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GAS CHROMATOGRAPH MOISTURE ANALYZER

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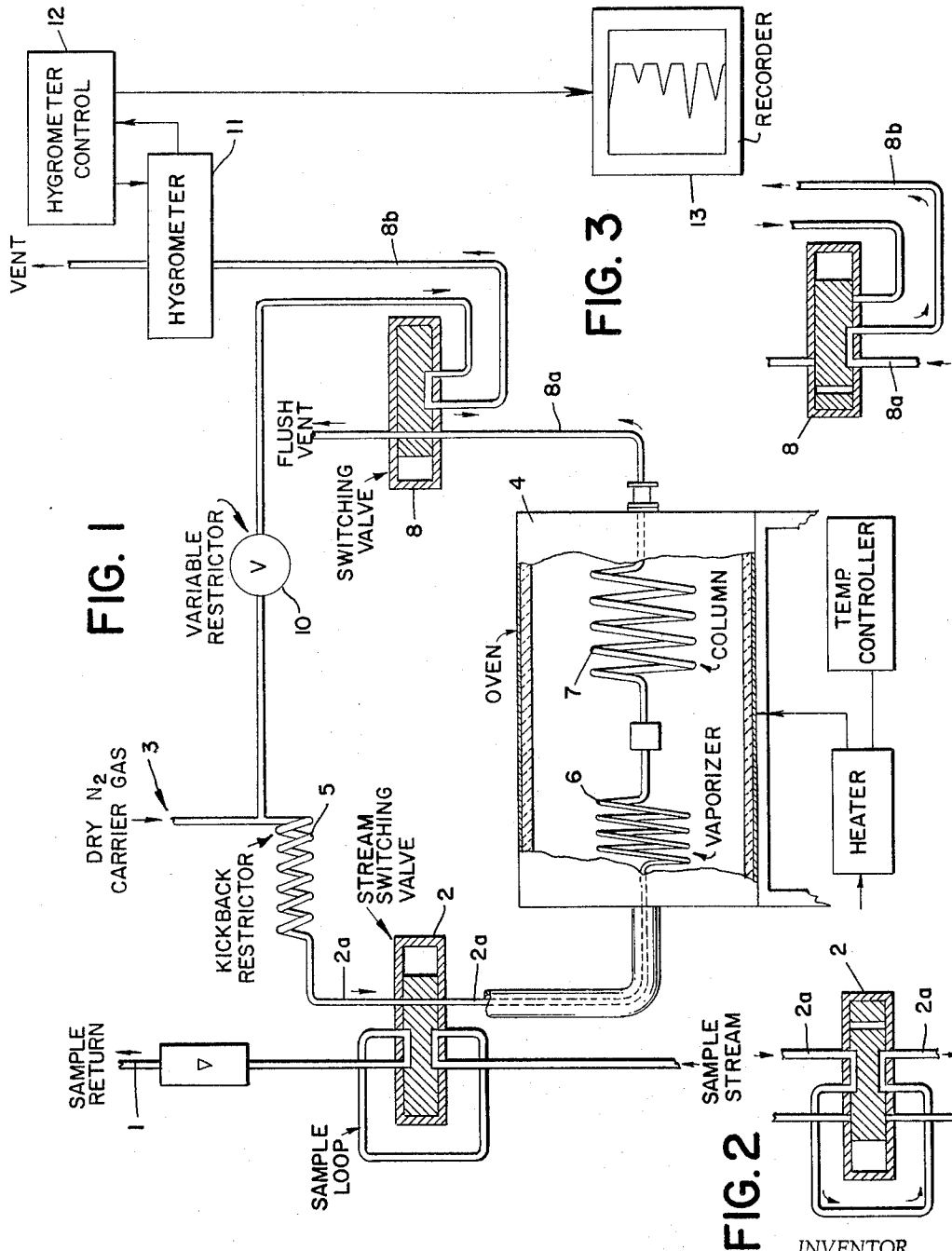


FIG. 1

FIG. 3

FIG. 2

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GAS CHROMATOGRAPH MOISTURE ANALYZER
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4 Claims. (Cl. 73-53)

This invention relates generally to chromatograph systems and, more particularly, to the use of a combined chromatograph-hygrometer system for moisture analysis of hydrocarbons.

The presence of water in small quantities in liquid or gaseous hydrocarbons is harmful to refinery processes and the control of moisture content is necessary to assure proper results. Heretofore, it has generally not been possible without elaborate techniques to determine moisture content on stream in a water-sensitive process and then only after considerable delay. Consequently, information relating moisture content to processes has necessarily been disjointed or perhaps completely unconnected with the condition which had caused the system's moisture content.

In accordance with the present invention it is now possible to determine moisture content in extremely small traces required by an on-stream system in a manner that such information may be directly related to a process very nearly concurrently with the process stream.

More specifically, an on-stream sample is first admitted to the moisture analyzer of the invention. Using a dry carrier gas, the sample is carried to a vaporizer and therefrom to a chromatographic column. The latter is constructed to pass entirely the hydrocarbons in the sample, while absorbing and holding for a predetermined time all of the moisture in the sample. By appropriate means, the initial hydrocarbon portion or fraction passed from the chromatographic column is flushed or otherwise removed, preferably by using dry carrier gas and after the complete removal of the hydrocarbon fraction, the output of the chromatographic column is routed to a hygrometer, for example, of the electrolytic type. The construction of the chromatographic column is such that after the aforementioned predetermined time, the moisture of the on-stream sample absorbed therein is gradually released (eluted) and the hygrometer, being maintained at constant temperature and voltage, will vary its current output, depending upon the degree of moisture sensed. The hygrometer may be connected to a recorder which preferably will maintain a continuous graphic record of current variations sensed by the hygrometer which, therefore, constitute a measure of the moisture content of the sample.

The following presents a specific embodiment of the invention and a description thereof in accordance with the accompanying drawing, in which:

FIG. 1 illustrates schematically a gas chromatograph-hygrometer moisture analyzer in accordance with the above-outlined principle of the invention; and

FIGS. 2 and 3 represent details of alternate valve positions of FIG. 1.

Referring to the drawing, sample stream 1 is under the control of a stream switching valve 2 which may be actuated to release a sample comprising, for example, 2 milliliters of a hydrocarbon from a direct or on-stream portion of a chemical process. The sample may be in a given instance, propylene or ethylene, at 100-200 p.s.i. The sample will first be trapped in the valve and sample loop as shown in the position of valve 2 of FIG. 1. Actuation of the valve to its alternate position of FIG. 2 causes the sample loop to be connected into line 2a through the valve 2. The sample will thus be carried by a slug of dry nitrogen carrier gas from its source 3 (under a

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pressure of perhaps 30 lbs.) toward and into an oven 4. Intermediate the carrier gas source 3 and the sample is a kickback restrictor 5 whose function is to prevent passage of the sample hydrocarbon beyond such restrictor, while permitting expansion of the sample because of the disparity between the initial on-stream pressure of 100-200 p.s.i. of the sample and the 30 lbs. of carrier gas pressure.

Accordingly, the sample carried by the dry carrier gas is fed to a vaporizer 6 in an oven 4 which is maintained at a constant temperature of 200° F. The vaporizer prepares the sample containing both hydrocarbon and moisture for introduction into a chromatographic column 7 also situated in the oven 4.

As is known in the art of constructing chromatographic columns, the absorption agent used in the column may be selected to absorb and retain for a predetermined time the moisture in the sample while passing completely the hydrocarbon portion or fraction thereof. In the present embodiment, wherein it is postulated that the hydrocarbon sample itself may consist of propylene or ethylene, the agent used in the chromatographic column may consist of polyethylene glycol having a molecular weight of 750. Such agent having an affinity for moisture only will, therefore, absorb the latter and pass the hydrocarbon fraction.

The hydrocarbon fraction passing through the column will proceed with the carrier gas to a valve 8 which, initially, via line 8a and through valve 8, will be connected to a vent. As a consequence, the initial hydrocarbon fraction of the test sample passed by the chromatographic column will be flushed through the valve 8 and therefrom vented for an initial period which may be in the order of 13-14 minutes. During this time, the column 7 will completely absorb all of the moisture content of the test sample, in perhaps the first 3-4 minutes of the period with the remainder acting to clear the column completely of the hydrocarbon fraction. It will be seen that a second portion of the dry carrier gas may proceed from the source 3 through a variable restrictor 10 which will be set to feed carrier gas at approximately 100 ccs./min. to the valve 8. When the latter is in the position of FIG. 1, dry gas will proceed through valve 8 via line 8b to a hygrometer 11 (to be described) in order to purge the hygrometer of any moisture therein.

After the initial period of 13-14 minutes, the valve will be switched to route the output of the chromatographic column to the hygrometer 11. Hygrometer 11 will be a sensitive electrolytic hygrometer, for example, such as a "Beckman" hygrometer, suitable to measure 1-1000 parts per million of water in the test sample and presently manufactured by the Beckman Instrument Company of Fullerton, California. Briefly the hygrometer comprises a moisture detector wherein moisture released by the chromatographic column, subsequent to separating out the hydrocarbon fraction of the sample, will be absorbed on phosphorous pentoxide (P_2O_5). After about 15 minutes from the beginning of passage of the sample through the column 7, the absorbed moisture therein will be released (eluted) to the hygrometer for detection therein.

The hygrometer has a control 12 which maintains the hygrometer at constant temperature and voltage. Current variations as an output from the hygrometer will result from the electrolytic breakdown of the moisture in the hygrometer cell. Such variations in the current output of the cell will be fed as indicated to a recorder 13, preferably of a continuous graphic record variety whose trace, when calibrated, therefore represents moisture content of the sample sensed by the hygrometer. This information may then, of course, be related to the sample itself which is of known volume.

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By the foregoing, it is now therefore possible to assure nearly continuous, on-stream monitoring of a refinery process and moisture presence at selected critical points. The information is very closely related in time to the actual operation of the process such that the effect of moisture in the process and control of the process itself in accordance therewith may be directly correlated.

It will be understood that the foregoing description relates merely to a representative embodiment and that, for example, various moisture detectors other than the specific electrolytic hygrometer illustrated and described may be used with similar results. Furthermore, other changes may be made from the described particular embodiment without departing from the teachings of the invention. Accordingly, in order to appreciate the true spirit and scope of the invention, attention is directed to the appended claims.

What is claimed is:

1. A gas chromatograph-hygrometer moisture analyzer for a hydrocarbon sample containing hydrocarbon and moisture portions comprising chromatographic means for absorbing all moisture from said sample product for a predetermined time while passing through said chromatographic means the hydrocarbon portion thereof, means for passing said hydrocarbon portion sequentially and initially from said chromatographic means, a hygrometer, and means for passing the moisture portion of said sample to said hygrometer subsequent to the elimination of the hydrocarbon portion of said sample from said chromatographic means.

2. The analyzer of claim 1 in which there are means for removing said sample from an on-stream portion

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of a process, a vaporizer, means comprising a dry carrier gas for passing said sample to said vaporizer, means for passing said sample from the vaporizer, a switching valve for receiving the output of said chromatographic means and initially positioned to vent the hydrocarbon portion of said sample, said valve being constructed in combination with conduit means for passing said moisture portion to said hygrometer, and means connected to the hygrometer for recording the moisture content of said sample.

3. The analyzer of claim 2 in which said hygrometer is an electrolytic type hygrometer maintained at constant voltage, wherein current variations therefrom comprise a measurement of moisture content in said sample and the current output of said hygrometer is connected to a recorder capable of continuously graphically recording said variations of current.

4. The analyzer of claim 3 in which the chromatographic means comprises a column having an absorption agent of polyethylene glycol having a molecular weight in the order of 750, said vaporizer and column are located within an oven, and dry gas means is connected to said switching valve for flushing said hygrometer when the switching valve is positioned to vent said hydrocarbon portion from the chromatographic column.

References Cited by the Examiner

UNITED STATES PATENTS

2,934,693 4/1960 Reinecke et al. ---- 73—23.1 X

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