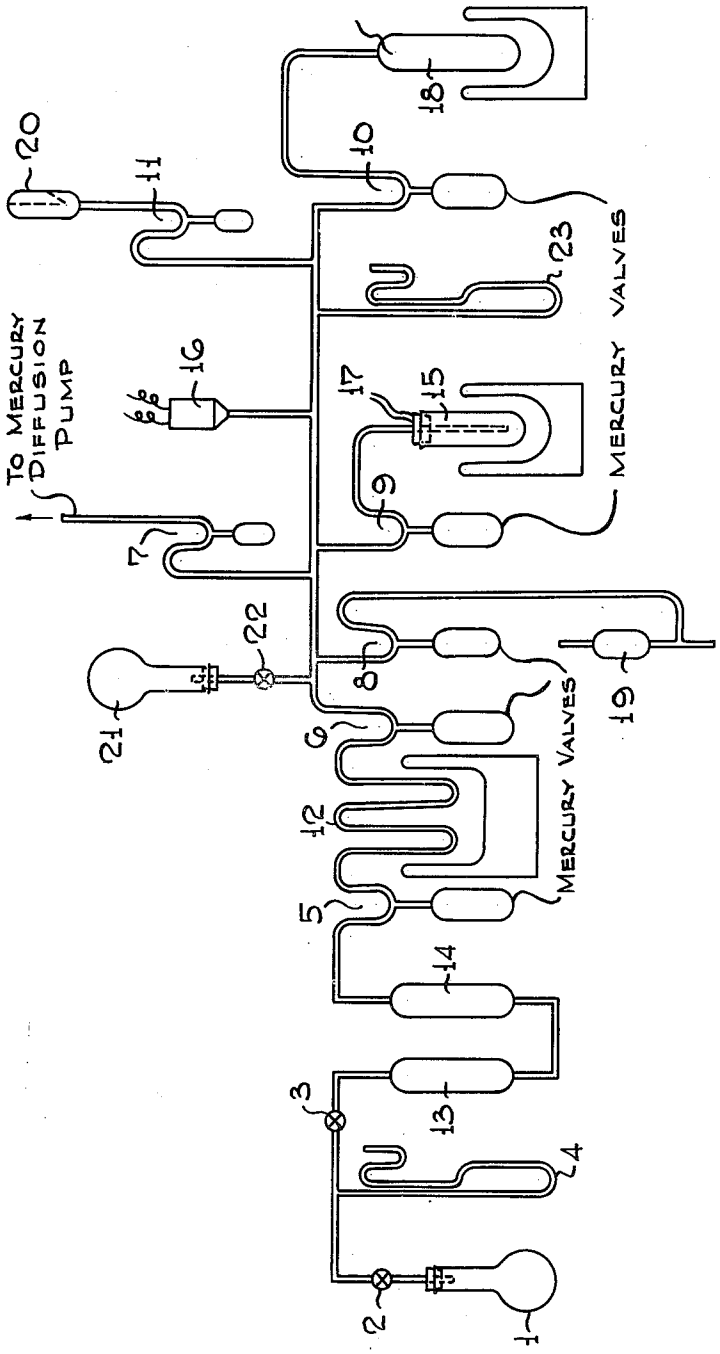
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PROCESS FOR HYDROCARBON GAS MIXTURE ANALYSIS

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PROCESS FOR HYDROCARBON GAS MIXTURE ANALYSIS

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1 Claim. (Cl. 23—232)

1

The present invention is concerned with an improved process for analyzing light hydrocarbon gases. The invention is more particularly concerned with a method for determining the analysis and composition of petroleum gases wherein the concentration of various light constituents in the gas is relatively small. My method comprises removing the methane and segregating constituents boiling in the range of hydrocarbons containing from 2 to 5 carbon atoms in the molecule. This latter fraction is then handled in a manner as hereinafter described.

It is well known in the art to analyze various gas compositions by many types of gas analysis apparatus. While these methods are generally satisfactory for ordinary gases they are not particularly adaptable for determining the actual composition of gas mixtures secured in the production of petroleum oils. These latter gas compositions for example may contain relatively large quantities of certain constituents and relatively minor quantities of other constituents. In accordance with my process, I am able to accurately analyze gas compositions, particularly those compositions containing from 2 to 5 carbon atoms in the molecule and resulting from the production of petroleum oils.

My invention may be readily understood by reference to the drawing illustrating one embodiment of the same. Referring specifically to the drawing, the gas sample to be analyzed is collected in pipette 1. This entire system is evacuated and is of a known capacity. Stopcock or valve 3 is closed and stopcock 2 is opened. The sample is allowed to expand into the mercury manometer 4 where the pressure of the sample can be read.

The amount of sample taken into the system from pipette 1 is determined by the pressure on manometer 4. The desired amount of sample is allowed to flow through valve 3 into the system. When the desired amount of sample has passed into the system, valve 3 is closed. The gas passes through ascarite and phosphorus pentoxide 13 and 14 where the carbon dioxide and water vapor are removed.

The gas, free of undesirable carbon dioxide and water vapor, is introduced into trap 12 which is immersed in liquid nitrogen at a temperature of —196° C. In this unit gases boiling above the boiling point of methane are condensed. During this operation the system is controlled so that a mercury diffusion pump is withdrawing uncondensed gases comprising methane from the system through valve 7. Other gases which are removed from the system comprise relatively large quantities of uncondensed oxygen and nitrogen. Pumping is continued until the pressure on the system is below about 2 millimeters of mercury. At this point, valve 5 is closed and pumping is continued on the remainder of the system until the pressure is lowered to the vapor pressure of the mercury in the system.

2

At this point, the sample contained in trap 12 is transferred to distillation trap 15. This is preferably accomplished by removing the nitrogen bath and substituting a Dry Ice-acetone bath, the temperature of which is about —80° C. The distillation trap 15 is cooled to —196° C., thus causing the sample to recondense in the distillation trap. The pressure changes involved in the transfer of the sample from zone 12 to zone 15 are watched by using the Pirani gauge 16. When the reading on the Pirani gauge is again approximately zero, the transfer is complete and valve 6 is closed.

The cold bath around the distillation trap 15 is lowered until a slow rise in temperature is noted on the thermocouple 17. A rise in pressure shown by the Pirani gauge 16 indicates that the distillation temperature for a compound has been reached. The cold bath is adjusted so that the temperature remains constant and the fraction is taken off by opening valve 10 and condensing it in combustion trap 18 which is maintained at a temperature of —196° C. by immersion in a liquid nitrogen bath. When the pressure no longer goes up with valve 10 closed, the fraction has all been distilled off and valve 9 is closed isolating the distillation trap.

The volume of the fraction in zone 18 is determined by bringing the temperature of zone 18 to about —80° C. and opening valves 10 and 8. The sample is allowed to expand into the McLeod gauge 19 where the pressure is determined. The volume of the system is known so that the volume of sample can be calculated.

The sample is also allowed to expand into Langmuir viscosity gauge 20 by which the molecular weight of the sample is determined. (Procedure described in "Procedures in Experimental Physics," by Strong, pages 146–147).

The sample is next recondensed into the burning trap 18 and oxygen is added from bulb 21 by opening stopcock 22 slightly until the pressure in the system is about 2 millimeters of mercury as shown by manometer 23. Valve 10 is closed, the burning trap 18 is brought to room temperature and the sample is burned for about one minute with either high voltage or radio frequency glow discharge. When burning is completed, the trap is again cooled to a temperature of —196° C. Valves 7 and 10 are opened and the excess oxygen is pumped off. The after-burning reading is taken on the McLeod gauge 19 by closing valve 7, opening valves 8 and 10 and raising the temperature of trap 18 to a temperature of —80° C. The after-burning reading gives a measure of the carbon dioxide formed during the combustion of the sample. The ratio of the after-burning reading to the before-burning reading shows the number of carbon atoms per molecule in the fraction.

The system is thoroughly evacuated by opening valves 7, 8, 10 and 11 and pumping until the system is completely degassed. Valves 7, 8, 10 and

11 are closed and valve 9 is opened. The temperature is adjusted and the procedure is repeated for the next fraction.

Distillation temperatures are reproducible within 2° C. and by calibrating the apparatus with known gases, a method of identification is obtained. Molecular weight determination is accurate within 2 molecular weight units on compounds having molecular weights up to 72. Heavier compounds suffer loss of accuracy due to dilution with traces of lighter gases.

My invention is directly applicable in the analysis of petroleum gases comprising light hydrocarbon constituents. It is especially applicable when these light hydrocarbon constituents contain appreciable quantities of methane, oxygen and nitrogen and relatively small quantities of constituents having from 2 to 5 carbon atoms in the molecule.

The general procedure used in my process is to segregate hydrocarbon constituents having 2 and more carbon atoms in the molecule from the methane, oxygen and nitrogen as described. I then segregate a fraction containing from 2 to 5 carbon atoms in the molecule in a distillation zone. My next step is to progressively segregrate the lowest boiling constituent from the remaining constituents by cooling the fraction to a temperature of —196° C. I then allow the temperature to rise until a rise in pressure is indicated on the gauge. This rise in pressure indicates that the distillation temperature for the particular compound has been reached. I hold the temperature constant until the pressure on the gauge again drops to zero indicating that the particular compound has been removed.

This operation consists in distilling the lowest boiling constituent, condensing the same in a segregated zone, revaporizing the segregated constituent and determining the molecular weight. The vaporized constituent is recondensed and expanded into a McLeod gauge and a pressure reading taken. A determined quantity of oxygen is added and the sample burned and condensed. Oxygen is removed from the burnt sample and the amount of CO_2 determined. By this procedure I am able to accurately analyze a light hydrocarbon fraction to a high degree of accuracy.

The terms "Langmuir viscosity gauge," "Pirani gauge" and "McLeod gauge" as used in the specification and claims refer to these types of gauges and apparatus as they are known and described in standard textbooks, such as for example in Strong, "Procedures in Experimental Physics," pages 138–148 (Prentice-Hall, Inc., 1946).

The process of my invention is not to be limited by any theory as to mode of operation, but only in and by the following claims in which it is desired to obtain all novelty insofar as the prior art permits.

What is claimed is:

Process for analyzing a gas mixture for its content of hydrocarbons of two to five carbon atoms wherein such hydrocarbons are present in minute quantities in admixture with methane and with relatively large quantities of oxygen and nitrogen which comprises placing said mixture in a separation zone at a temperature of about —196° C. and at a pressure below about 2 millimeters of mercury, whereby hydrocarbons boiling above methane are condensed while methane, oxygen and nitrogen remain uncondensed, removing methane, oxygen and nitrogen from the condensed hydrocarbon gases, transferring the remaining condensed gases comprising a hydrocarbon fraction of 2 to 5 carbon atoms from said separating zone into a distillation zone maintained at a temperature of about —196° C. and at a pressure of about that of the vapor pressure of mercury, bringing said distillation zone into communication with an evacuated combustion zone cooled to a temperature of about —196° C., raising the temperature of said distillation zone sufficiently to cause a measurable increase in pressure in said zone, maintaining said increased temperature until the completion of distillation of the hydrocarbon exhibiting the lowest boiling point in the hydrocarbon fraction is indicated by a drop in pressure, cutting off communication between said distillation zone and said combustion zone, raising the temperature in said combustion zone to about —80° C., measuring the pressure exerted by the resultant expanded hydrocarbon gas in a zone of known volume whereby the quantity of said lowest boiling hydrocarbon is determined, determining the molecular weight of said lowest boiling hydrocarbon by measuring its viscosiity at the indicated pressure, recondensing said hydrocarbon gas in said combustion zone by recooling said zone to about —196° C., introducing oxygen into said combustion zone under a pressure of about 2 millimeters of mercury, isolating said combustion zone and raising its temperature to ordinary room temperature, burning the mixture of hydrocarbon gas and oxygen by means of an electrical discharge, condensing the combustion products by recooling said combustion zone to about —196° C., removing excess oxygen, raising the temperature of the combustion zone to about —80° C., measuring the pressure exerted by the resultant expanded gas in a zone of known volume and determining the amount of carbon dioxide produced by said burning by comparing said last named pressure with the pressure exerted by said particular hydrocarbon when the temperature of said combustion chamber was previously raised to about —80° C. prior to said burning, and successively distilling each higher boiling hydrocarbon in said distillation zone and subjecting the thus separated hydrocarbon to the viscosity measuring, burning and associated steps in the manner aforesaid whereby each hydrocarbon of from 2 to 5 carbon atoms and the composite concentration of hydrocarbons of two to five carbon atoms in the gas sample are determined.

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