Jan. 6, 1970 B. O. AYERS 3,488,155

ANALYSIS OF GAS STREAMS

Filed July 18, 1966

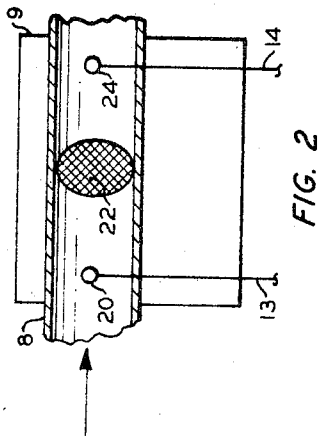

FIG. 2

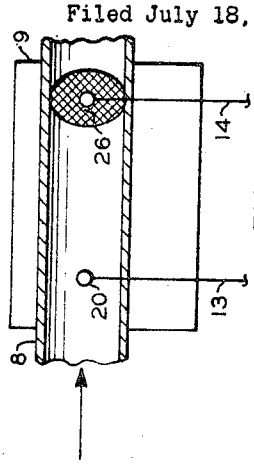

FIG. 3

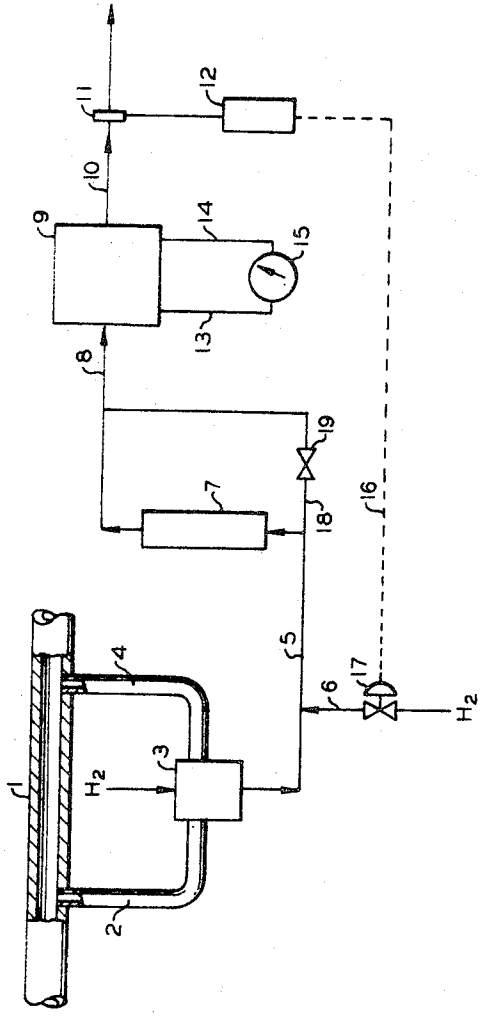

FIG. 1

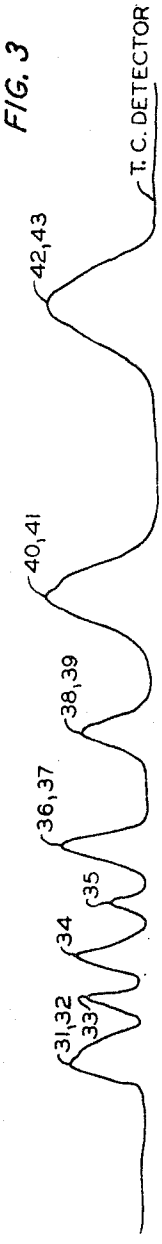

FIG. 4a

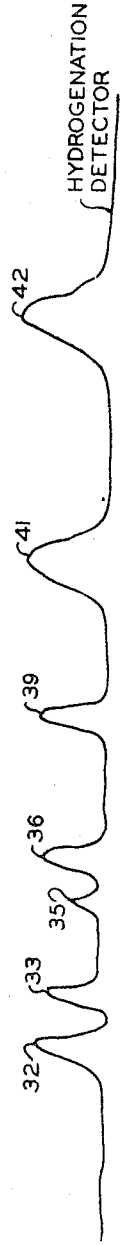

FIG. 4b

INVENTOR
B. O. AYERS

BY Young & Quigg
ATTORNEYS

United States Patent Office 3,488,155
Patented Jan. 6, 1970

3,488,155

ANALYSIS OF GAS STREAMS

Buell O. Ayers, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

Filed July 18, 1966, Ser. No. 565,842
Int. Cl. G01n 33/04, 33/06
U.S. Cl. 23—232 13 Claims

ABSTRACT OF THE DISCLOSURE

A process and apparatus in which hydrogen is added to a gaseous hydrocarbon stream which may contain hydrogenatable material, and the amount of hydrogenatable material is indicated by the difference in temperature of said gas stream, measured first before and second during or after hydrogenation over a hydrogenation catalyst. The components of said gaseous hydrocarbon stream of different molecular weight may first be spaced apart by the differential rate of their passage through a gas chromatography column. By measuring the degree of hydrogenation, the composition of the stream can be controlled to contain a predetermined proportion of hydrogenatable material. By measuring the amount of hydrogen in the effluent from the hydrogenation zone, the composition of the stream can be controlled to contain the desired amount of hydrogen prior to hydrogenation.

This invention relates to analysis of gas streams. In one of its aspects it relates to a method for detecting the presence of hydrogenatable components in a gas stream by passing same over a hydrogenation catalyst and detecting a temperature rise due to hydrogenation of hydrogenatable components within said gas stream.

In another of its aspects the invention relates to an apparatus for detecting the presence of hydrogenatable components in a gas stream, the apparatus comprising a hydrogenation catalyst support means, and means for detecting a temperature rise due to hydrogenation of gas streams passing across a hydrogenation catalyst on said support means.

Analysis of gas streams is an important part in maintaining proper controls for many chemical processes. It is known to detect oxidizable components by passing the same over an oxidizing means in the presence of oxygen and measuring the rise in temperature due to the oxidation by resistance or thermistor means.

Olefins may be detected by oxidation but cannot be distinguished from other oxidizable components by oxidation detectors.

I have now discovered that olefins can be selectively detected in a stream of non-hydrogenatable hydrocarbons by hydrogenating the olefins in the stream and then sensing the temperature rise due to hydrogenation.

By various aspects of this invention, one or more of the following, or other, objects can be obtained.

It is an object of this invention to provide a method and apparatus for detecting olefins in a stream of saturated hydrocarbons.

A further object of this invention is to provide a method and apparatus for detecting hydrogenatable hydrocarbons in a stream containing the same and non-hydrogenatable hydrocarbons.

It is a still further object of this invention to provide a method and apparatus for selectively detecting and distinguishing between terminally bonded olefins and internally bonded olefins in a stream containing the two types of olefins.

It is a still further object of this invention to provide a method and apparatus for maintaining fixed ratios of hydrocarbons to olefins in a gas process stream.

Yet another object of this invention is to provide a method and apparatus for detecting the presence of oxygen and other hydrogen reducible materials in a saturated hydrocarbon stream.

Other aspects, objects, and several advantages of this invention are apparent to one skilled in the art from a study of this disclosure, the drawings, and the appended claims.

According to the invention, hydrogenatable components of a gas stream are analyzed by passing same in the presence of hydrogen over hydrogenation catalyst under hydrogenating conditions and detecting a temperature change due to hydrogenation as a signal representative of the amount of hydrogenatable material in the gas stream.

The hydrogenatable materials can be any materials which exothermally or endothermally add hydrogen under hydrogenating conditions. Generally, the materials will be unsaturated hydrocarbons, aldehydes, ketones, alcohols, ethers, organic nitro-compounds (in the presence of amine) and oxygen. The process is especially suitable for detection of olefins in a gas stream of saturated hydrocarbons.

The catalysts which are suitable for the process are any hydrogenation catalysts including Raney nickel, platinum black and palladium black. The preferential catalyst for detecting olefins is palladium black.

As has been hereinbefore mentioned, it is necessary that the feedstream to the detector be under hydrogenating conditions. Thus, it may be necessary to heat the feedstream up to a hydrogenation temperature. Suitable hydrogenation temperatures are 125 to 295° C. Unsaturated compounds can be efficiently hydrogenated at 150–180° C. Alcohols can be hydrogenated at 200–265° C.

In one embodiment of the invention, thermistors are placed upstream and downstream from the hydrogenation catalyst in a conduit. The temperature differential which is measured by the two thermistors is indicative of the amount of hydrogenatable material in the feedstream. The signals from the thermistors are transmitted to a suitable measuring device which converts the signals into a reading representative of the amount of hydrogenatable material in the stream. This measuring device is therefore a hydrogenation detector.

In another embodiment of the invention, the hydrogenation catalyst is coated directly onto the downstream thermistor and the temperature rise due to the hydrogenation is detected in the same manner as above.

In still another embodiment of the invention, amounts of terminally bonded and internally bonded olefins are selectively determined. A mixture of hydrocarbons containing terminally bonded and internally bonded olefins are passed to a gas chromatography column and then separated. The separated mixture is passed over the hydrogenation catalyst. The terminally bonded olefin will pass over the catalyst first and must be detected first. Thus, the amount of terminally bonded olefin can be determined. Then the internally bonded olefins will pass over the catalyst and the differential temperature rise for the internally bonded olefins will give an indication of the amount of internally bonded olefins present.

The various proportions of internally and terminally bonded olefins can also be determined without a chromatographic column by simply passing the mixture of gases to a hydrogenation catalyst and detecting the temperature rise due to the hydrogenation of the two types of olefins. Since the heat of hydrogenation for the two types of olefins is different, the amount of terminally bonded olefins can be determined with respect to the internally bonded olefins if the amount of olefins is known. Standard samples with various percentages can be used to make a calibration scale and the temperature

rise due to the hydrogenation of the two types of olefins can be compared with the standard scales.

The invention will now be described with reference to the drawings in which FIGURE 1 is a schematic drawing showing an embodiment of the invention as it relates to a gas chromatography column, FIGURE 2 shows a specific detecting device, and FIGURE 3 shows a modified detecting device.

FIGURE 4*a* is a chart made by a standard thermal conductivity detector (not shown) of the nonhydrogenated mixed olefin and paraffin effluent from a chromatographic column, and

FIGURE 4*b* is a similar chart made by the present hydrogenation detector **9** and **15** of the same nonhydrogenated effluent from the same chromatographic column **7**.

Referring now to FIGURE 1, a gas stream containing hydrogenatable hydrocarbons is passed through line **1**. A portion of the gas stream is removed through line **2**, passed through sampler valve **3** and a sample thereof is taken through line **5** or returned through line **4** to conduit **1**. Hydrogen is used as a purge gas and is also used as a carrier gas and passes with the sample through line **5**. Make-up hydrogen can also be added through line **6** as will be hereinafter described. The sample, according to one embodiment of the invention, passes through gas chromatography column **7** which is packed with a suitable material to separate the components of the sample stream. The separated components pass through line **8** to sensor **9** in which the hydrogenatable components in stream **8** are hydrogenated. The rise in temperature is detected within detector **9** and a signal representative of the temperature rise is transmitted via lines **13** and **14** to indicator **15** which will give a reading proportional to the amount of hydrogenatable material in gas stream **8**. Sensor **9** therefore is a hydrogenation detector having a hydrogenation detector indicator **15**. Suitable calibration curves can be made from standard samples and the reading from indicator **15** can be easily converted into a percentage hydrogenatable material in gas stream **8** as is understood by one skilled in the art. The effluent from detector **9** is passed through line **10**. The amount of hydrogen in line **10** is detected by hydrogen detector **11** and a signal representative of the hydrogen in stream **10** is sent to recorder controller **12**. In the event that the hydrogen content in stream **10** drops below a predetermined limit, a signal will be sent by line **16** to valve **17** to allow more hydrogen to pass through line **6** into line **5**. It is desirable in carrying out the process that all of the hydrogenatable material be hydrogenated. Therefore, an excess of hydrogen is required in the process. Alternately and preferably, valve **17** and line **6** can be connected to line **8** to add excess hydrogen between the column and the detector. Addition of hydrogen upstream from the column would change the retention time of the components in the column.

According to another embodiment of the invention, the chromatography column can be by-passed by passing the sample in line **5** through line **18** to line **8**. In this case valve **19** will be opened. In the event that it is desirable to use the chromatography column, valve **19** will be closed. The chromatography column will be by-passed in the event that there is only one hydrogenatable material in the sample stream to be detected or when there are two hydrogenatable materials having different heats of hydrogenation as has been hereinbefore described.

If it is desirable to heat the feed to a hydrogenation temperature, this heating is preferably done between column **7** and detector **9**. This method will allow the column **7** to be operated at any desired temperature.

Referring now to FIGURE 2, there is shown an embodiment of the invention in which there are two thermistors **20** and **24** to detect the temperature of the gas in line **8**. A suitable hydrogenation catalyst such as palladium can be deposited on mesh **22** and placed between the two thermistors. As the gas passes through the stream, hydrogenation of the hydrogenatable materials takes place at **22** and the temperature rise therefrom is detected at **24**.

According to another embodiment of the invention, as shown in FIGURE 3, the hydrogenation catalyst is placed directly onto the thermistor, represented by **26**. The coating of the catalyst has been greatly exaggerated for purposes of illustration.

Thermistors **20**, **24** and **26** can be any suitable means for measuring the temperature of the gas stream. A suitable thermistor is Veeco AX 1189–2B6 which is normally an 8K resistor at 75° F.

The hydrogen detector **11** can be any suitable hydrogen detector.

The indicator **15** can be any suitable means for comparing two signals and giving an indication of the relative difference between the signals. A Wheatstone bridge circuit or other suitable means can be employed.

The hydrogenation detecting means **9** and **15** of the invention can be used to maintain a predetermined percentage of olefins in a gas stream. The olefins can be detected by the hydrogenation detector **9** and **15** and more or less olefins or make-up hydrocarbons can be supplied to the stream in accordance with the measured olefin content.

EXAMPLE I

A sample containing the components listed in Table A was passed through a ⅛ inch x 16 feet long gas chromatography column containing 10 percent Squalane on 81 mesh Chromosorb G at 40° C. The effluent from the column was passed to a standard thermal conductivity detector (not shown). The results of the detection in the thermal detector are shown in FIGURE 4*a*. The numbers correspond to the components listed by the same number in Table A.

TABLE A

(31)—normal pentane
(32)—3-methylbutene-1
(33)—1,3-butadiene
(34)—2,2-dimethylbutane
(35)—2-methylbutene-1
(36)—trans pentene-2
(37)—2-methylpentane
(38)—3-methylpentane
(39)—2-methylbutene-2
(40)—normal hexane
(41)—4-methylpentene-1
(42)—cyclopentene
(43)—3,3-dimethylpentane

EXAMPLE II

A second sample having the same components as Table A was passed through the same gas chromatography column as Example I under the same conditions. The effluent from the column was passed to a hydrogenation detector **9** and **15** according to the invention. The results of this detection are seen in FIGURE 4*b*.

It can be seen from the above that the invention can be used to advantage to detect the presence of olefins, and for separating pairs of components which are not separated by conventional gas chromatography.

I claim:

1. A method for detecting the presence of a hydrogentable material in a gas stream containing the same and hydrogen, said gas stream being heated to hydrogenation temperature, comprising measuring the temperature of said gas stream, passing said gas stream over a hydrogenation catalyst under hydrogenation conditions, and measuring the temperature of said gas stream after hydrogenation, whereby the change in temperature indicates hydrogenatable materials.

2. A method according to claim **1** wherein olefins are detected in said gas stream.

3. A method according to claim 1 where said gas stream is first passed through a gas chromatography column to separate the various components and hydrogenatable materials are serially detected by sensing the resulting change in temperature of said gas stream for each material as it is hydrogenated in serial order.

4. A method according to claim 1 wherein said hydrogenation catalyst is selected from the group consisting of Raney nickel, platinum black and palladium black.

5. A method according to claim 4 wherein said catalyst is palladium.

6. A method according to claim 1 wherein said hydrogenation material is oxygen.

7. A method according to claim 1 wherein the ratio of hydrocarbons to olefins is maintained in said gas stream by further using the signal detected from said temperature change as an indication of the amount of olefins in said hydrocarbon stream, comparing said amount with a predetermined amount, and adjusting the percentage of olefins in said stream according to said comparison by changing the amount of at least one of the hydrocarbons and the olefins of said stream in an amount sufficient to maintain said predetermined hydrocarbons to olefins ratio.

8. A method according to claim 1 wherein the hydrogen remaining in the gas after hydrogenation is measured and used to control the rate of addition of hydrogen to said stream before hydrogenation so that said hydrogenation will be substantially complete.

9. An apparatus for detecting the presence of hydrogenatable material in a gas stream containing the same and hydrogen comprising conduit means heated to hydrogenation temperature, in said conduit means a hydrogenation catalyst support means having a hydrogenation catalyst thereon, and a means for detecting a temperature change in said conduit means due to hydrogenation of said hydrogenatable material.

10. An apparatus according to claim 9 wherein there is further provided a gas chromatography column upstream from said conduit means and in open communication with said conduit means.

11. An apparatus according to claim 9 wherein said detecting means comprises a first thermistor and a second thermistor, said second thermistor being downstream

from said first thermistor, said first and second thermistors being operably connected to a comparing and indicating means which means gives an indication of the difference between the signal generated from said first and said second thermistor means, and wherein said hydrogenation catalyst support means is between said first and said second thermistor means.

12. An apparatus according to claim 9 wherein said detecting means comprises two thermal detector means, one downstream from the other, wherein said detecting means comprises a first and a second thermal detection means, said second thermal detection means being downstream from said first thermal detection means, said second detection means having thereon said hydrogenation catalyst support means, and said first and said second thermal detector means being operably connected to a comparing and sensing means which gives a visual indication of the difference between the signal generated from said first and said second thermal detecting means.

13. The apparatus according to claim 9 wherein there is further provided a hydrogen detector in the outlet from said conduit means, and means controlled by said hydrogen detector to vary the rate at which hydrogen is added to the inlet of said conduit means so that said hydrogenation will be substantially complete.

References Cited

UNITED STATES PATENTS

2,762,568	9/1956	Sullivan.	
2,901,329	8/1959	Kapff.	
2,905,536	9/1959	Emmett et al.	23—232
3,030,191	4/1962	Ridgway et al.	23—232

FOREIGN PATENTS

832,423	4/1960	Great Britain.

MORRIS O. WOLK, Primary Examiner

R. M. REESE, Assistant Examiner

U.S. Cl. X.R.

23—254

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,488,155 Dated January 6, 1970

Inventor(s) Buell O. Ayers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, Claim 6, lines 12,13 "hydrogenation" should be corrected to read -- hydrogenatable --.

Column 6, Claim 12, lines 13, 14 - between the words "second" and "detection" should be inserted -- thermal --.

SIGNED AND
SEALED
JUL 14 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents