July 2, 1963 P. M. BROWN ETAL 3,096,157

METHOD AND APPARATUS FOR ANALYZING FUEL-AIR MIXTURES

Filed Nov. 18, 1960 2 Sheets-Sheet 1

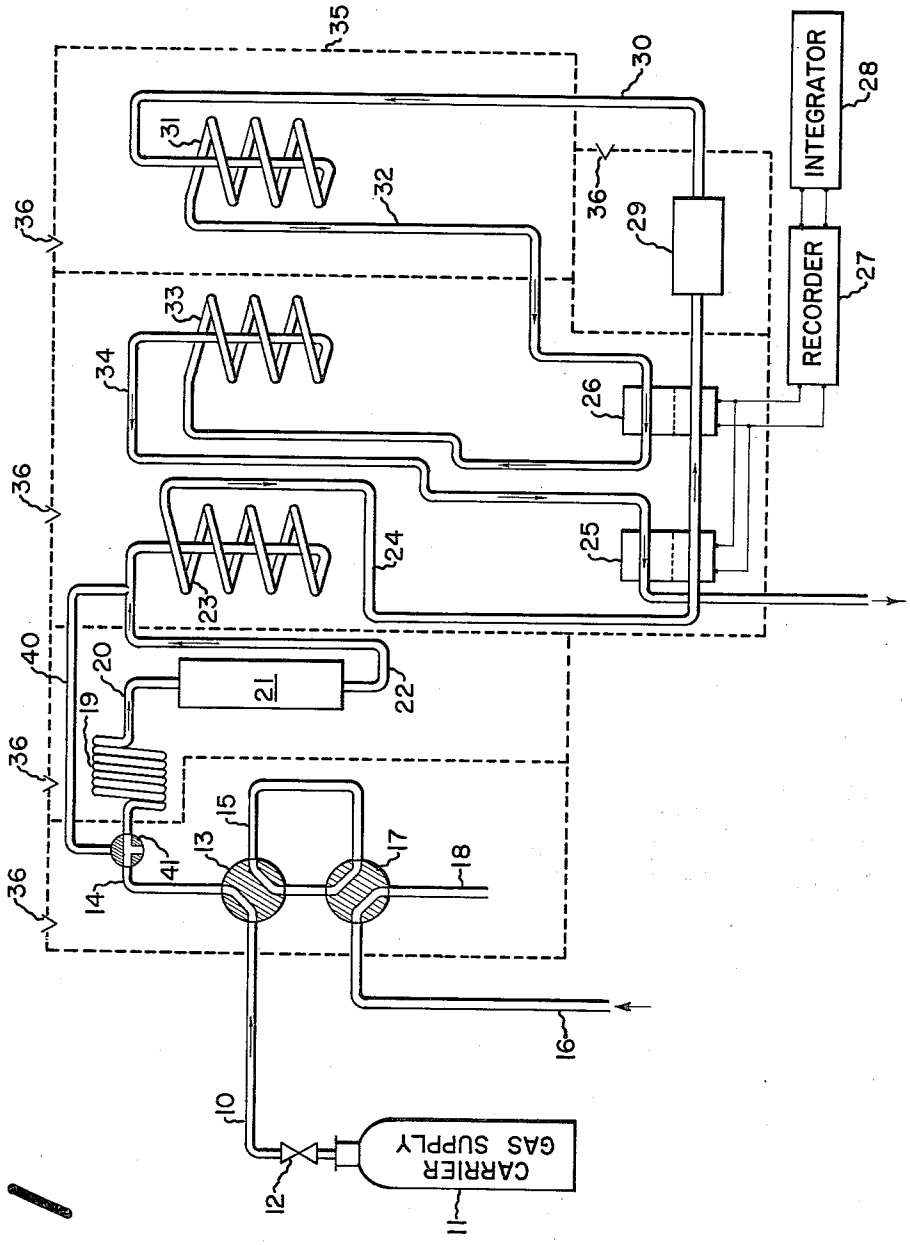


FIG. 1

INVENTORS
PAUL M. BROWN
DONALD R. O'MALLEY

BY

ATTORNEY

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FIG. 2

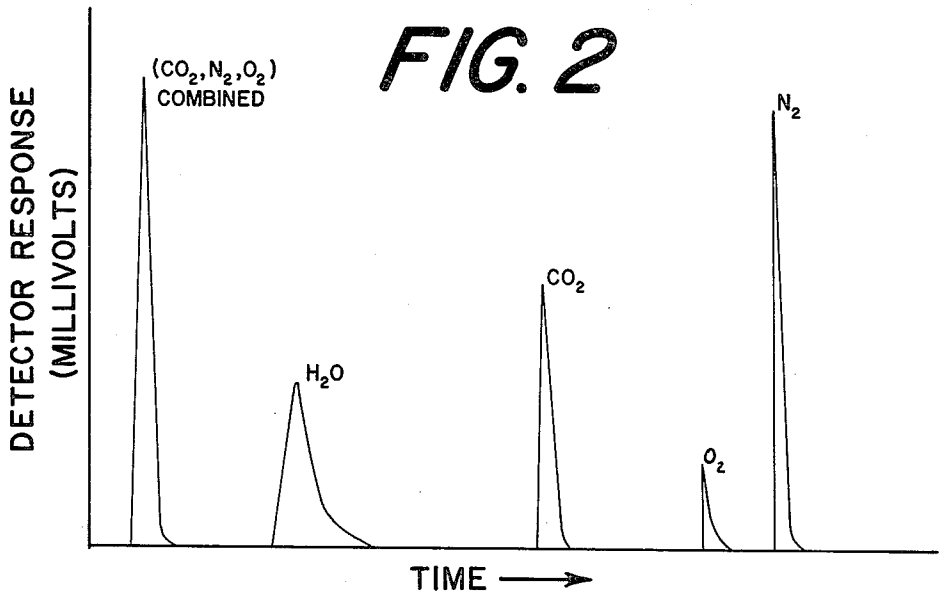


FIG. 3

WEIGHT OF CO_2 $= \frac{CO_2}{CO_2 + H_2O + N_2}$ (POUNDS PER POUND OF SAMPLE)

WEIGHT OF H_2O $= \frac{H_2O}{CO_2 + H_2O + N_2}$ (POUNDS PER POUND OF SAMPLE)

WEIGHT OF N_2 $= \frac{N_2}{CO_2 + H_2O + N_2}$ (POUNDS PER POUND OF SAMPLE)

WEIGHT OF AIR $= \frac{\text{WEIGHT OF } N_2}{0.75} = W_A$

WEIGHT OF CARBON $= \frac{12}{44} \times \text{WEIGHT OF } CO_2 = W_C$

WEIGHT OF HYDROGEN $= \frac{2}{18} \times \text{WEIGHT OF } H_2O = W_H$

$$\text{AIR/FUEL} = \frac{W_A}{W_C + W_H}$$

$$\text{C/H RATIO} = \frac{W_C}{W_H}$$

INVENTORS
PAUL M. BROWN
DONALD R. O'MALLEY
BY
ATTORNEY

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METHOD AND APPARATUS FOR ANALYZING FUEL-AIR MIXTURES

Paul M. Brown, O'Hara Township, Allegheny County, and Donald R. O'Malley, Fox Chapel Borough, Allegheny County, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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This invention generally relates to analyses of gas mixtures. More particularly, the invention relates to a method and apparatus for analyzing hydrocarbon fuel-air mixtures and/or the products resulting from combustion of such mixtures.

The control of combustion processes is based generally on analysis of the combustion products. From analysis of combustion products, the air requirements can readily be calculated and the air-fuel ratio of a fuel mixture supply properly regulated so as to achieve the highest degree of combustion efficiency. Thus, means for accurately analyzing hydrocarbon fuel-air mixtures either prior to or subsequent to combustion are highly desired. The system employed for such analysis should not only provide a high degree of accuracy, but should be simple in operation. Moreover, the system employed for analysis of the products resulting from combustion of hydrocarbon fuel-air mixtures should not depend upon the particular fuel which is subjected to combustion nor the extent to which the air-fuel mixture is burned.

The present invention provides a method and apparatus for accurately analyzing hydrocarbon fuel-air mixtures. In specific and preferred embodiment, the invention provides a method and apparatus for analyzing the products resulting from combustion of hydrocarbon fuel-air mixtures to thereby determine the air-fuel ratio of the mixture or the carbon to hydrogen ratio of the hydrocarbon fuel itself with a high degree of accuracy and without consideration of the particular hydrocarbon fuel undergoing combustion or the extent to which the combustion process has progressed.

In accordance with the present invention, a measured sample of a hydrocarbon fuel-air mixture or gaseous products resulting from combustion of such mixtures is substantially completely oxidized to convert the oxidizable carbon and hydrogen constituents of the mixture to carbon dioxide and water, respectively. The oxidation is accomplished by subjecting the gas sample to combustion so as to complete the conversion of any unburned fuel and to insure that substantially all carbon present is converted to carbon dioxide. At this stage the principal components of the oxidized gas sample are carbon dioxide, water, and nitrogen; the nitrogen resulting from the air originally present in the hydrocarbon fuel-air mixture. These components are then separated by gas chromatography and quantitatively determined. The carbon dioxide, water, and nitrogen values obtained are then converted to express the carbon-hydrogen ratio of the hydrocarbon fuel or the air-fuel ratio of the air-fuel mixture.

Both gas elution adsorption chromatography and gas-liquid partition chromatography are employed in the practice of the present invention. In both species of gas chromatography a sample gas is injected into one end of a chromatographic column packed with a suitable material so that the various compounds pass through the column at different rates and the components of the mixture emerge from the column at different times. In the chromatogram which is thereby obtained, each component of the mixture shows up as a separate peak and from the time it takes for it to appear, identification can be made; the size of the peak provides a measure of the concentration of each component. In gas adsorption chromatography a mixture of gaseous materials is separated on the basis of the difference in affinity for a solid adsorbent material which is employed in the chromatographic column. In gas-liquid partition chromatography the column is packed with an inert granular material on which has been deposited a coating of a high-boiling organic liquid such as dioctyl phthalate. The column is then eluated with an inert carrier gas such as helium. The components of the gaseous mixture partition between a gas phase in the interstitial spaces of the column and a liquid phase absorbed in the high boiling organic liquid coating of the granular solid particles. The velocity with which a particular component moves is dependent upon its partition coefficient, the latter being a measure of the solubility of the component in the stationary liquid phase.

The invention will be more fully understood from the following description when read in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a schematic view of the associated elements of a preferred embodiment of the apparatus of the present invention;

FIGURE 2 is a typical chromatogram obtained utilizing the method and apparatus of the invention; and

FIGURE 3 shows the mathematical equations employed to obtain the carbon-hydrogen ratio of the hydrocarbon fuel or the air-fuel ratio of the hydrocarbon fuel-air mixture from the water, carbon dioxide, and nitrogen values plotted in FIGURE 2.

In FIGURE 1 the numeral **10** designates a carrier gas inlet line which connects with a carrier gas supply source **11**. Valve **12** regulates the flow of carrier gas through line **10**. The carrier gas passes through line **10** to a four-way valve **13**. This valve directs the carrier gas either to preheater inlet line **14** or to sample chamber **15** which is adapted to contain a predetermined volume of the gas to be analyzed. The gas mixture which is to be analyzed flows through sample inlet line **16**. The gas stream entering line **16** may be the main stream or a portion withdrawn from the main stream as a representative sample thereof. A four-way valve **17** is positioned in line **16** to direct the gas flow to either sample chamber **15** or outlet line **18** which permits escape from the system of gas in excess of the predetermined volume desired for examination.

Line **14** leads to a preheater **19** which is in the form of a coiled tube wherein the gas stream is heated to the temperature of the combustor **21**. After passing through preheater **19**, the gas stream passes via conduit **20** to combustor **21**. Combustor **21** can be conventional apparatus suitable for effecting oxidative combustion reactions. In a preferred embodiment combustor **21** is a column of suitable dimensions in which there is placed an oxidizing agent such as copper oxide which supplies the oxygen needed for combustion. Combustor **21** can also take the form of a ceramic tube closed by a heater coil through which tube the gas stream and oxygen pass. The outlet of combustor **21** connects with conduit **22** which leads to a chromatographic column **23**, which in the modification of the drawings is in the form of a long coiled tube. Column **23** is filled with partitioning materials which are capable of separating water from the other components of the gas stream. The effluent gas stream from column **23** passes by way of conduit **24** through gas detecting devices **25** and **26** which are arranged in series for greater sensitivity. The gas detecting devices **25** and **26** can be any of the conventional devices employed for detecting changes in the composition of gas streams, such as thermal conductivity cells, gas density balances, and the like. The electrical potential or signal produced by

the gas detecting devices 25 and 26 is registered by recorder 27, which again can be any of the conventional potentiometric recording devices such as, for example, a conventional self-balancing electronic strip chart recorder which continuously plots potentiometer deflections against time. The various peaks on the curve plotted by the recording potentiometer correspond to the various components detected in the gas stream analyzed. The area of the curve under the various peaks indicates the concentration of the various components. In a preferred optional embodiment of the invention, a conventional integrator 28 can be employed in conjunction with the recorder 27 so as to automatically integrate the curve and provide the integrated numerical value for the various components. The integrator 28 can be a mechanical integrator of the ball-and-disk type, for example, or a circuit containing electronic integrating means can be used, as is well known in the art.

After passing through the detecting devices 25 and 26, the effluent stream from chromatographic column 23 passes through desiccator 29 which contains a water-absorbing material such as calcium chloride, "Drierite" (calcium sulfate), or the like. The water-free effluent from desiccator 29 consisting predominantly of carbon dioxide, nitrogen, and possibly oxygen is passed by conduit 30 to a second chromatographic column 31, which column contains a suitable adsorbent for separating the carbon dioxide component from the other components of the gas stream. The effluent from column 31 passes via line 32 through gas detecting device 26 to again produce a signal which is registered by recorder 27. The gas stream is then directed through chromatographic column 33 which contains a suitable adsorbent for preferentially separating the nitrogen present in the gas stream. The effluent from column 33 passes by line 34 through gas-detecting device 25 for determination of the amount of nitrogen in the stream. For proper temperature control the various elements of the apparatus are enclosed in a thermostated cell block 35 which is adapted to be heated and maintained at selected temperature levels. Thermostats 36 are provided to control the temperature throughout the various sections of cell block 39. Line 40 controlled by valve 41 permits by-passing of combustor 21.

To analyze gas mixtures in accordance with the present invention, a carrier gas from supply source 11 is flowed through line 10. The carrier gas can be any of the inert carrier gases known to be suitable for use in gas chromatography. It should be understood that by the term "inert carrier gas" we mean that the gas is inert with respect to the chromatographic separation. Suitable carrier gases include helium, argon, and the like. At the initiation of the analysis, the four-way valve 13 is positioned to direct the carrier gas from line 10 into inlet line 14 by-passing sample chamber 15. The combustion gas mixture to be analyzed is introduced through line 16 and flows through four-way valve 17. Valve 17 is positioned to direct the gas stream into sample chamber 15 which is calibrated to contain a known volume of gas at a particular temperature. It is preferred to maintain the sample chamber 15 at a temperature above about 100° C. to prevent liquid condensation. When the sample chamber 15 is completely filled with the predetermined volume of the gas to be analyzed, valve 17 is switched to direct the gas stream through outlet line 18 for escape from the system. The valve 17 can be operated manually or automatically by means well known in the art.

After the desired gas sample is obtained in sample chamber 15, valve 13 is switched either manually or automatically to direct the carrier gas from line 10 into sample chamber 15. The carrier gas sweeps the gas sample from chamber 15 into inlet line 14 and into preheater 19 where the gas stream is heated sufficiently so as to undergo substantially complete combustion. From preheater 19 the gas sample to be analyzed passes via line 20 into combustor 21. As previously stated, combustor 21 preferably

contains an oxidizing agent such as copper oxide and is maintained at a temperature above about 700° C. to insure substantially complete oxidation of the oxidizable carbon present in the gas stream. The oxidation or combustion products consisting mainly of carbon dioxide, water, nitrogen, and oxygen pass from combustor 21 through line 22 to chromatographic column 23 wherein the water is separated from the other components of the gas stream in accordance with known principles of gas chromatography. Column 23 is filled with a relatively low surface area granular material on which there is adsorbed a partitioning liquid which preferentially separates water from the other combustion products. A suitable granular packing material for use in column 23 is a crushed firebrick known commercially as Johns-Manville Corporation, Insulated Firebrick (Sil-O-Cel, C_{22}) of 40–80 mesh particle size. Other granular packing materials which can be employed include Haloport, which is a linear polymer of tetrafluoroethylene and which is marketed by the F. & M. Scientific Company of New Castle, Delaware, and Celite 545 which is a sintered diatomaceous earth marketed by Johns-Manville Corporation. Suitable partitioning liquid for coating the granular packing material are the high molecular weight polyethylene glycols which are marketed by Union Carbide Corporation and which are designated as Carbowax 20,000 etc. Preferably chromatographic column 23 is maintained at an elevated temperature of about 125° C. or above to reduce the time required for elution of water from the column. The carrier gas elutes the various components of the gas stream from column 23. The carbon dioxide, nitrogen, and oxygen components of the gas stream move through column 23 at a faster speed and emerge from the column before the water component of the gas stream which is separated by the partitioning liquid. The effluent emerges from column 23 via line 24 and passes through the detecting channel of the gas detecting devices 25 and 26. As indicated previously, the gas detecting devices 25 and 26 can be any of the conventional devices commonly employed in the art for detecting changes in the composition of gas streams. Perhaps, the most common of these detecting devices are thermal conductivity cells. The conventional conductivity cell employs a Wheatstone bridge, two arms of which are heated with platinum wires. One of the wires extends into a reference region through which a reference gas flows and the other extends into a testing region through which the gas being analyzed flows. The effluent stream from the chromatographic column 27, consisting of carrier gas and the separated components of the feed mixture that are eluted from the column, flows through the testing region of the thermal conductivity cell. When a gas is in contact with a heated platinum wire of the cell, the wire is cooled to an extent that depends upon the thermal conductivity of the gas, and when the composition of gas flowing through the testing region changes, its thermal conductivity changes and the temperature of the platinum wire changes correspondingly. As a result of the temperature change of the wire, its electrical resistance changes. The variations in the differences between the resistances of the platinum wires in the testing and reference regions are reflected in the unbalance of the Wheatstone bridge as indicated by recording potentiometers. The recorded deviations can be related to the composition of the gas being analyzed. As indicated previously, an integrating device of conventional type can be employed in conjunction with recorder 27 so as to provide a direct indication of the amount of the various components detected in the effluent stream from column 23.

After determination of the water component in the gas stream, the effluent from column 23 is passed through desiccator 29. Desiccator 29 contains a material which preferentially adsorbs the water and thus removes it from the system. Such water-adsorbing materials as calcium chloride, "Drierite," or calcium sulfate and the like can

be employed in desiccator 29 for this purpose. Upon emerging from desiccator 29, the water-free gas stream consisting of carrier gas, carbon dioxide, nitrogen, and possibly oxygen passes via line 30 into chromatographic column 31 wherein separation of the carbon dioxide is achieved. Column 31 can be either a gas adsorption chromatography column or a gas-liquid partition chromatography column. Materials such as silica gel and the like which adsorb carbon dioxide in preference to other components of the gas stream can be employed in column 31. Column 31 is operated at a temperature which can be conveniently maintained constant such as for example about 40° C. The carbon dioxide being more strongly held by the partitioning or adsorption material employed in column 31 is the last component to be eluted from the column by the carrier gas. The effluent emerging from column 31 passes via line 32 through the gas detecting device 26 so that the amount of carbon dioxide in the gas stream is detected. After passing through gas detecting device 26 the effluent stream passes into chromatographic column 33 which contains a material which preferentially separates the nitrogen component of the stream.

A valuable class of materials which can be employed in column 33 for separation of nitrogen from oxygen with which it may be associated comprises the crystalline or dehydrated zeolites known as "molecular sieves." As is known in the art, molecular sieves are crystalline dehydrated zeolites, natural or synthetic, having a well-defined physical structure. Natural zeolites which can be dehydrated to serve as molecular sieves include materials such as chabasite, phacolite, gmelinite, harmotome, and like materials of rigid three-dimensional structure. Suitable natural zeolites are relatively rare. This has led to the development of synthetic zeolites which upon dehydration are effective molecular sieves. The zeolites that can be dehydrated to form molecular sieve adsorbents are hydrous aluminum silicates, usually containing one or more sodium, potassium, calcium, or barium cations, although zeolites containing hydrogen, ammonium, or other metal cations are known. These zeolites have a characteristic three-dimensional aluminum silicate anionic network, the cations neutralizing the anionic charge. Upon dehydration, the three-dimensional lattice network of the crystal is maintained, leaving intercommunicating channels, pores, or interstices of molecular dimensions within the crystal lattice. For each dehydrated zeolite of this type, the cross-sectional diameter of the channels is a characteristic and is substantially uniform throughout the crystal. The synthetic crystalline, partially dehydrated metallo-alumino silicate zeolitic adsorbents are presently available items of commerce marketed by Linde Air Products Company, 30 East 42nd Street, New York, New York under the name of "Molecular Sieves" 5X, 13X, and so forth, and these have pore diameters of 5 and 13 Angstroms, respectively.

The chromatographic column 33 is operated at a temperature which can be easily maintained relatively constant such as, for example, about 40° C. The effluent from column 33 is passed through gas detecting device 25 for the determination of the nitrogen content of the gas mixture.

Thus, as a result of the foregoing procedure, the amount of nitrogen, carbon dioxide, and water are determined. From these values, the air-fuel ratio of the fuel supply mixture and the carbon-hydrogen ratio of the hydrocarbon fuel can be determined.

The present invention can be advantageously employed for analyzing gas mixtures resulting from combustion of hydrocarbon fuels in general. By means of the invention the air-fuel ratios of hydrocarbon fuel supply mixtures can be accurately and rapidly determined. Thus, it is possible by means of the present invention to determine the air-fuel ratios required for proper combustion in internal combustion engines, jet engines, boilers, furnaces, gas turbines, and the like. One special application of the invention is in the analysis of exhaust gases from automotive-internal combustion engines to determine the combustion efficiency of the engine, as well as the amount of undesirable combustion products such as unburned hydrocarbons which pass into the atmosphere. Thus, the invention finds particular utility in air pollution control programs where it is essential to have means for accurately and rapidly analyzing exhaust gases of automotive engines.

A further understanding of the invention can be obtained from the following illustrative examples.

Example I

The exhaust gas of an automotive engine is to be analyzed in the apparatus illustrated in the drawing. The purpose is to determine the air-fuel ratio of the fuel mixture supplied to the engine. These ends are accomplished by determining quantitatively the carbon dioxide, nitrogen, and water content of the engine exhaust gas.

At the start of the process, four-way valve 13 is positioned so as to direct the carrier gas from line 10 into inlet 14, preheater 19, combustor 21, and thence through the remainder of the system. Upon its emergence from chromatographic column 23, the carrier gas flows through detecting devices 25 and 26.

The exhaust gas from the automotive engine which is to be analyzed enters the system through line 16. Four-way valve 17 is set to direct the incoming gas into sample chamber 15. When the sample chamber 15 is filled with the predetermined volume of exhaust gas, valve 17 is switched to permit the exhaust gas to flow through outlet line 18 and to escape from the system. After obtaining the desired sample of the exhaust gas in chamber 15, valve 13 is switched to direct the flow of carrier gas through sample chamber 15 to sweep the exhaust gas sample therefrom. The carrier gas sweeps the exhaust gas sample from sample chamber 15 into inlet line 14, and thence into preheater 19. In preheater 19, the exhaust gas sample is heated to a temperature of about 750° C. From preheater 19, the gas is passed into combustor 21. Combustor 21 contains a quantity of copper oxide catalyst which supplies oxygen needed to complete the combustion of all combustible components in the gas stream. Combustor 21 is operated at a temperature of about 750° C. or above. As a result of oxidation or combustion in combustor 21, all of the oxidizable carbon present in the gas sample is converted to carbon dioxide while the hydrogen is converted to water. The oxidized products from combustor 21 are then passed through chromatographic column 23. This column is packed with granular Celite particles which are coated with Carbowax 400, which material preferentially separates the water from the gas stream. The effluent from column 23 passes via line 24 through the testing channels of the thermal conductivity cells 25 and 26. The electrical signal produced by the thermal conductivity cells 25 and 26 is registered by the recording potentiometer 27 and a curve indicating changes in the composition of the gas stream is traced on a chart. Integrator 28 automatically integrates the area of the curve which represents the water component of the gas stream to provide directly the numerical value for the water present in the exhaust gas sample. The effluent stream from chromatographic column 23 after passing through the thermal conductivity cells 25 and 26 passes into desiccator 29 wherein calcium chloride is employed to adsorb the water and remove it from the system. The remainder of the gas stream then passes through chromatographic column 31 which is a column four feet in length packed with silica gel of about 30–100 mesh particle size to effect separation of carbon dioxide. The carbon dioxide which is held more strongly in column 31 is the last component to emerge from the column. The carbon dioxide is quantitatively determined by passing the effluent from column 31 through thermal

conductivity cell 26. After determining its carbon dioxide content, the gas stream proceeds through line 32 into chromatographic column 33. Column 33 is filled with 5A molecular sieves which are available commercially from Linde Air Products Company under the designation "Molecular Sieves 5X." The nitrogen is preferentially absorbed by the molecular sieves in column 33. The quantity of nitrogen is determined by passing the effluent from column 33 through thermal conductivity cell 25 which transmits to recorder 27 an electrical signal proportional to the amount of nitrogen detected.

A plot of the thermal conductivity cell readings against time is shown in FIGURE 2 of the drawings. The water, carbon dioxide, and nitrogen components of the gas stream are represented by individual peaks and the size of each peak provides a measure of the concentration of these components. By substituting these determined values in the equations illustrated in FIGURE 3, the air-fuel ratio of the fuel mixture supplied to the engine and the carbon-hydrogen ratio of the fuel is readily determined.

In Example I, we have described the procedure for analyzing the exhaust from an automotive engine to determine the air-fuel ratio of the fuel mixture burned in the engine. The method and apparatus of the invention are readily adapted for analyzing combustion gas streams such as the exhausts from automotive engines to determine the efficiency of the combustion process which occurs in the engine, and also the total unburned hydrocarbons in the engine exhaust. This application of the invention is described in the following example.

Example II

In addition to carbon dioxide and water, the exhaust gases of internal combustion engines, such as automotive engines, frequently contain carbon monoxide and unburned or partially burned hydrocarbons. These latter partially burned hydrocarbons are characteristically carbonyl compounds, alcohols and/or peroxides and may be conveniently designated by the term "total unburned hydrocarbon." The determination of this value gives an indication of the amount of pollutants being discharged into the atmosphere as well as the combustion efficiency of the engine, and is accomplished as follows:

The exhaust gas from the automotive engine which is to be analyzed enters the system through line 16. The four-way valve 17 is set to direct the incoming gas into sample chamber 15. After trapping the desired sample of exhaust gas in chamber 15, valve 13 is switched to direct the flow of carrier gas through chamber 15 to sweep the exhaust gas from the inlet chamber into line 14. Valve 41 is positioned to direct the gas sample from line 14 through line 40 directly to the inlet of chromatographic column 23 by-passing preheater 19 and combustor 21. The water content of the gas sample is separated and detected in column 23 and the effluent therefrom is passed successively through chromatographic columns 31 and 33 for separation and detection of the carbon dioxide and nitrogen components as in Example I. After detection of these components a second sample of the same gas is introduced through sample chamber 15 and line 14 to preheater 19 where the temperature of the gas stream is raised, and thence into combustor 21 for conversion of substantially all of the combustibles present in the sample to carbon dioxide and water. The effluent from combustor 21 then passes successively through chromatographic columns 23, 31, and 33 for determination of the increase in carbon dioxide and water content of the gas sample after being subjected to combustion in combustor 21. The difference in the values of carbon dioxide and water before and after combustion in combustor 21 provides a direct measure, after calculation of carbon and hydrogen weights of the total unburned hydrocarbon as a fraction of the total fuel charge or as an absolute concentration per unit volume of exhaust gas.

Example III

An alternative procedure to that described in Example II for determining the amount of unburned hydrocarbons in exhaust gas involves first pretreating the exhaust gas to remove carbon dioxide and water contained therein. This can be accomplished by contacting the exhaust gas sample with calcium or potassium hydroxide to remove the carbon dioxide and a suitable desiccant such as anhydrous alumina, etc. to remove water. The gas remaining after this treatment contains substantially only nitrogen, oxygen, and unburned or partially burned hydrocarbons. The exhaust gas sample is then analyzed as described in detail in Example I. The carbon dioxide and water values obtained from the analysis provide a direct measure of the amount of unburned hydrocarbons in the exhaust gas sample.

While the description in the preceding examples relates specifically to analysis of automotive engine exhaust, it is to be understood that the same procedure is followed for analysis of the gaseous products of combustion of other internal combustion engines, jet engines, boilers, furnaces, gas turbines, and the like.

From the foregoing it is apparent that we have developed a method and apparatus which can be used to rapidly and accurately analyze gaseous products resulting from combustion of hydrocarbon fuels. It is possible by means of the invention to rapidly determine the air-fuel ratio and the carbon-hydrogen ratio of hydrocarbon fuels in a relatively simple manner without having knowledge as to the particular hydrocarbon fuel employed or the extent to which the fuel has undergone combustion. Moreover, the invention makes it possible to accurately determine the air-fuel ratios which extend over exceptionally wide ranges.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

We claim:

1. A method of analyzing gaseous mixtures of hydrocarbon fuels and air which comprises: extracting a sample of predetermined volume of the gaseous mixture to be analyzed, subjecting the said sample to oxidative combustion under conditions to effect substantially complete combustion of the combustible components of said sample, and then passing said oxidized gas sample through a series of chromatographic separation zones adapted selectively to separate the various components of said oxidized gas sample and detecting the separated components of the oxidized gas sample as they emerge from the separation zones selective therefor.

2. A method of analyzing gaseous mixtures of hydrocarbon fuels and air which comprises: extracting a sample of predetermined volume of the gaseous mixture to be analyzed, subjecting the said sample to oxidative combustion under conditions whereby the resulting oxidized gas sample contains as its principal components carbon dioxide, water, and nitrogen, and then sequentially passing said oxidized gas sample through a series of chromatographic separation zones, each zone being adapted to preferentially separate one of the principal components of the oxidized gas sample, and detecting the separated carbon dioxide, water, and nitrogen components of the oxidized sample, as they emerge from the separation zones selective therefor.

3. A method of analyzing gaseous mixtures of hydrocarbon fuels and air which comprises: extracting a sample of predetermined volume of the gaseous mixture to be analyzed, subjecting the said sample to oxidative combustion under conditions whereby the resulting gas sample contains as its principal components carbon dioxide, water, and nitrogen, then passing the oxidized gas sample to a chromatographic separation zone to separate the water present in the gas sample, detecting said separated water as it emerges from the chromatographic separa-

tion zone, subsequently removing the separated water from the system, passing the substantially water-free oxidized gas sample to a second chromatographic separation zone to separate carbon dioxide, detecting the carbon dioxide component of the oxidized gas sample as it emerges from the chromatographic separation zone, passing the substantially water-free oxidized gas sample to a third chromatographic separation zone to separate nitrogen from the sample, and detecting the separated nitrogen of the oxidized gas sample as it emerges from the chromatographic separation zone.

4. A method of analyzing gaseous mixtures resulting from combustion of hydrocarbon fuels and air which comprises: continuously passing a stream of carrier gas through a combustion zone which is maintained under oxidative conditions to effect substantially complete combustion of the combustible gaseous substances passing through said zone, while so passing the carrier gas stream introducing upstream of the said combustion zone a predetermined volume of the gas mixture to be analyzed, passing the carrier gas and the oxidized gas sample from the combustion zone to a series of chromatographic separation zones adapted selectively to separate the various components of said gas sample, detecting and measuring the separated components of the oxidized gas sample as they emerge from the separation zones selective therefor.

5. A method of analyzing gaseous mixtures resulting from combustion of hydrocarbon fuels to determine the amount of unburned hydrocarbons therein which comprises: extracting a sample of predetermined volume of the gaseous mixture to be analyzed, chromatographically separating the carbon dioxide and water components of the gas sample, detecting and measuring the separated water and carbon dioxide components of the gas sample, and then subjecting a second sample of the gaseous mixture to oxidative combustion under conditions whereby the combustible components of the gas sample are substantially completely oxidized, chromatographically separating the carbon dioxide and water components in the oxidized gas sample in a series of chromatographic zones adapted selectively to separate said carbon dioxide and water components, detecting and measuring the separated carbon dioxide and water components in the oxidized gas sample as they emerge from the separation zones selective therefor to provide a comparison between the amount of carbon dioxide and water in the gas sample before and after oxidation of the gas sample.

6. A method of analyzing gaseous mixtures of hydrocarbon fuels and air which comprises: extracting a sample of predetermined volume of the gas mixture to be analyzed, passing said gas sample through a bed which contains an oxidation catalyst and which is maintained at an elevated temperature sufficient to effect substantially complete oxidation of the oxidizable components in said gas sample whereby the resulting gas sample contains as its principal components carbon dioxide, water, and nitrogen, then passing the oxidized gas sample through a chromatographic separation column packed with a material capable of preferentially separating the water present in the gas sample, detecting the separated water as it emerges from the said chromatographic column, subsequently removing the separated water from the system, passing the substantially water-free oxidized gas sample to a second chromatographic separation column packed with a material capable of preferentially separating the carbon dioxide present in the gas sample, detecting the separated carbon dioxide as it emerges from the said chromatographic separation column, and then passing the substantially water-free oxidized gas sample to a third chromatographic separation column packed with a material capable of preferentially separating the nitrogen component of the gas sample, and detecting the separated nitrogen of the oxidized gas sample as it emerges from the chromatographic separation column.

7. A method of determining the fuel-air ratio of an engine exhaust which comprises: extracting a sample of predetermined volume of the engine exhaust, subjecting the said sample to oxidative combustion under conditions whereby the resulting gas sample contains as its principal components carbon dioxide, water, and nitrogen, then passing the oxidized gas sample to a chromatographic separation zone to separate the water present in the gas sample, detecting said separated water as it emerges from the chromatographic separation zone, subsequently removing the separated water from the system, passing the substantially water-free oxidized gas sample to a second chromatographic separation zone to separate carbon dioxide, detecting the carbon dioxide component of the oxidized gas sample as it emerges from the chromatographic separation zone, passing the substantially water-free oxidized gas sample to a third chromatographic separation zone to separate nitrogen from the sample, detecting the separated nitrogen of the oxidized gas sample as it emerges from the chromatographic separation zone, and converting the water, carbon dioxide, and nitrogen values to express the air-fuel ratio of the original hydrocarbon fuel-air supply mixture.

8. A method of analyzing gaseous mixtures resulting from combustion of hydrocarbon fuels to determine the amount of unburned hydrocarbons therein which comprises: treating the gaseous mixture to be analyzed to remove carbon dioxide and water which may be contained therein, subjecting a sample of predetermined volume of the gaseous mixture to oxidative combustion under conditions whereby the combustible components of the gas sample are substantially completely oxidized, chromatographically separating the carbon dioxide and water components of the oxidized gas sample in a series of chromatographic zones adapted selectively to separate said carbon dioxide and water components, detecting and measuring the separated carbon dioxide and water components in the oxidized gas sample as they emerge from the separation zones selective therefor to provide an indication of the total amount of unburned hydrocarbons present in the sample.

9. Apparatus for analysis of gaseous mixtures resulting from combustion of hydrocarbon fuels comprising in combination: a sample chamber calibrated to contain a predetermined volume of gas sample at a particular temperature, a conduit system in communication with said sample chamber adapted to convey a stream of inert carrier gas, a conduit system in communication with said sample chamber adapted to convey a stream of a gaseous mixture to be analyzed, valve means in said gaseous mixture conduit system adapted to direct the gas to be analyzed to said sample chamber, valve means in said carrier gas conduit system for directing carrier gas through said sample chamber, a combustion unit in communication with said sample chamber and having an inlet through which said carrier gas and gas sample are admitted, said combustion unit being adapted for effecting substantially complete oxidative combustion of said gas sample, a conduit from said combustion unit leading to a first chromatographic separation column for selectively separating one component of the oxidized gas sample, an effluent line from said chromatographic separation column passing through a gas detecting device and thence to the inlet of a second chromatographic separation column, retention means positioned between the second chromatographic separation column and said gas detecting device, for selectively removing and retaining the component selectively separated in said first chromatographic separation column, an effluent line from said last-mentioned chromatographic separation column passing through a gas detecting device and thence to an inlet of a third chromatographic column, an effluent line from said last-mentioned chromatographic separation column passing through a gas detecting device.

10. The apparatus of claim 9, wherein the gas detecting means comprises a thermal conductivity cell.

11. Apparatus for analysis of gaseous mixtures resulting from combustion of hydrocarbon fuels comprising in combination: a sample chamber calibrated to contain a predetermined volume of gas sample at a particular temperature, a conduit system in communication with said sample chamber adapted to convey a stream of inert carrier gas, a conduit system in communication with said sample chamber adapted to convey a stream of a gas mixture to be analyzed, valve means in said gas mixture conduit system adapted to direct the gas to be analyzed to said sample chamber, valve means in said carrier gas conduit system for directing carrier gas through said sample chamber, a heater unit in communication with said sample chamber adapted for raising the temperature of the carrier gas and gas sample, a combustion unit having an inlet through which said carrier gas and gas sample is admitted, said combustion unit being adapted for effecting substantially complete oxidative combustion of the gas sample, a conduit from said combustion unit leading to a first chromatographic separation column for selectively separating water from the oxidized gas sample, an effluent line from said chromatographic separation column passing through a gas detecting device and thence to the inlet of a second chromatographic separation column, desiccating means positioned between the second chromatographic separation column and said gas detecting device, for selectively removing and retaining water selectively separated in said first chromatographic separation column, an effluent line from said last-mentioned chromatographic separation column passing through a gas detecting device and thence to an inlet of a third chromatographic separation column, an effluent line from said last-mentioned chromatographic separation column passing through a gas detecting device, and means for maintaining the said sample chamber and chromatographic separation columns at selected relatively constant temperatures.

12. Apparatus for analysis of gaseous mixtures resulting from combustion of hydrocarbon fuels comprising in combination: a sample chamber calibrated to contain a predetermined volume of gas sample at a particular temperature, a conduit system in communication with said sample chamber adapted to convey a stream of inert carrier gas, a conduit system in communication with said sample chamber adapted to convey a stream of a gaseous mixture to be analyzed, valve means in said gaseous mixture conduit system adapted to direct the gas to be analyzed to said sample chamber, valve means in said carrier gas conduit system for directing carrier gas through

said sample chamber, a combustion unit in communication with said sample chamber and having an inlet through which said carrier gas and gas sample are admitted, said combustion unit being adapted for effecting substantially complete oxidative combustion of said gas sample, a conduit from said combustion unit leading to a first chromatographic separation column for selectively separating water from the oxidized gas sample, an effluent line from said chromatographic separation column passing through a gas detecting device and thence to the inlet of a second chromatographic separation column, desiccating means positioned between the second chromatographic separation column and said gas detecting device, for selectively removing and retaining water selectively separated in said first chromatographic separation column, an effluent line from said last-mentioned chromatographic separation column passing through a gas detecting device and thence to an inlet of a third chromatographic column, an effluent line from said last-mentioned chromatographic separation column passing through a gas detecting device, a by-pass conduit for said combustion chamber providing direct communication from said sample chamber to said first chromatographic separation column.

13. Apparatus for analysis of combustible gaseous mixtures comprising the combination of a combustion chamber for subjecting a sample of the gaseous mixture to be analyzed to substantially complete oxidative combustion, means in association with the combustion chamber for establishing a flow of inert carrier gas through said chamber, means for introducing a measured sample of the gaseous mixture to be analyzed into the carrier gas stream, a series of chromatographic separation means adapted selectively to separate the principal components of the oxidized gas sample, means for detecting the separated components of the oxidized gas sample as they emerge from the chromatographic separation means selective therefor.

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