

[54] **APPARATUS FOR THE DRAWING OF SAMPLES OF GASEOUS MIXTURES TO BE ANALYZED**[72] Inventors: **Francesco Garilli**, Catania; **Michelangelo Marino**, Augusta (Siracusa), both of Italy[73] Assignee: **Montecatini Edison S.p.A.**, Milan, Italy[22] Filed: **Sept. 18, 1970**[21] Appl. No.: **73,462**[52] U.S. Cl. **73/421.5 R**[51] Int. Cl. **G01n 1/22**[58] Field of Search **73/421.5 R, 421.5 A**[56] **References Cited****UNITED STATES PATENTS**

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[57] **ABSTRACT**

An apparatus for drawing samples of gaseous mixtures to be analyzed, such as the gaseous mixtures present at the outflow of a cracking furnace, includes a plurality of baffles arranged longitudinally inside a hollow columnar passageway so as to provide a serpentine pathway for the gaseous mixture flowing therethrough. A thermoregulator, which comprises a sleeve or jacket through which a temperature controlling fluid such as air or steam flows, surrounds the columnar passageway substantially along its length to regulate the temperature therewithin. A thermometer located at the head of the passageway, near a sampling duct through which the desired gaseous mixture is passed to an analyzer, controls the flow of fluid within the thermoregulator by sensing the temperature of the passing mixture so as to maintain this temperature at a desired value. This value is dependent on the fraction desired for analysis. Solid particles contained in a mixture are deposited on the baffles as the mixture flows through the serpentine pathway. Self-washing of these baffles is accomplished by condensation of the higher boiling fractions.

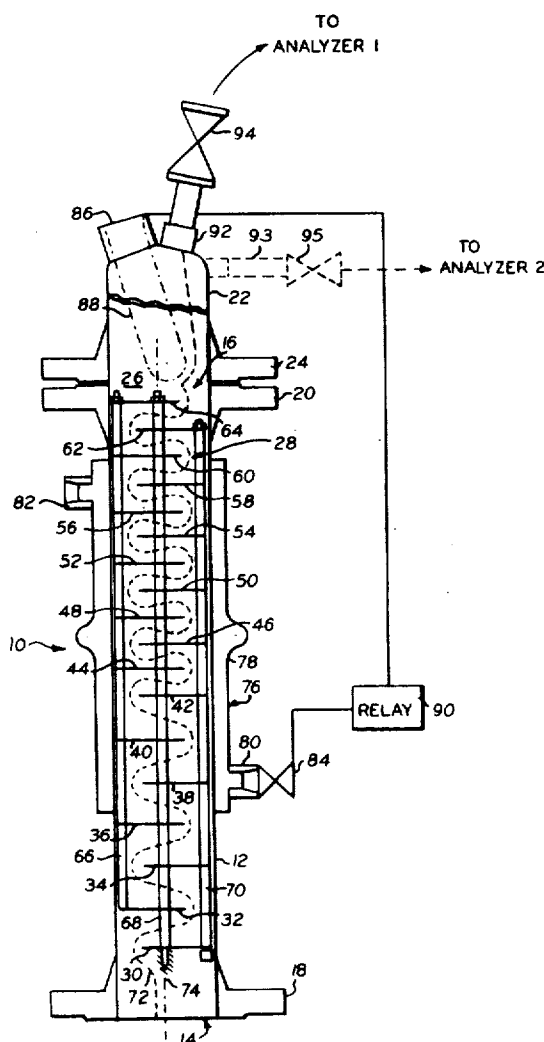
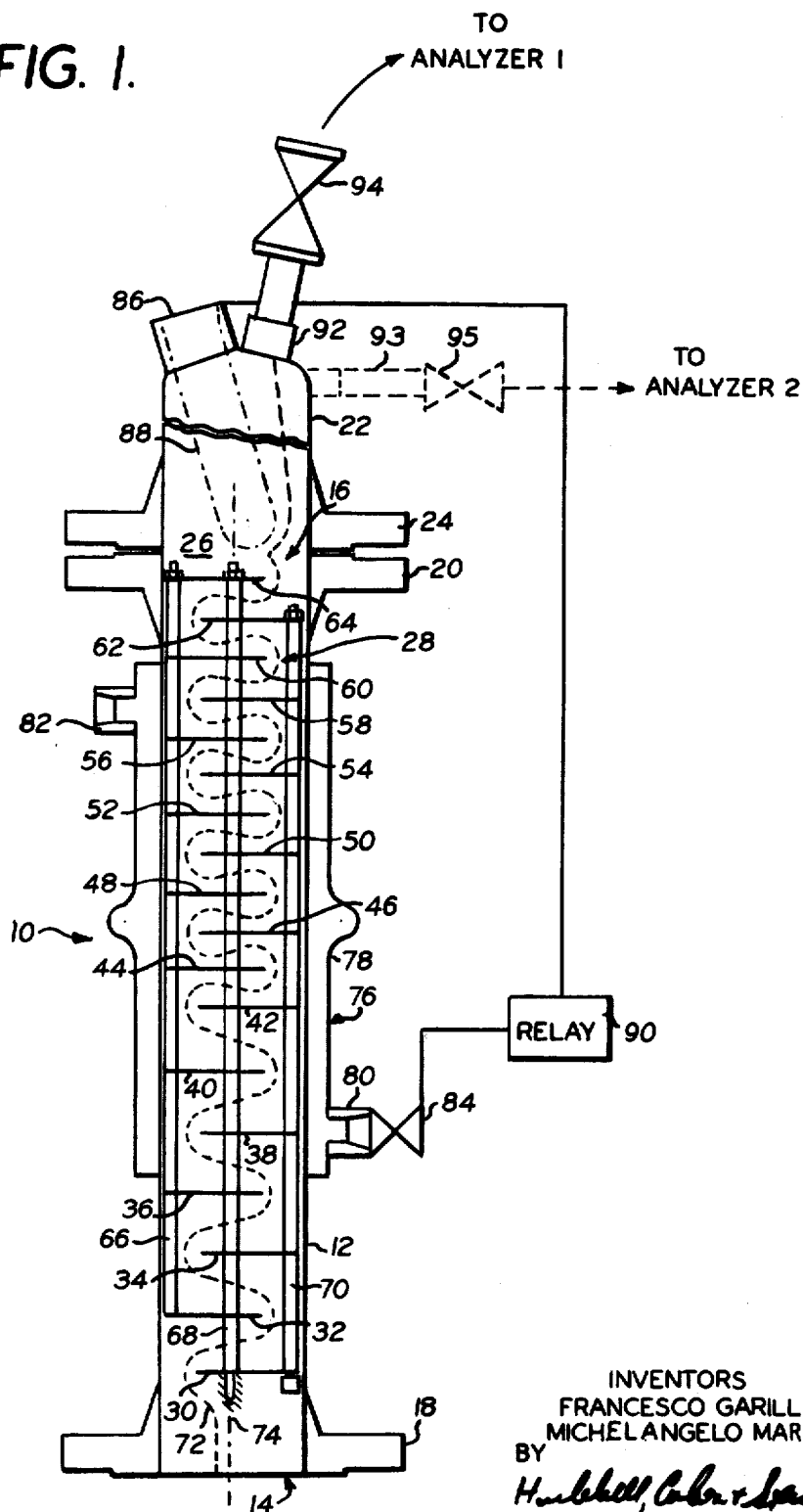
8 Claims, 4 Drawing Figures

FIG. 1.



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FIG. 2A.

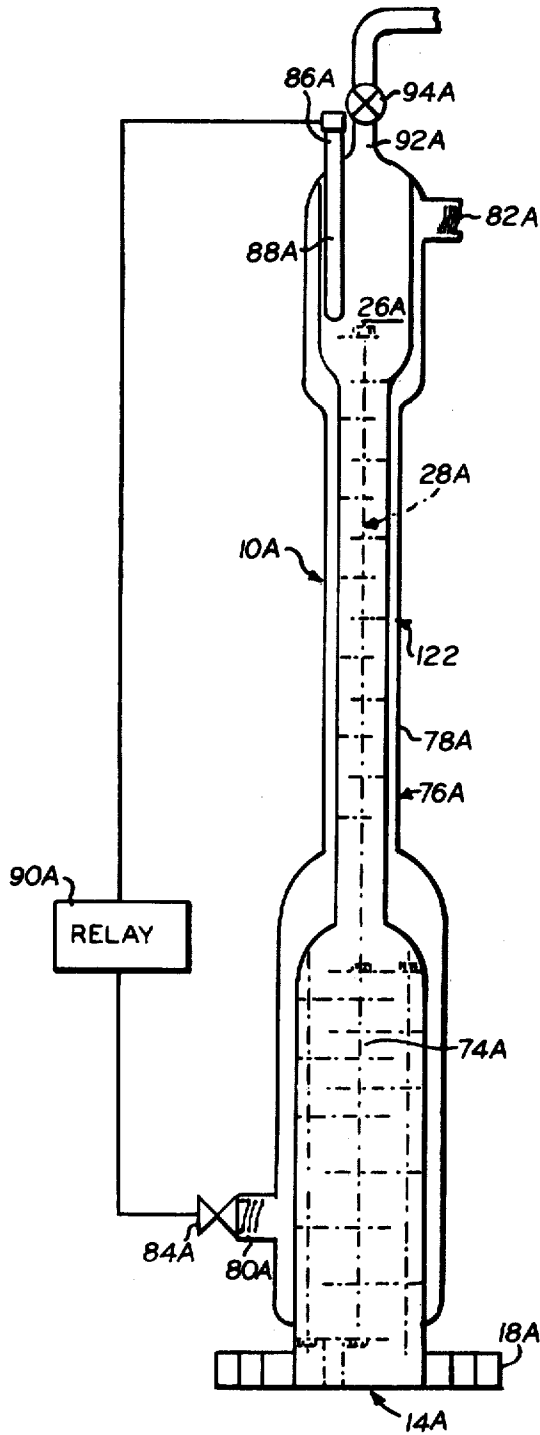
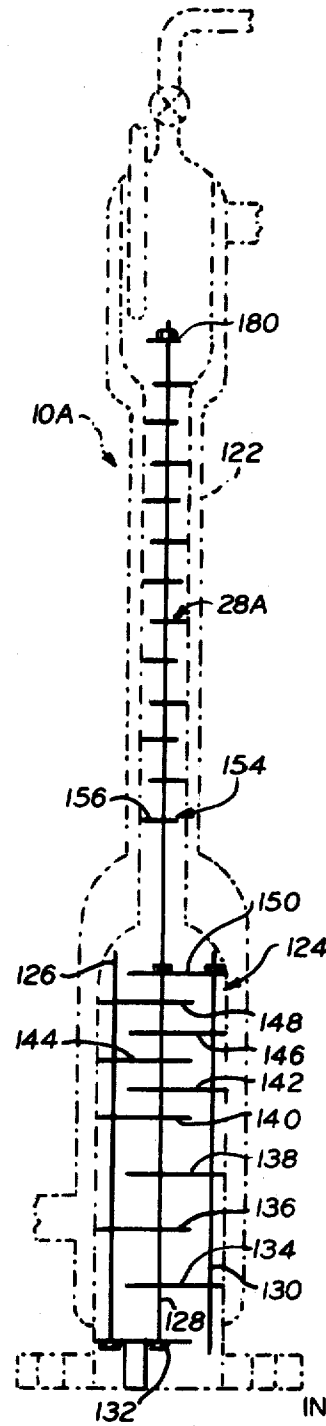


FIG. 2B.

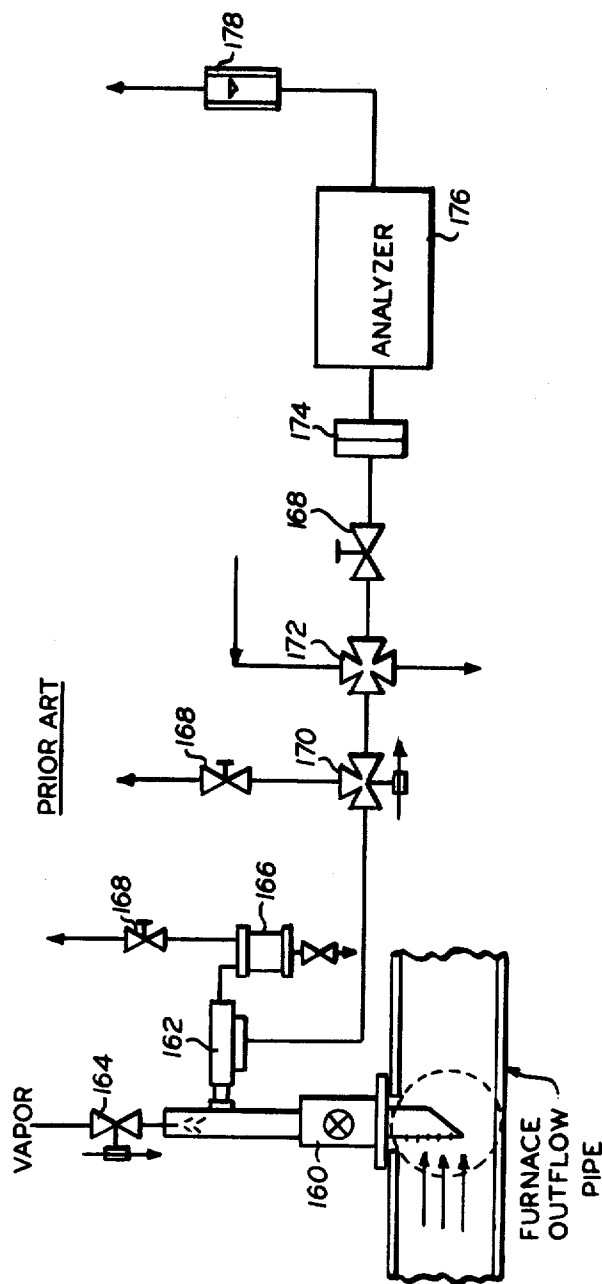


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FIG. 3.



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APPARATUS FOR THE DRAWING OF SAMPLES OF GASEOUS MIXTURES TO BE ANALYZED

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an apparatus for the drawing of samples of mixtures of gases to be analyzed from an effluent containing undesirable substances such as pitchy or solid substances.

2. Description of the Prior Art

Devices for the drawing of samples of mixtures of gases to be analyzed, hereinafter termed samplers, are well known. Such devices have been utilized in the analysis of the mixtures formed during the operation of a cracking furnace. For the satisfactory running of such furnaces, complete information about the proportions of the products that have formed in the process must be available continuously within the shortest possible time. However, this requirement causes considerable difficulties as far as the drawing of samples of the outflow mixture inasmuch as solid products formed during the process tend to obstruct or clog the sampling device as well as accumulate or pile up in the duct connecting the sample drawing apparatus to the analyzing apparatus. For example, in "steam cracking" of virgin naphtha, wherein "virgin naphtha" is defined as a blend of crude oil or petroleum having a boiling point of between 35° centigrade and 160° centigrade, complex mixtures are formed which consist of between 62 and 70 percent hydrogen and hydrocarbons such as methane, ethylene, ethane, propylene, propane, normal and iso-butane, butenes and gasoline (b.p. 35° - 220°C), 30 to 38 percent water, and, for a small residual part such as between 1.2 and 1.4 percent, consists of solids and liquids, such as solid compounds containing condensed benzene rings and coke, and liquid compounds containing condensed benzene rings. This small residual part of the mixture which contains these solid products is what tends to interfere with the sampling operation.

Prior art attempts to overcome this problem have involved using extractable or removable samplers which are subjected to periodic cleaning, or internal washing by means of a washing fluid such as a jet of water vapor. These prior art attempts, however, have not yielded satisfactory results. If the sampler is only cleaned periodically, the partial progressive obstruction that continues to build up until the sampling apparatus is completely blocked, influences the representativeness of the sample by altering the proportions between the light hydrocarbons, that is hydrocarbons having from one through four carbon atoms, and the heavy hydrocarbons, that is hydrocarbons having five or more carbon atoms. In the other case, if a washing fluid is introduced into the sampler, although the solid residues are eliminated, the composition of the sample is altered. For example, if water vapor is utilized for this washing, no determination can be made as to the quantity of water in the outflow of the cracking furnace. Furthermore, when washing fluids are utilized, some of the components of the gasoline fraction, in particular benzol, toluene, or xylois can not be quantitatively determined as these substances are normally present in such washing fluids. Therefore, when a washing fluid is utilized, analysis is limited to a determination of the low molecular weight components, generally from methane to the butanes.

These disadvantages of the prior art are overcome by the present invention.

SUMMARY OF THE INVENTION

An apparatus for drawing samples of gaseous mixtures to be analyzed, such as the gaseous mixtures present at the outflow of a cracking furnace, includes a plurality of baffles arranged longitudinally inside a hollow columnar passageway so as to provide a serpentine pathway for the gaseous mixture flowing therethrough. The apparatus is preferably mounted on the outflow pipe of the furnace so as to sample the outflow therefrom. A thermoregulator, which comprises a sleeve or

jacket through which a temperature controlling fluid such as air or steam flows, surrounds the columnar passageway substantially along its length to regulate the temperature within the passageway. The flow of fluid within the thermoregulator is controlled by means of a thermometer which is located at the head of the passageway near the sampling duct through which the desired gaseous mixture is passed to an analyzer. The thermostat senses the temperature of the passing mixture and maintains the head of the passageway at a desired value by controlling the operation of an inlet valve of the thermoregulator so as to control the flow of fluid thereto, an outlet pipe for the fluid also being provided. The desired value is dependent on the fraction which it is desired to obtain for analysis.

The solid particles, or products, contained in the outflow mixture from the furnace are deposited on the baffles as the mixture flows through the serpentine pathway. The higher boiling fractions contained in the mixture passing through the apparatus condense and flow towards the bottom of the passageway, the condensing higher boiling fractions acting as a "self-wash" for the baffles which thereby prevents particle build-up. The baffles may be mounted on rods of an assembly which is removable from the interior of the columnar passageway for additional cleaning.

BRIEF DESCRIPTION OF DRAWING

FIG. 1 is a sectional elevation of a preferred embodiment of the present invention;

FIG. 2A is a sectional elevation of an alternative embodiment of the present invention with the baffle assembly removed;

FIG. 2B is an elevational view of the baffle assembly removed from the embodiment shown in FIG. 2A; and

FIG. 3 is a diagrammatic illustration of a prior art sampling and analysis apparatus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings in detail and especially to FIG. 1 thereof. The sampling apparatus of the present invention, generally referred to by the reference numeral 10, preferably includes a cylindrical upstanding hollow column or pipe portion 12 having an inlet end 14 and an outlet end 16. As shown and preferred, flanges 18 and 20 are located at the inlet end 14 and outlet end 16, respectively. Flange 18 is preferably utilized for coupling the sampling apparatus 10 to a similarly flanged outlet pipe (not shown) of a system, such as a cracking furnace (not shown) from which the mixture of gases to be analyzed is provided. Flange 20 is preferably coupled to a similarly flanged head piece or capping portion 22 for the column 12, which headpiece portion 22 has a flange 24. Flange 24 is coupled to flange 20 in a conventional manner, such as by bolts (not shown). Headpiece portion 22, which is preferably a cylindrical hollow member having the same inner diameter as the column 12, when coupled to column 12 forms a continuous hollow columnar passageway 26 to the inlet end 14 of the column 12.

As shown and preferred, the interior 26 of the column portion 12 contains a baffle assembly, generally referred to by the reference numeral 28. The baffle assembly 28 preferably includes a plurality of planar or disc-like plates, illustratively shown as comprising 18 such plates 30 through 64, inclusive, which are preferably mounted on three rods 66, 68, and 70, in a staggered arrangement, each plate being secured to two of the three rods 66, 68, and 70. Plates 32, 36, 40, 44, 48, 52, 56, 60, and 64 are secured to rods 66 and 68, and plates 30, 34, 38, 42, 46, 50, 54, 58, and 62 are secured to rods 68 and 70, to complete the baffle assembly 28 as an integral structure. Preferably, the plates 32, 36, 40, 44, 48, 52, 56, 60, and 64 secured to rods 66 and 68 are arranged in the baffle assembly 28 so as to each be between a pair of upper and lower adjacent plates secured to rods 68 and 70, equidistantly therefrom, to preferably form a serpentine pathway, illustratively shown by

the dotted line 72, through the baffle assembly 28. The baffle assembly 28 preferably has a width substantially equal to the inner diameter of the column 12 so as to substantially extend completely across the hollow interior 26 of the column 12. Furthermore, as shown and preferred, the length of the baffle assembly 28, which is substantially the distance between plates 30 and 64, is substantially equal to the length of the longitudinal axis 74 of the column portion 12 so as to extend substantially therealong. Furthermore, as shown and preferred, the spacing between plates 30 and 34, 34 and 38, 38 and 42 is equal, as is the spacing between plates 42 and 46, 46 and 50, 50 and 54, 54 and 58, and 58 and 62 mounted on rods 68 and 70 of the baffle assembly 28, with the spacing between the plates closer to the outlet end 16 being smaller than the spacing of the plates closer to the inlet end 14.

The column 12 is preferably surrounded by a conventional thermoregulator 76 which includes a jacket or sleeve portion 78 which preferably completely surrounds the column 12 and extends substantially along the longitudinal axis 74 of the column 12 for a sufficient distance to control the temperature of the mixture located in the headpiece portion 22, in a manner to be described in greater detail hereinafter. The thermoregulator 76, jacket portion 78 includes an inlet pipe 80 through which the thermoregulating fluid such as air or steam flows, and an outlet pipe 82 for the thermoregulating fluid. Preferably, an intake valve 84 is associated with the inlet pipe 80 to control the flow of the thermoregulating fluid to the jacket 78 from a heat exchanger (not shown), outlet pipe 82 also being connected to the heat exchanger (not shown).

Preferably, the headpiece portion 22 includes a conventional thermostat 86 having a sensing portion 88 extending into the interior 26 of the headpiece portion 22 close to the top 64 of the baffle assembly 28, which is the outlet thereof, for sensing the temperature of the mixture of gases at this point in the column 12. Furthermore, preferably, the thermostat 86 is connected to a conventional relay means 90 which controls the opening and closing of the intake valve 84 to regulate the flow of the thermoregulating fluid to the jacket 78 and thus regulate the temperature of the mixture of gases in the headpiece portion 22. The thermostat 86 may be set to any desired value in a conventional manner. An outlet pipe 92 is provided in the headpiece portion 22 through which the mixture of gases to be sampled may flow to an analyzer (not shown). Preferably, the outlet pipe 92 is located near the sensing portion 88 of thermometer 86 so that the temperature sensed will be of the mixture of gases flowing to the analyzer (not shown). A conventional gate valve 94 is provided on the outlet pipe 92 for regulating the flow therethrough of the gases to the analyzer. If desired, more than one outlet pipe, such as pipe 93 and valve 94 shown by dotted lines in FIG. 1, could be provided from the headpiece 22 for drawing several samples contemporaneously to be transferred to different analyzers (not shown).

OPERATION

Now describing the operation of the embodiment shown in FIG. 1. The sampling apparatus 10 is preferably installed on the outflow pipe for the gases coming from the heat exchangers (not shown) of a furnace, such as a cracking furnace, which outflow pipe, as was previously mentioned, has a flange similar to flange 18 and is coupled thereto to form a continuous passageway to inlet 14 of the sampling apparatus 10 for the mixture of gases flowing through the outflow pipe of the furnace. The thermostat 86 is set at a desired value depending on the desired fraction to be drawn through outlet pipe 92 to the analyzer. For example, if it is desired to draw a sample consisting of the gaseous fraction $H_2 \rightarrow C_4$'s plus the aromatic fraction and water, which sample is free of residual substances, from the mixture of gases, liquids and solids coming from a virgin naphtha cracking furnace placed downstream of the heat exchanger, where the temperature is dropped to 350° to 300° centigrade, the thermometer 86 is set so as to maintain

the temperature of the effluent at the head 16 of the column 12 at a value in the range between 105° and 115° centigrade. Furthermore, if it is desired to draw and analyze the gaseous fraction C_1 's through C_4 's, the thermometer 86 need only be set to maintain this temperature at a value in the range of 40° to 50° centigrade. The thermometer 86, which is set for the desired value, will regulate the flow of the thermoregulating fluid in the thermoregulator 76 to maintain this value for the effluent at the head 16 of the column 12.

As the mixture of gases flows through the outflow pipe from the furnace into the column 12, this mixture of gases, liquids and solids sinuously flows through the baffle assembly 28 towards the head 16 of the column 12. As this mixture sinuously flows through the staggered baffles or plates 30 through 64 inclusive, the dragged solid particles are deposited on the plates 30 through 64 inclusive, with the majority of the solid particles being deposited on the lower plates, such as 30 through 44 inclusive.

Furthermore, the high boiling fractions, for example, those having a boiling point of about 230° centigrade, which have a higher boiling point than the temperature which the thermostat 86 is set for, condense and are deposited toward the bottom of the column 12. The condensing higher boiling point fractions cause the fractions and particles deposited on the baffles or plates 30 through 64, inclusive, to once again be dragged into the current of the effluent coming from the heat exchanger through the outflow pipe. In this manner, the condensing higher boiling point fractions cause a self-washing of the baffles 30 through 64, inclusive.

If the temperature of the effluent at the head 16 of the column 12 drops below a certain preestablished limit, the relay 90 is operated by the thermostat 86 to increase the opening of the inlet valve 84 so as to permit more thermoregulating fluid to flow therethrough to raise the temperature, or, if this temperature rises above a certain preset value, then the thermostat 86 operates relay 90 to partially close down that valve 84 so as to lower this temperature. All that is required, if it is desired to draw a different fraction, is to vary the temperature at the head 16 of the column 12 so that this temperature corresponds to the associated temperature of the fraction to be drawn.

For purposes of illustration and not by way of limitation, the following examples are given in order to better illustrate the operation of the apparatus of the present invention.

EXAMPLE 1

An analysis was carried out on the gases flowing out of the coils of a cracking furnace for virgin naphtha, using the sample drawing apparatus shown in FIG. 1 in order to draw samples for analysis. For purposes of comparison, this analysis was also carried out using a commercially available prior art apparatus employing an extractable sampler 160 such as the prior art apparatus shown in FIG. 3 wherein the apparatus includes the extractable sampler 160, a centrifugal filter 162, a two-way solenoid valve 164, a condensate separator 166, three needle valves or pin valves 168—168, a three-way electrovalve 170, a four-way valve 172, a filter 174, an analyzer 176, and a rotameter 178. The analyses and the resultant comparison were limited to the hydrocarbons having from one to four carbon atoms only, because an analysis of the refined gasoline produced in cracking cannot be properly performed using an extractable sampler 160. For this reason the thermoregulation of the column 12 of the apparatus 10 of the present invention was based on 45° centigrade. The operational conditions of the furnace were as follows.

The temperature of the coils at the outlet of the furnace was 760° C, the ratio of vapor/virgin naphtha was 0.56, the inlet pressure was 8.8 kg/cm², the outlet pressure was 1.2 kg/cm², and the temperature in the effluent or outflow was 375° C.

Under these conditions a gas-chromatographic analysis yielded the following results enumerated in Table I for the percent by weight (percent b.w.) of the components from H_2 to

the hydrocarbons having four carbon atoms, no separation between propane and propylene (C_3 's) nor between the butanes and the butenes (C_4 's) having been carried out.

TABLE I

Comparison between the analysis of the components from H_2 to C_4 of gaseous mixtures flowing out of a cracking furnace for virgin naphtha, carried out by drawing two samples each (56 days apart) with the apparatus 10 of the present invention (columns I and III) and with a commercial extractable sampler 160 (columns II and IV).

I First Sample Components % b.w.	II First Sample % b.w.	III Second Sample % b.w.	IV Second Sample % b.w.
H_2 0.7	0.7	0.7	0.7
CH_4 19.9	20.0	20.0	20.1
C_2 28.0	28.1	27.8	27.8
C_2^+ 8.2	8.3	8.1	8.2
C_3 's 25.9	25.8	26.1	26.1
C_3^+ 's 17.3	17.0	17.2	17.1
Total: 100.0	99.9	99.9	100.0

C_x^- and C_x^+ means saturated (+) or unsaturated (-) hydrocarbons at x carbon atoms. These tests, repeated after 56 days of operation, proved the repeatability of the sample.

EXAMPLE 2

In another test, an analysis cycle was carried out every 10 minutes, with the apparatus 10 of the present invention for a cracking furnace for virgin naphtha operating under the same operational conditions as in Example 1. A determination of the hydrogen content of the mixture was carried out in parallel on an automatic chromatograph. The results of these analyses appear below in Table II and are expressed in molar fractions.

TABLE II

Gas chromatographic analysis of a gaseous mixture flowing out of a cracking furnace for virgin naphtha, carried out by drawing samples every 10 minutes with the apparatus 10 of the present invention

Components, percent by vol.:	Time, min.									
	0	10	20	30	40	50	60	70	80	90
H_2	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
CH_4	27.9	27.8	27.9	28.0	27.8	27.8	27.8	27.8	27.6	28.0
C_2	24.2	24.3	24.3	24.3	24.3	24.3	24.3	24.3	24.3	24.3
C_2^+	7.2	6.9	7.1	7.0	6.9	6.8	7.1	7.0	6.8	7.0
C_3	15.1	15.3	15.1	15.0	15.3	15.3	15.2	15.3	15.4	15.2
C_3^+	15.1	15.3	15.1	15.0	15.3	15.3	15.2	15.3	15.4	15.2
C_4	6.7	6.7	6.6	6.6	6.7	6.7	6.7	6.6	6.7	6.5
Gasoline from cracking, percent by volume.....	8.9	9.0	8.9	9.0	9.1	9.4	9.1	8.9	9.3	8.9

Assuming that no variation of any of the parameters has occurred, the following analytical changes appearing in Table III would result.

TABLE III

Components	minimum	maximum	Average	spread
CH_4 % by vol.	27.6	28.0	27.8	± 0.2
C_2 % by vol.	24.1	24.3	24.2	± 0.1
C_2^+ % by vol.	6.8	7.2	7.0	± 0.2
C_3 % by vol.	15.0	15.4	15.2	± 0.2
C_3^+ % by vol.	6.5	6.7	6.6	± 0.1
Gasoline from cracking % by vol.	8.9	9.4	9.15	± 0.25

On the basis of the results obtained and of the minimum analytical changes observed it can be seen that the sample drawn is really representative through time.

ALTERNATIVE EMBODIMENT

Now referring to FIGS. 2A and 2B and describing an alternative embodiment of the present invention. The embodiment

shown in FIGS. 2A and 2B is substantially identical with the embodiment shown in FIG. 1 with the exception that the head-piece portion 22 and column portion 12 of the embodiment shown in FIG. 1 comprise one continuous portion instead of the two coupled portions of the embodiment shown in FIG. 1, and the baffle assembly 28A is a different staggered assembly of baffles or plates than that of the embodiment shown in FIG. 1. Furthermore, the configuration of the column assembly 122 is different from that of the sampling apparatus 10 shown in FIG. 1. The thermoregulator 76 surrounds the column assembly 122, extending substantially along the entire length of the longitudinal axis 74A thereof and being substantially symmetrical therewith. Components in FIGS. 2A and 2B which are identical with components in FIG. 1 will be given the same reference numeral followed by the subscript "A" as will be those which are functionally identical, and will not be described in greater detail hereinafter.

Suffice it to say, that the baffle assembly 28A, comprises a lower portion 124 having three upstanding rods 126, 128 and 130 upon which are arranged, in staggered fashion so as to create a serpentine pathway for gases flowing therethrough, baffles or plates 132 through 150, inclusive, with plates 132, 136, 140, 144, and 148 being secured to rods 126 and 128, and plates 134, 138, 142, 146, and 150 being secured to rods 128 and 130. Preferably, the spacing between plates 132 and 134, 134 and 136, 136 and 138, and 138 and 140 is equal, as is the spacing between plates 140 and 142, 142 and 144, 144 and 146, 146 and 148, and 148 and 150, the spacing between plates 140 to 150, inclusive, being closer than the spacing between plates 132 to 140, inclusive.

Furthermore, center rod 128 extends upwardly beyond the ends of rods 126 and 130 so as to form a center shaft for the upper portion of the column assembly 122. This upper portion 154 of the center rod 128 also preferably contains a plurality of baffles or plates 156 through 180, inclusive, arranged in a staggered fashion so as to provide a further serpentine pathway for the gaseous mixture flowing through the interior 26A of the column assembly 122. This baffle assembly 28A is

easily removable from the column assembly 122 for additional cleaning. The operation of this sampling apparatus 10A is identical with that previously described with reference to the embodiment shown in FIG. 1 and will not be described in greater detail hereinafter.

By utilizing the sampling apparatus of the present invention, a sample of effluent such as from a cracking furnace, which sample is relatively free of solid particles and which is representative through time may be continuously drawn. Furthermore, such samples may be drawn relatively free of clogging thereby requiring minimal maintenance. Moreover, the fractions which are drawn may be easily varied by varying the temperature at the head of the column. In addition, the apparatus of the present invention enables an analysis of the refined cracking gasoline (at a boiling point of 35° to 220° C) and the water present as well as the gases flowing from a cracking furnace (such as hydrogen, methane, ethane,

ethylene propane, propylene, butanes and butenes). As a result, the yields of valuable products such as propylene and butadiene may be quantified immediately.

It is to be understood that the above described embodiments of the invention are merely illustrative of the principles thereof and that numerous modifications and embodiments of the invention may be derived within the spirit and scope thereof.

What is claimed is:

1. An apparatus for drawing a desired sample fraction from a gaseous effluent mixture comprising
means having a substantially columnar passageway for receiving said effluent, said columnar passageway having an inlet and an outlet, said effluent being received at said inlet,
means for providing a serpentine pathway for said effluent, said serpentine pathway providing means being located within said columnar passageway between said inlet and said outlet,
means for tapping said desired sample fraction from said outlet, and
means for maintaining a desired temperature in a region adjacent said sample outlet tap, said desired temperature being substantially equivalent to the desired fraction boiling point.
2. An apparatus in accordance with claim 1 wherein said temperature maintaining means includes means for varying said temperature to a different value to obtain a different desired fraction, said different value being substantially equivalent to the different desired fraction boiling point.
3. An apparatus in accordance with claim 1 wherein said temperature maintaining means includes a sleeve-like means having an inlet and an outlet, said sleeve-like means substan-

tially surrounding said columnar passageway, a thermoregulating fluid being contained within said sleeve-like means and flowing therethrough for maintaining said desired temperature.

4. An apparatus in accordance with claim 3 wherein said temperature maintaining means further includes temperature sensing and controlling means for sensing the temperature in said region and controlling the flow of said thermoregulating fluid within said sleeve-like means to maintain said desired temperature.

5. An apparatus in accordance with claim 1 wherein said tapping means includes a plurality of outlet taps for contemporaneously tapping a plurality of samples of said desired fraction.

6. An apparatus in accordance with claim 3 wherein said tapping means includes a plurality of outlet taps for contemporaneously tapping a plurality of samples of said desired fraction.

7. An apparatus in accordance with claim 1 wherein said effluent is from a virgin naphtha cracking furnace, and said temperature maintaining means maintains said desired temperature in a range substantially between 105° and 115° C whereby said desired sample includes a gaseous fraction including hydrogen through hydrocarbons having four carbon atoms, a gasoline fraction and water.

8. An apparatus in accordance with claim 1 wherein said effluent is from a virgin naphtha cracking furnace, and said temperature maintaining means maintains said desired temperature in a range substantially between 40° and 50° C whereby said desired sample includes a gaseous fraction including hydrocarbons having from one to four carbon atoms.

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