently prefer Yokogawa TDLS200 analyzer, but there is no criticality in this selection. The analyzer is capable of directing a beam of light, tuned to a selected wave length, typically tuned within a narrow band (*e.g.*, a resolution of less than 0.02 nm) of wavelengths, from the transmitter **60** through the gas stream in the sample path **52** to the receiver **62** and generating a signal representative of the received signal. Based on the signal, the logic and computation unit **64** is capable of calculating the concentration of ammonia in the gas stream, and will do so. Based on this signal representative of the ammonia concentration, a process controller, *e.g.*, for the SCR reactor and ammonia supply will control one or more operational parameters.

[031] Detail and arrangement of the probes **44** are illustrated schematically in **Fig. 3**, with **Fig. 4** showing a cross section of one probe **44** taken along line **4-4** in **Fig. 3**. It can be seen that each probe **44** comprises a hollow tube having an internal passage defined by a tube wall having at least one opening through the tube wall and means for connecting the internal passage to an intake line. **Fig. 4** shows tube **44** having a central opening **45** with a hole **47** therethrough. As seen in **Fig. 3**, there can be a plurality of holes. Means, which may be simple brackets (represented by the outer dotted lines at **44** in **Fig. 1**, are provided to enable locating a plurality of the probes within the flowing gas stream in duct **21** and to position them effectively to permit communication between the internal passage **47** in the tubes with the gas in the flowing gas stream in duct **21**. At least one valve **70** is provided for each hollow probe to control gas flow through a probe. By proper placement of the probes within duct **21**, depending on the particular flow patterns that have been determined by suitable modeling, *e.g.*, computational fluid dynamics or cold flow modeling, the valves **70** can be operated manually or by a controller to take samples at predetermined locations within the duct **21**. This will enable taking samples from particular locations, samples representative of the entire cross section, or samples that are an average of a particular cross section. It will be possible by judicious placement of the probes **44** and operation of the valves **70** to map the concentrations of ammonia at a plurality of load settings and will

permit continuous control. The invention provides the ability to test at various locations along the flue gas path as boiler load changes without the need to install transmitter and receiver pairs at each location to be tested. While lacking the full mapping capability, it will be possible to install the above apparatus with a single probe, without any valve and still take advantages of some aspects of the invention.

[032] Systems employing the process and apparatus combine the disclosed features and incorporate details as necessary for a wide variety of industrial applications.

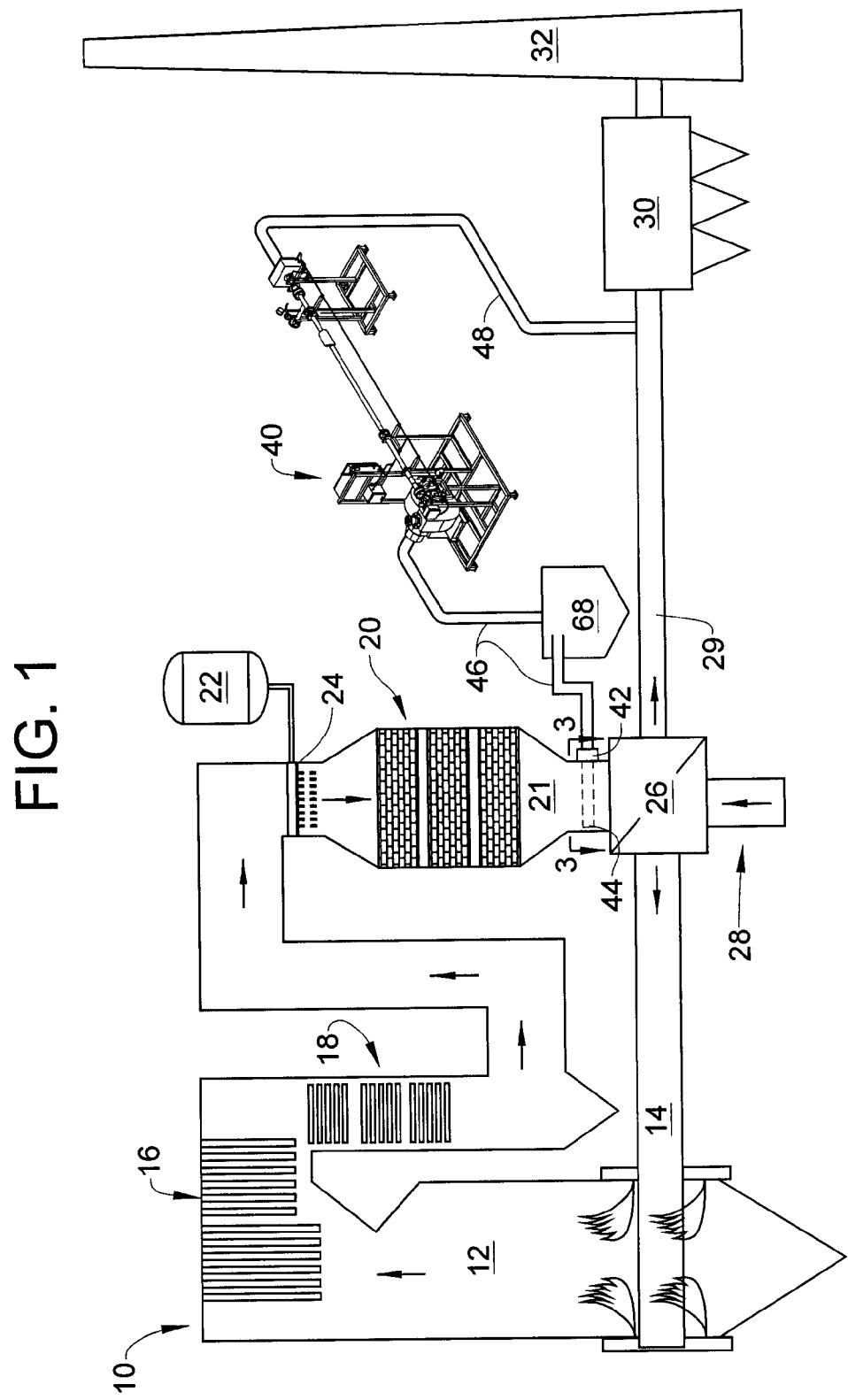
[033] The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the invention. It is not intended to detail all of those obvious modifications and variations, which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within the scope of the invention which is defined by the following claims. The claims are meant to cover the claimed components and steps in any sequence which is effective to meet the objectives there intended, unless the context specifically indicates the contrary.

What is claimed is:

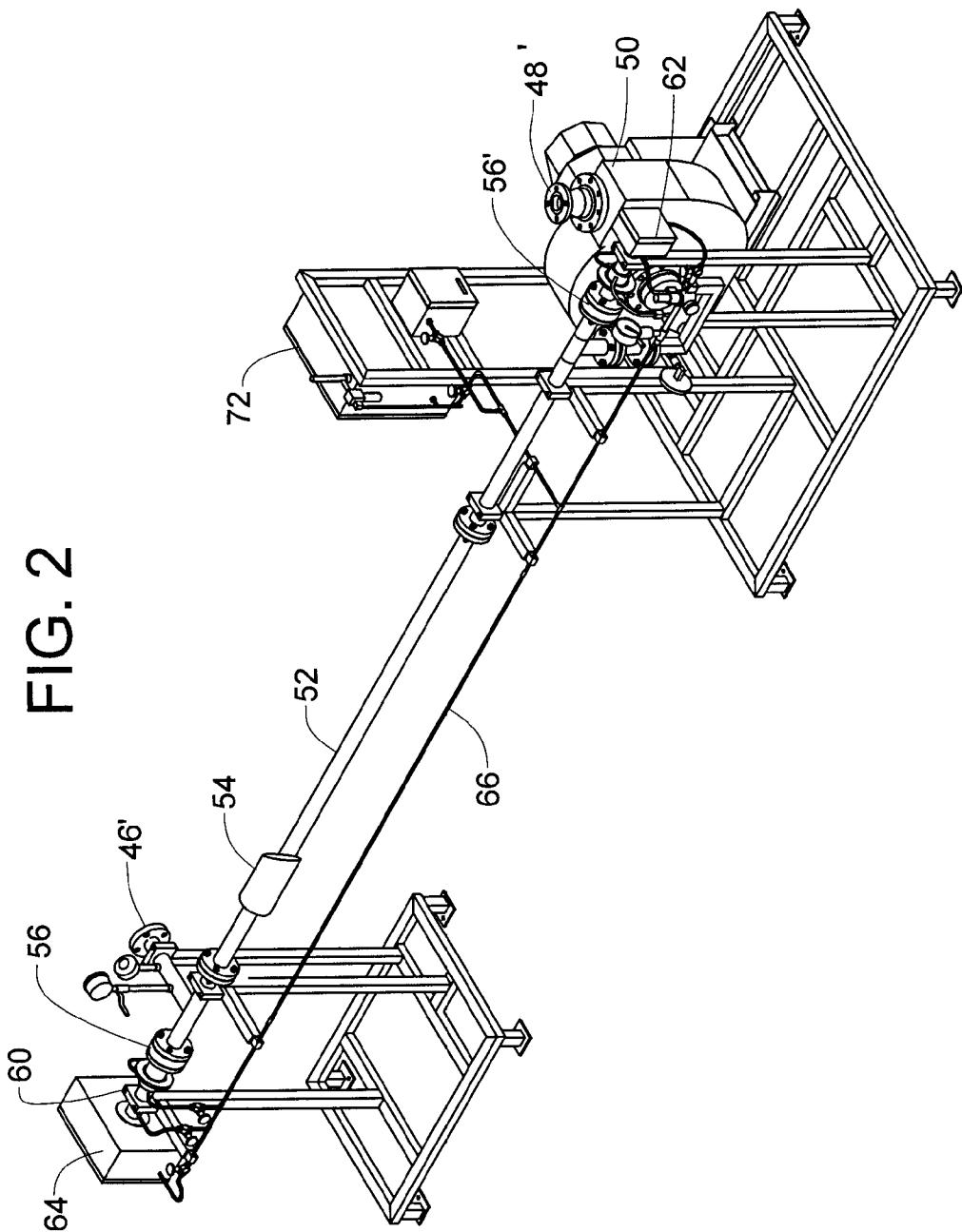
1. A process for continuously monitoring ammonia (or other gas species) in an apparatus utilizing flowing gas streams containing ammonia, comprising:
 - a. providing at least one hollow probe, each comprising a hollow tube having an internal passage defined by a tube wall having at least one opening through the tube wall and means for connecting the internal passage to an intake line;
 - b. locating at least one of said probes within the flowing gas stream positioned to permit communication between the internal passage in the tubes with the gas in the flowing gas stream;
 - c. creating a negative pressure differential between each internal passage of each probe and the flowing gas stream;
 - d. directing flow of gases from the flowing gas stream through a sample path positioned between a transmitter and a receiver for a tunable diode laser;
 - e. maintaining the temperature of the gases in the sample path at a predetermined value;
 - f. directing a beam of light, tuned to a selected wave length, from the transmitter through the gas stream in the sample path to the receiver and generating a signal representative of the received signal;
 - g. based on the signal calculating the concentration of ammonia in the gas stream.
2. A process according to claim 1, further including utilizing the concentration of ammonia as calculated to control one or more operational parameters.
3. A process according to claim 1 wherein the sample stream is redirected from the sample path to recombine with the flowing gas stream.
4. A process according to claim 1 wherein a plurality of probes are provided and providing at least one valve for each hollow probe to control gas flow through a probe;

5. An apparatus for continuously monitoring ammonia (or other gas species) in an apparatus utilizing flowing gas streams containing ammonia, comprising:
 - a. at least one hollow sampling probe, each comprising a hollow tube having an internal passage defined by a tube wall having at least one opening through the tube wall and means for connecting the internal passage to an intake line;
 - b. means for locating said probe or probes within the flowing gas stream positioned to permit communication between the internal passage in the tubes with the gas in the flowing gas stream;
 - c. means for creating a negative pressure differential between each internal passage of each probe and the flowing gas stream;
 - d. means for directing flow of gases from the flowing gas stream through a sample path positioned between a transmitter and a receiver for a tunable diode laser;
 - e. means for maintaining the temperature of the gases in the sample path at a predetermined value;
 - f. means for directing a beam of light, tuned to a selected wave length, from the transmitter through the gas stream in the sample path to the receiver and generating a signal representative of the received signal;
 - g. means for, based on the signal, calculating the concentration of ammonia in the gas stream.
6. The apparatus of claim 5, further including means for utilizing the concentration of ammonia as calculated to control one or more operational parameters.
7. The apparatus of claim 5, wherein a plurality of probes are employed and at least one valve is provided for each hollow probe to control gas flow through a probe.
8. A system comprising apparatus features of claim 5.

1/3



2/3



3/3

FIG. 3

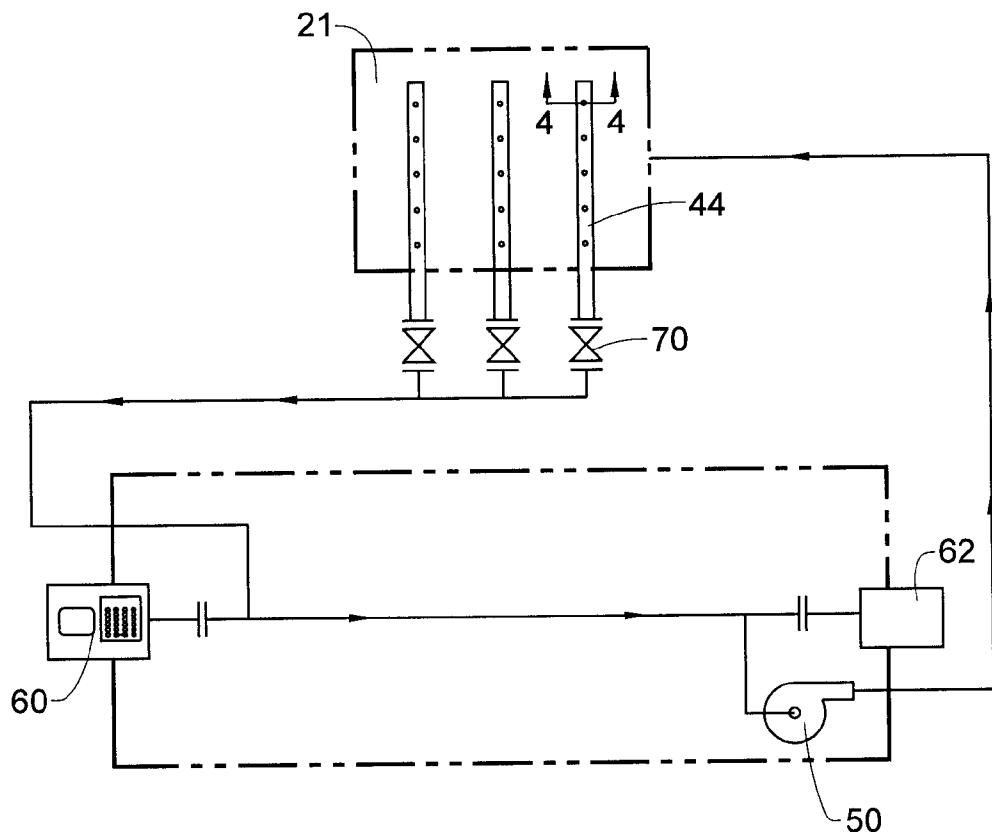


FIG. 4

