

Oct. 2, 1956

J. W. HUTCHINS ET AL

2,765,409

METHOD OF AND APPARATUS FOR ANALYZING HYDROCARBON GASES

Filed Oct. 30, 1950

2 Sheets-Sheet 1

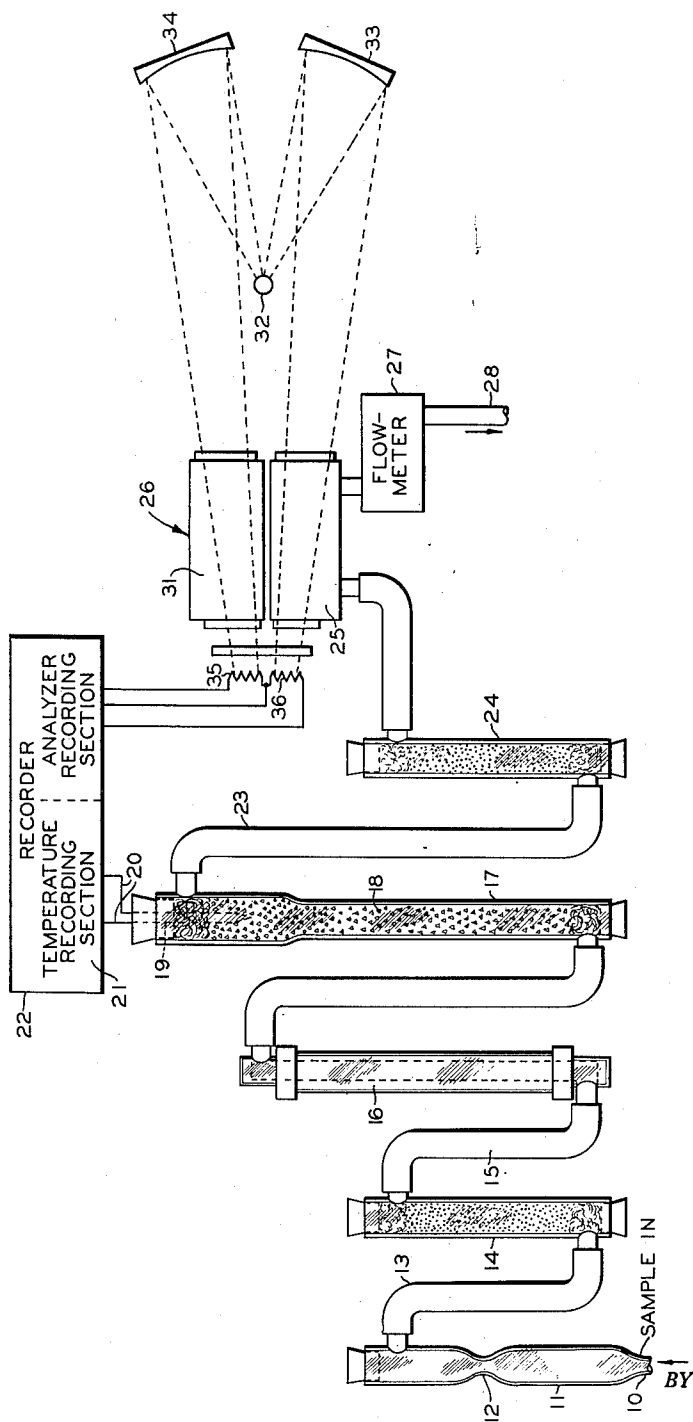


FIG. 1.

INVENTORS.
J. W. HUTCHINS
E. C. MILLER

Hudson & Young
ATTORNEYS

Oct. 2, 1956

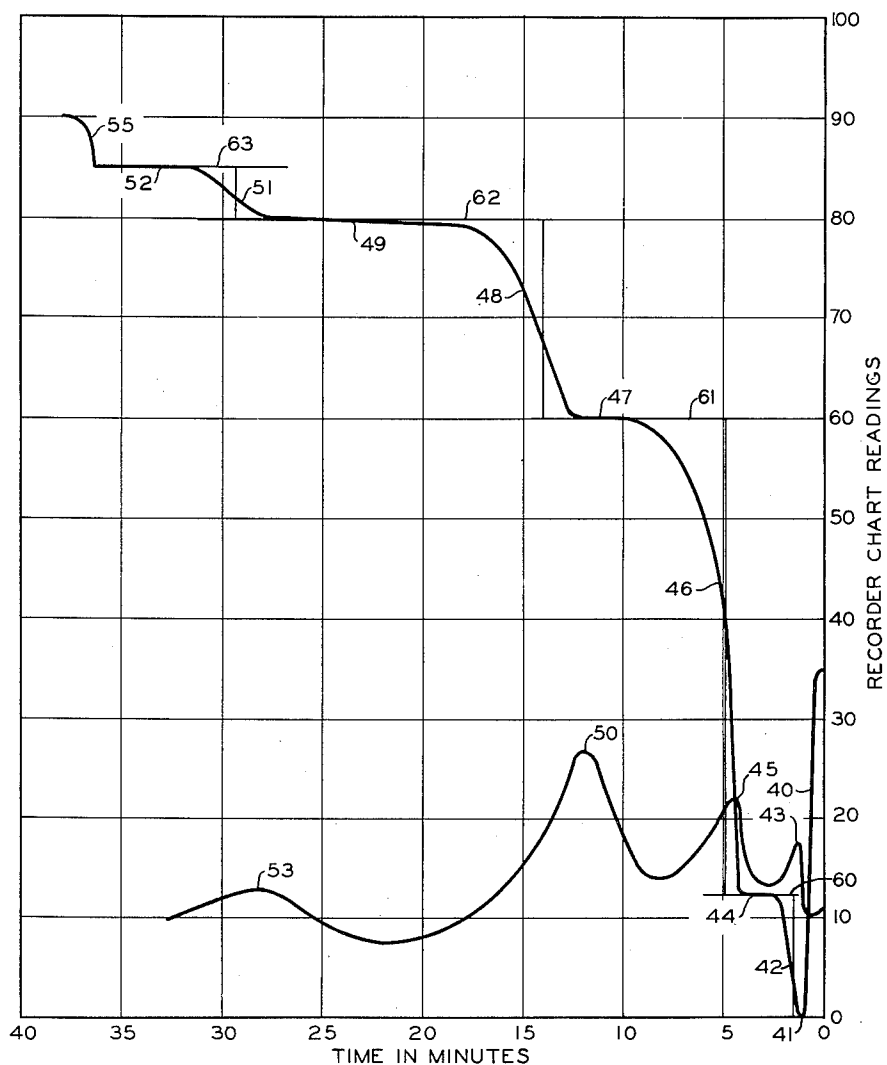
J. W. HUTCHINS ET AL

2,765,409

METHOD OF AND APPARATUS FOR ANALYZING HYDROCARBON GASES

Filed Oct. 30, 1950

2 Sheets-Sheet 2



INVENTORS.

J. W. HUTCHINS
E. C. MILLER

BY

Hudson & Young
ATTORNEYS

1

2,765,409

METHOD OF AND APPARATUS FOR ANALYZING HYDROCARBON GASES

Joseph W. Hutchins and Elmer C. Miller, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

Application October 30, 1950, Serial No. 192,908

12 Claims. (Cl. 250—43.5)

This invention relates to a method of analyzing hydrocarbon gases. In one specific aspect, it relates to a method of and apparatus for analyzing natural gas or cracked gas.

Heretofore, there has been no convenient method of analyzing hydrocarbon gases in a quick and efficacious manner when it has been desired to obtain such rapid analysis at the site of a gas well. In one prior method, an analysis has been made to determine the gasoline content, that is, the proportion of C_5 and higher hydrocarbons, by passing the gas through a tube of activated charcoal containing a measured amount of this substance, the charcoal being distilled after a predetermined amount of gas has been passed therethrough to determine the content of C_5 and higher hydrocarbons which are selectively adsorbed by the charcoal. In this method, the distillation is carried out after a desired degree of saturation has been reached but considerable difficulty has been encountered in determining when this degree of saturation has been attained. The activated charcoal adsorbs the hydrocarbons selectively in the order of increasing number of carbon atoms and, as it becomes saturated with a particular hydrocarbon component of the feed gas, the temperature of the charcoal rises. As a result, as each component is adsorbed, a high temperature or hot zone moves from the bottom to the top of the charcoal and this movement can be followed by touch. By thus following a number of high temperature zones, corresponding to the respective components selectively adsorbed, through the charcoal tube by touch, an operator can determine very closely when the charcoal has reached its optimum degree of saturation.

The method of our invention enables this crude procedure of following a high temperature zone by touch, up through the charcoal-containing tube, to be eliminated. Further, quantitative analysis of the lower boiling hydrocarbons in the gas is readily obtained, which analysis could not readily be furnished by the previously known method, since only the most readily adsorbed hydrocarbons, that is, those boiling in the gasoline range, could be determined by this previously used method. This quantitative analysis is extremely valuable in determining whether the residue gas from a particular natural gas stream is a rich gas or a lean gas, that is, whether or not it contains a high proportion of ethane and propane with respect to the quantity of methane.

It is an object of this invention to provide an improved method of and apparatus for analyzing natural gas or cracked gas.

It is a still further object to provide a method which is rapid in operation, and sufficiently accurate for practical purposes.

Various other objects, advantages and features of the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawings:

Figure 1 is a flow diagram of suitable apparatus for carrying out our method; and

2

Figure 2 is a view of a recorder tape produced by the apparatus of Figure 1.

Referring now to Figure 1, the gas sample to be analyzed is fed through a line 10 to a vessel 11 containing a fritted disc filter 12. From this tube, gas is conveyed by a line 13 to a tube 14 containing a suitable material for absorbing carbon dioxide and hydrogen sulfide for a purpose to be hereinafter described. A suitable material for this purpose is a sodium hydroxide asbestos preparation, which is known in the trade as "Ascarite." From the tube 14, the gas is passed through a line 15 and a flow controller 16, which maintains a constant flow rate, to the lower end of a tube 17 which is filled with activated charcoal 18, or other suitable selective adsorption material. A thermocouple 19 is disposed at the top of the tube, this thermocouple being connected by leads 20 to a recording galvanometer 21 which conveniently forms a part of a recorder 22. The effluent from the selective adsorption zone defined by the activated charcoal within tube 17 is removed by a line 23 and passed through a desiccating tube 24 for the removal of moisture to a sample cell 25 forming a part of the optical system of an infra-red analyzer 26. From the cell 25, the stream under analysis passes through a flowmeter 27 to a waste conduit 28 or other suitable type of disposal.

The analyzer 26 includes a standard cell 31, a source 32 for passing twin beams of radiation to the respective mirrors 33, 34 from which the beams are reflected and passed through the cells 25, 31, respectively, to a pair of bolometers 35 and 36. The bolometers are connected in a Wheatstone bridge circuit, preferably of the type shown in the copending application of Joseph W. Hutchins, Serial No. 103,158, filed July 5, 1949, entitled "Analyzer," now Patent No. 2,579,825. This bridge circuit actuates a suitable recording apparatus which can conveniently be included within the recorder device 22. The recorder produces a trace which is representative of the infra-red absorption produced by the material passing through the cell 25, as compared with the absorption of a standard fluid in cell 31. As shown in the aforementioned copending application, the recorder can also include a recalibrating system which periodically passes a standard fluid through cell 25 and readjusts the bridge circuit to compensate for changes produced by drift of circuit components and other disturbing factors.

The operation of our method will be explained in connection with the analysis of a stream of natural gas containing nitrogen, carbon dioxide, hydrogen sulfide, hydrogen, methane, ethane, and higher hydrocarbons of various isomeric forms. The gas stream, however, does not ordinarily contain an appreciable quantity of olefins or other unsaturated hydrocarbons. The hydrogen sulfide and carbon dioxide are removed in tube 14 for the reason that the former compound causes corrosion and fogging of silver chloride windows with resultant inaccuracies in the reading of the instrument while the carbon dioxide produces a strong unwanted infra-red absorption band. The desiccating material in tube 24 removes water from the effluent of the adsorption zone which also would interfere with proper operation of the infra-red recording device.

As flow of the natural gas stream through tube 17 is initiated, there is an initial period during which the air is purged from the adsorption zone and sample cell, this period being indicated by line 40, Figure 2. Following a very short period 41 during which the charcoal becomes saturated with hydrogen and nitrogen, methane begins to appear in the effluent from the adsorption zone, the remaining hydrocarbon components being adsorbed within the tube 17. The appearance of methane in the effluent stream produces an increase in infra-red absorption which

3

is reflected by a rising portion 42 of the graph and a corresponding rise 43 in the temperature curve produced by galvanometer 21. The curve levels out and forms a plateau 44. During this period, the charcoal is becoming saturated with ethane and the effluent contains substantially all the methane present in the feed together with an additional small quantity which is desorbed from the charcoal by the ethane and higher hydrocarbons. When the charcoal becomes saturated with ethane, this material also appears in the effluent, thus producing a further increase in the infra-red absorption characteristics of the effluent and causing a temperature rise 45 and a sloping portion 46 upon the infra-red analyzer curve. This sloping portion 46 merges into a second plateau 47, during which period the charcoal is becoming saturated with propane, and the effluent gases contain all the methane and ethane in the feed together with a small proportion of these materials which are desorbed from the charcoal by the propane and heavier hydrocarbons. In similar fashion, a sloping portion 48 and a plateau 49 of the curve indicate the presence of propane in the effluent as does the temperature rise 50, the effluent containing methane, ethane and propane during this period. When the charcoal becomes saturated with butane, a similar sloping portion 51 and plateau 52 are formed together with a temperature rise 53 indicating that the charcoal has become saturated with butane and this material now appears in the effluent together with the other hydrocarbons previously noted. The sloping portion 55 indicates the time at which the charcoal becomes saturated with pentane and higher hydrocarbons and this material starts to appear in the effluent.

In utilizing our method as an improvement upon the previously known analysis scheme hereinbefore mentioned, the feed to the tube 17 is stopped immediately at the beginning of plateau 52. At this time, the activated charcoal has adsorbed thereon substantially all of the pentanes and higher hydrocarbons, that is, the components boiling within the gasoline range. The charcoal can then be distilled to determine the total amount of these gasoline range hydrocarbons in the amount of gas fed to the testing unit, as determined by flow controller 16. This is greatly superior to the prior method of following temperature changes, as by touching the sides of the tube and following the several high temperature zones up the tube.

By an inspection of the recorder chart, or by comparing this chart with similar charts made from samples of known compositions, the amounts of methane, ethane, propane, and butane in the sample can be roughly determined. This enables a rough determination to be made of the richness of residue gas to be obtained from a natural gasoline plant and the amount of natural gasoline obtained from this particular sample. The recorder chart can be utilized to obtain a more accurate quantitative analysis of the gas by constructing an idealized curve such as is shown as a fine line upon Figure 2, the vertical ordinates being constructed so that an equal area of a sloping portion of the curve is included on each side of each such ordinate. During the period 41, it is known that the air originally present in the system is being evacuated, the volume passing out of the system during this interval being measured by flowmeter 27. During the plateau period 60, it is known that the effluent consists substantially of methane together with nitrogen and hydrogen. The percentage of each material in the effluent is determined from the vertical position of plateau 60 by comparing the height of this plateau with the deflection obtained upon the recorder chart by a stream of pure methane. By applying the percentage thus obtained to the total volume of effluent as measured by flowmeter 27, the amounts of methane, nitrogen and hydrogen leaving the system during this period are calculated.

During the plateau portion 61, it is known that the

4

effluent consists substantially of nitrogen, hydrogen, methane and ethane, the relative proportions of these constituents being determined by comparing the height of plateau portion 61 with the height of plateau portion 60 and the deflection produced upon the tape by a stream consisting of pure ethane. This percentage is applied to the gas leaving the system during this period as measured by flowmeter 27 to determine the amounts of methane, ethane, nitrogen and hydrogen therein. In a similar manner, plateau portion 62 determines the proportions of nitrogen, hydrogen, methane, ethane and propane leaving the system, as determined by flowmeter 27, during the interval represented by this portion 62 of the graph and plateau portion 63 determines the proportions of nitrogen, hydrogen, methane, ethane, propane, and butane in effluent leaving the system during this period as determined by flowmeter 27. The percentage compositions being determined as indicated with respect to methane and ethane. By adding the amounts of the several constituents leaving the system during the respective periods defined by the plateaus 60 to 63, inclusive, analysis is carried out quantitatively to a rather high degree of accuracy, at any rate, to a precision suitable for practical work.

Many refinements can be made upon this system of analysis. For example, the material adsorbed by the charcoal can be distilled and added to the proportions of the various components to obtain a still better approximation of the content of the gas entering the system during the period from the beginning of the measurement to the end of plateau portion 63. Alternatively, where the analysis of the lighter components is of paramount importance, it can be assumed that the charcoal zone contains, at the end of the test, substantially all of the pentanes and higher hydrocarbons together with an estimated amount of butane and negligible amounts of the lower hydrocarbons.

The slope of the portions 42, 46, 48 and 51 is due, in part, to changes in composition of the effluent from the adsorption zone and in part to the fact that a certain time lag is produced by the volume of the sample cell and conduit leading thereto through the drier, which causes the curve to be of a sloping nature rather than straight, as in the idealized curve. The first variation can be compensated for by graphical integration of the sloping portions of the curve while the second factor can be compensated for by applying a correction factor based upon the known volumes of the conduits, drier, tube and sample cell. Finally, the adsorptive powers of the charcoal vary in accordance with the size of the carbon chain in the molecules of test gas. This produces a distortion of the lengths of the plateau portions which can be compensated for by applying a correction factor based upon the known adsorption coefficients of the charcoal for different hydrocarbon materials. When these factors are taken into account, an extremely precise quantitative analysis can be performed.

It is to be understood that the method of our invention is not to be limited to natural gas or cracked gas but is applicable to the analysis of many different types of hydrocarbon streams, as those skilled in the art will understand. Furthermore, materials other than charcoal can be used in the selective adsorption zone provided that they have suitable selective adsorption properties for the components of the test stream. Finally, ultraviolet or even visible radiation can be substituted for infra-red radiation. The use of ultraviolet radiation is advantageous in many cases in that there is a considerable variation between the absorption characteristics of saturated and unsaturated materials for ultraviolet radiation. As a result, streams containing a substantial proportion of both types of hydrocarbons can be advantageously analyzed by the use of ultraviolet radiation.

While the invention has been described in connection with present, preferred embodiments thereof, it is to be understood that this description is illustrative only and is

5

not intended to limit the invention, the scope of which is defined by the appended claims.

We claim:

1. The method of analyzing a mixture of hydrocarbon gases which comprises passing a mixture of hydrocarbon gases to be analyzed through a zone wherein the components of said mixture are selectively adsorbed, whereby the components of said gaseous mixture appear, in succession, in the effluent gas stream from said zone in the order of increasing number of carbon atoms per molecule, directing a beam of radiation through the effluent stream from said zone, and measuring the intensity of said radiation beam after it has passed through said effluent stream, said mixture of hydrocarbon gases being passed through said zone while the intensity of said radiation beam is being measured.

2. The method of analyzing a mixture of hydrocarbon gases which comprises passing a mixture of hydrocarbon gases to be analyzed through a zone wherein the components of said mixture are selectively adsorbed for a period of time sufficient for the components of said gaseous mixture to appear, in succession, in the effluent gas stream from said zone in the order of increasing number of carbon atoms per molecule, directing a beam of radiation through said effluent stream from said zone, and measuring the intensity of said radiation beam after it has passed through said effluent stream.

3. The method of analyzing a mixture of hydrocarbon gases which comprises passing a mixture of hydrocarbon gases to be analyzed through a zone wherein the components of said mixture are selectively adsorbed, whereby the components of said gaseous mixture appear, in succession, in the effluent gas stream from said zone in the order of increasing number of carbon atoms per molecule, directing a beam of infrared radiation through the effluent stream from said zone, and measuring the intensity of said beam of radiation after it has passed through said effluent stream, said mixture of hydrocarbon gases being passed through said zone while the intensity of said radiation beam is being measured.

4. The method in accordance with claim 3 further comprising the step of measuring the temperature of the outlet end of said zone while said gas is being passed there-through.

5. The method of analyzing a gas selected from the group consisting of natural gas and cracked gas which comprises passing such a gas to be analyzed through a zone wherein the hydrocarbon components of said gas are selectively adsorbed, whereby the hydrocarbon components of said gaseous mixture appear, in succession, in the effluent gas stream from said zone in the order of increasing number of carbon atoms per molecule, directing a beam of radiation through the effluent stream from said zone, and measuring the intensity of said radiation beam after it has passed through said effluent stream, said gas being passed through said zone while the intensity of said radiation beam is being measured.

6. The method of analyzing a stream of natural gas which comprises removing carbon dioxide, hydrogen sulfide and water vapor from a stream of natural gas, passing the resulting stream of said natural gas at a uniform rate through a zone containing a mass of adsorbent wherein the components of said gas are selectively adsorbed, whereby the hydrocarbon components of said gas appear, in succession, in the effluent gas stream from said

6

zone in the order of increasing number of carbon atoms per molecule, directing a beam of infrared radiation through the effluent stream from said zone, and measuring the intensity of said radiation beam after it has passed through said effluent stream, said gas being passed through said zone during the time the intensity of said radiation beam is being measured.

7. The method in accordance with claim 6 further comprising the steps of terminating the flow of gas through said zone when a particular hydrocarbon component appears in the effluent stream from said zone, and thereafter distilling said mass of adsorbent to determine the hydrocarbon components adsorbed thereon.

8. Apparatus for analyzing a mixture of gases comprising, in combination, a vessel filled with a material which selectively adsorbs hydrocarbon gases in accordance with the number of carbon atoms per molecule, means for passing a mixture of hydrocarbon gases to be analyzed through said vessel whereby the hydrocarbon components of said gaseous mixture appear, in succession, in the effluent gas stream from said vessel in the order of increasing number of carbon atoms per molecule, a cell having radiation transparent windows, means to direct the effluent gas from said vessel through said cell, a source of radiation, means to direct a beam of radiation from said source through said cell, and means to measure the intensity of said radiation beam after its passage through said cell.

9. The combination in accordance with claim 8 wherein said vessel is filled with activated charcoal.

10. The combination in accordance with claim 8 wherein said source of radiation provides radiation in the infrared spectrum.

11. The combination in accordance with claim 8 further comprising means to measure the rate of flow of the effluent gas from said vessel.

12. The combination in accordance with claim 8 further comprising temperature measuring means disposed in said vessel adjacent the outlet opening therein.

References Cited in the file of this patent

UNITED STATES PATENTS

1,522,848	Vorees et al. -----	Jan. 13, 1925
2,212,681	Dunn -----	Aug. 27, 1940
2,345,219	Sanderson -----	Mar. 28, 1944
2,373,113	Francis -----	Apr. 10, 1945
2,382,381	Calvert -----	Aug. 14, 1945
2,386,831	Wright -----	Oct. 16, 1945
2,395,489	Major et al. -----	Feb. 26, 1946
2,547,212	Jamison et al. -----	Apr. 3, 1951
2,575,519	Imhoff -----	Nov. 20, 1951
2,601,272	Frost -----	June 24, 1952
2,603,553	Berg -----	July 15, 1952

OTHER REFERENCES

Altieri: "Gas Analyses" pages 69, 75, 95-98, 114, 443, published by American Gas Assn., Inc., N. Y. C., 1945.

Mellon, M. G.: "Analytical Absorption Spectroscopy," 1950 ed., pp. 490, 504 and 505, John Wiley and Sons, N. Y.

Altieri: "Gas Analysis and Testing of Gaseous Materials," pp. 391-399. Published by American Gas Assn., Inc., N. Y. (1945).

Garner: "Charcoal As An Adsorbent," Natural Gas, vol. 5, No. 11, pp. 3, 4, 46, 48, 50, 54, 56, Nov. 1924.