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3,531,255

METHOD AND APPARATUS FOR ANALYZING HYDROCARBON COMPOSITIONS

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Figure 1

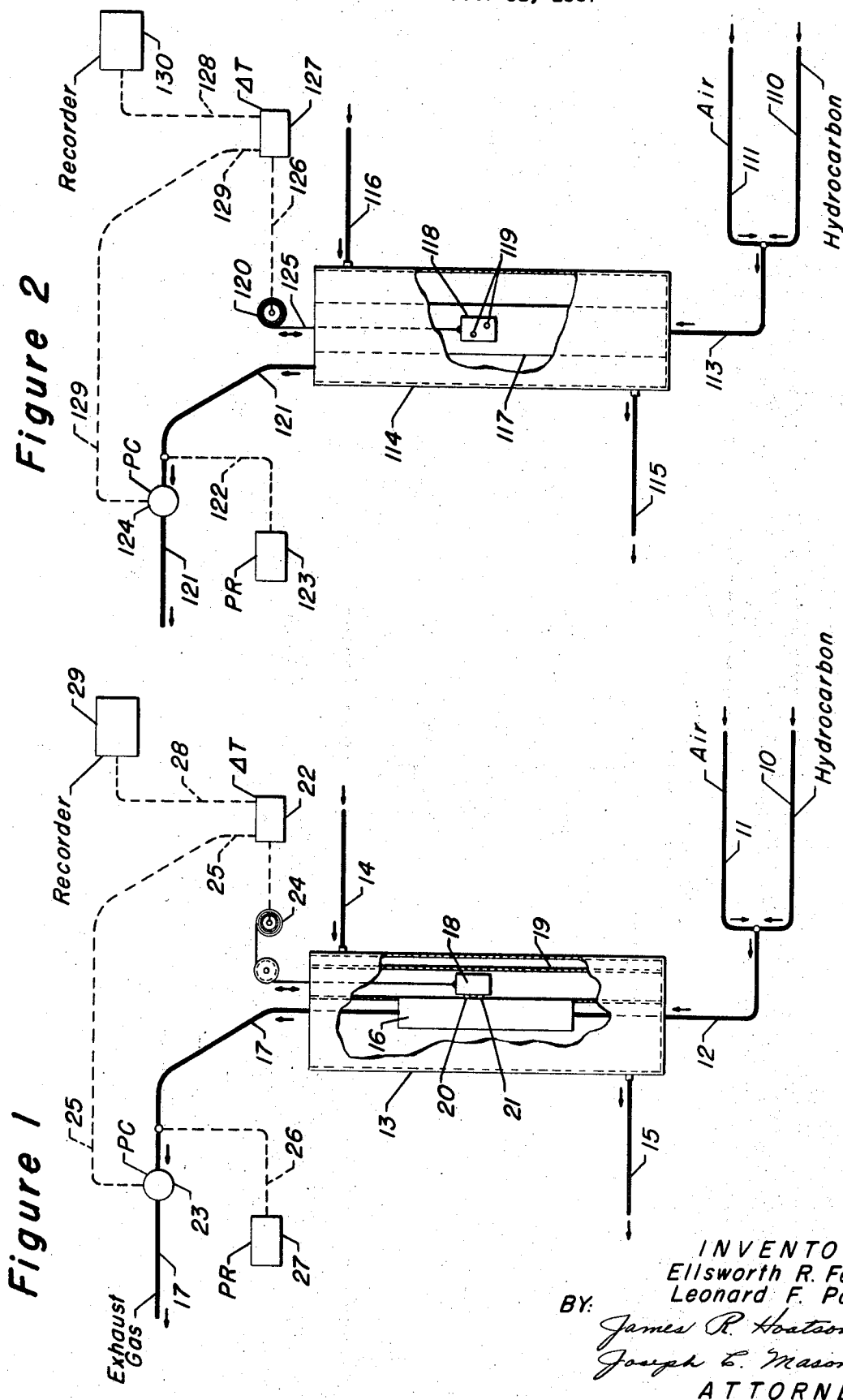
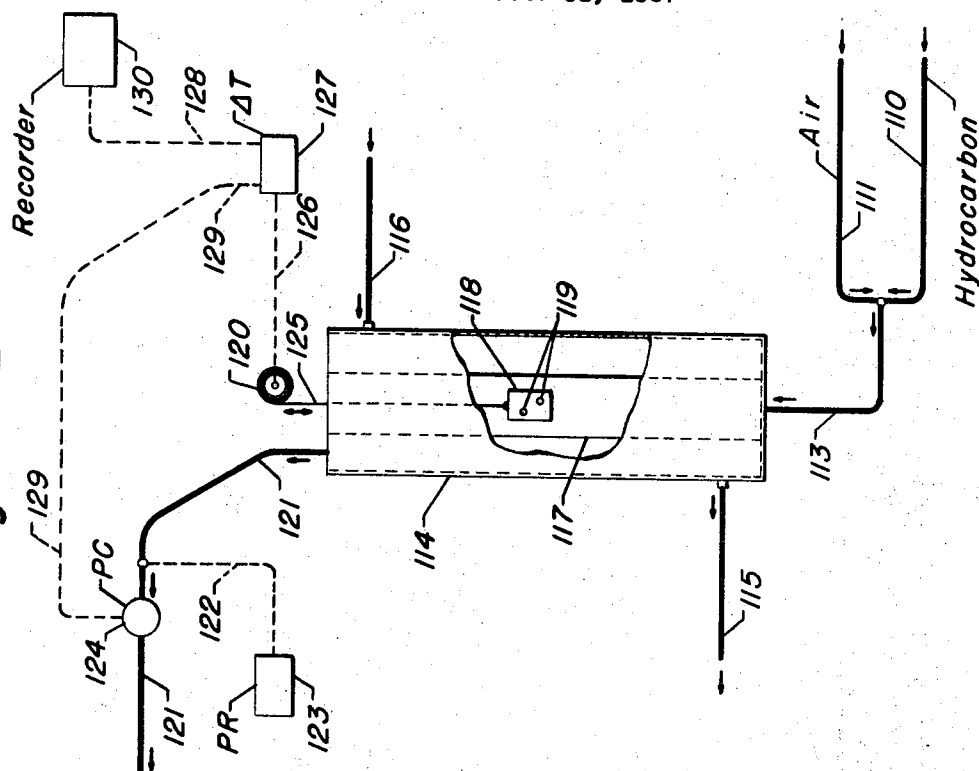


Figure 2



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3,531,255

METHOD AND APPARATUS FOR ANALYZING
HYDROCARBON COMPOSITIONSEllsworth R. Fenske, Palatine, and Leonard F. Pasik,
Mount Prospect, Ill., assignors to Universal Oil Products Company, Des Plaines, Ill., a corporation of DelawareFiled Oct. 31, 1967, Ser. No. 679,450
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U.S. Cl. 23—230

7 Claims

ABSTRACT OF THE DISCLOSURE

Method and apparatus for analyzing hydrocarbon compositions whereby, for example, octane rating of a stream is obtained. The hydrocarbon to be analyzed is burned in an apparatus under conditions which produce a cool flame. The position of the flame in the combustion chamber is located and the output signal from such flame position is correlated with a composition parameter, such as octane number.

BACKGROUND OF THE INVENTION

The present invention relates to a method and apparatus for analyzing hydrocarbon compositions. It particularly relates to an improvement in the method and apparatus for analyzing hydrocarbon mixtures which utilize a stabilized cool flame generator. It specifically relates to an improvement in the method and apparatus for determining a parameter, such as octane number, of a hydrocarbon composition utilizing cool flame combustion and utilizing the correlation between the location of the cool flame within the combustion chamber to said parameter.

Those skilled in the art are familiar with the phenomena of cool flames. Briefly, when a mixture of hydrocarbon vapor and oxygen within the explosion limit is held at conditions of pressure and temperature below the normal ignition point, partial oxidation reactions occur which generally result in the formation of by-products, such as aldehydes, carbon monoxide, and other partially oxidized combustion products. It is believed that these are the products of a chain reaction which also produced ions which then continue the reaction chain by attacking other hydrocarbon molecules. If such a mixture is contained and compressed and/or heated so that these chain reactions proceed at significant rates "cool flames" are observed usually after a suitable induction period. These cool flames are light emissions accompanied by the evolution of mild amounts of heat. In all respects the phenomena of cool flames is short of total combustion and short of total ignition and explosion. "Industrial and Engineering Chemistry," vol. 43, pp. 2329-2332, 1951, contains an article by Barusch and Paine which describes the results of work utilizing a continuous or stabilized cool flame. The utilization of this phenomena in the practice of the present invention is one of correlating the physical distance of the cool flame from the end of the combustion chamber with a composition parameter such as F-1 octane number.

A more complete explanation and description of the basic apparatus and basic method for measuring composition parameters utilizing cool flames is contained in copending patent application Ser. No. 471,670, filed July 13, 1965, now U.S. Pat. No. 3,463,613 issued Aug. 26, 1969. The contents of said copending application are incorporated herein by reference so that a greater detailed discussion need not be presented in this application. Those skilled in the art are referred directly to said copending application for additional details. As will be

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more fully developed hereinafter, the present invention describes and claims an improvement over the basic method and apparatus claimed in said copending application.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a method and apparatus for analyzing hydrocarbon mixtures.

It is another object of this invention to provide an improved method and apparatus for measuring a composition parameter of a hydrocarbon mixture such as F-1 octane number utilizing the cool flame phenomena.

Therefore, the present invention provides an analyzer for hydrocarbon composition which comprises in combination a combustion chamber; means for generating a stabilized cool flame within said chamber, said generating means using only the hydrocarbon to be analyzed as fuel therefor; means for sensing the physical position of said flame, said sensing means comprising traversing thermocouple means; and, readout means developing a signal responsive to said sensed flame position and correlatable to said hydrocarbon fuel composition.

Another embodiment of this invention includes the analyzer hereinabove wherein said sensing means is located within said combustion chamber.

A more specific embodiment of this invention includes an analyzer for hydrocarbons composition which comprises in combination a combustion chamber; means for generating a stabilized cool flame within said chamber, said generating means using only the hydrocarbons to be analyzed as fuel therefor; means for sensing the physical position of said flame, said sensing means comprising traversing thermocouple means; control means coupled to said sensing means and to said generating means sufficient to vary at least one combustion condition responsive to movement of said flame position thereby maintaining the position of said flame at a preselected plane; and, readout means developing a signal responsive to said varied condition and correlatable to hydrocarbon composition.

The present invention also provides a method for monitoring changes in hydrocarbon composition which comprises introducing a sample of hydrocarbon mixture into an elongated combustion chamber maintained under combustion conditions sufficient to generate therein a stabilized cool flame; traversing the combustion chamber in a substantially length-wise direction sufficient to determine the position of the flame; and, developing from said determined position an output signal correlatable to changes in the composition of said sample.

It is to be noted that the present invention as related to the analysis of hydrocarbon mixtures is carefully distinct from a chemical analysis means whereby a hydrocarbon mixture is broken down into its chemical components. In other words, the present invention does not necessarily relate to a method for analyzing, for example, a paraffinic hydrocarbon mixture so as to determine the relative amounts of propane, butane, pentane, etc. therein. On the other hand, the present invention is uniquely related to a method and apparatus which generates an output signal which is empirically correlatable with one or more conventional identifications or specifications of petroleum products, such as Reid Vapor Pressure, ASTM Distillation, knock characteristics such as Research Octane Number, Motor Octane Number, and the like. The specific nature of the correlation is basically a function of composition and carbon number and is further influenced by the presence or absence of hydrocarbon types such as paraffins, isoparaffins, olefins, diolefins, aromatics, etc. Thus, as presently conceived, it is contemplated that the present analyzer will be calibrated

for a particular hydrocarbon blend or charge stock and relatively small composition deviations therefrom can be accounted for by linear extrapolation. Such characteristic in no way detracts from the usefulness of this invention and is inconsequential where the apparatus is employed as an on-stream analyzer for the measurement and/or control of a particular petroleum refinery process stream since potential composition deviations will be relatively minor in such application.

Furthermore, as used herein, the term "output signal" or signal developed by the readout means is to be construed in its broadest meaningful sense and includes analog signals of all types such as amplitude-modulated, phase-modulated, or frequency-modulated electrical signals or pressure signals by conventional pneumatic transmission media, as well as digital representations of the foregoing. The output signal is further intended to include simple mechanical motion or displacement of a transducer member (whether or not mechanically, electrically, or pneumatically coupled to a visual display means, such as an indicating arm, recorder pin, or digital display board) including by way of illustration and not by way of limitation the expansion or contraction of a Bourdon tube, pressure spiral or helix; the displacement of a bellows-flapper, nozzle-diaphragm or differential transformer-core assembly; the movement of a bimetallic temperature responsive element; the motion of the slider of a self-balancing potentiometer, etc. The output signal may be transmitted without visual display directly to reset a final control unit such as a diaphragm motor valve or a sub-control loop in a cascade system. Preferably, however, the readout device will comprise or be coupled to an indicating or recording means, the scale or chart of which may further be calibrated in terms of the desired identifying composition parameter of the hydrocarbon sample, such as octane number, initial boiling point, 90% boiling point, vapor pressure, and the like. It is important to note however that in the practice of this invention the temperature difference which generated the output signal of the present invention may be directly correlatable to the composition parameter by virtue of the change in position or the temperature change output signal may be used to adjust one of the combustion parameters so as to maintain the cool flame in a predetermined position within said generating chamber.

Samples which can be analyzed by our invention include those normally gaseous and normally liquid hydrocarbon-containing mixtures comprising either at least one hydrocarbon containing from 1 to about 22 carbon atoms per molecule in admixture with one or more non-hydrocarbons, such as hydrogen, nitrogen, carbon monoxide, carbon dioxide, water, and hydrogen sulfide, or at least two different hydrocarbons containing from 1 to about 22 carbon atoms per molecule. The upper limit on carbon number is fixed by the operational requirement that the sample be vaporizable in the air stream under combustion conditions without undergoing any substantial thermal decomposition prior to the partial oxidation thereof. Therefore, in the context of the present invention, the term "hydrocarbon composition" is intended to embody all forms of hydrocarbon mixtures in which hydrocarbons predominate but which may also contain significant amounts of non-hydrocarbon materials. In the preferred and practical embodiment of this invention for the measurement of Research Octane Number, the feed-stock chargeable to the apparatus of the present invention include those within the gasoline boiling range, including straight-run gasoline, cracked gasolines, motor alkylate, catalytically reformed gasoline, hydrocracker gasoline products, etc.

The oxidizing agent used in this apparatus is preferably an oxygen-containing gas, such as air, substantially pure oxygen, or it may be a synthetic blend of oxygen with an inert or equilibrium-affecting diluent, such as nitrogen, carbon dioxide, or steam.

The generation of the stabilized cool flame is effected under combustion conditions generally including super-atmospheric pressure and elevated temperature although subatmospheric pressure may be used in some cases. For example, the pressure may be in the range from about 12 p.s.i.a. to about 165 p.s.i.a., with a maximum flame front temperature in the order of 600° F. to 1000° F. For measuring the composition of a gasoline boiling range hydrocarbon fraction, it is preferable to employ pressures in the range from 15 to 65 p.s.i.a., more preferably in the range from 16 to 50 p.s.i.a., together with an induction zone temperature in the range of from 550° F. to 850° F. Control of induction zone temperature can be effected by the amount of preheat imparted to the incoming sample and air streams and also by supplying heat from an external source to the combustion chamber itself. In any case, the permissible limits within which pressure and temperature may be independently varied without departure from stable operation can be determined by simple experiment for particular type of sample.

As previously mentioned the thermocouple sensing device may be placed either within the combustion chamber or outside of the combustion chamber. The important thing to note, however, is that the thermocouple sensing device must be placed in such a position that it can traverse in substantially lengthwise direction the combustion chamber in order to locate the position of the stabilized cool flame. In the event the thermocouple sensing means is located exterior to the combustion chamber, a thin-walled conduit should be used to contain such means. As will be noted from the detailed description of the apparatus, it is preferable to utilize a heat exchange medium completely surrounding the combustion chamber in order to minimize localized temperature changes within the combustion chamber and to remove as rapidly as possible the heat of combustion which is evolved from the reaction. Accordingly, the conduit should be placed directly against the combustion chamber so that there is a minimum of resistance between the interior of the combustion chamber and the thermocouple sensing means. Those skilled in the art are aware of thermocouple elements which are sensitive enough to pick up small temperature changes through the wall of a combustion chamber. This conduit need not be perfectly vertical or plum, but should have a substantial inclination from the horizontal so as to extend through substantially the entire length of the combustion chamber without occupying excessive space within the heat exchange zone and also to permit free travel of the thermocouple sensing device within it, e.g. a vertical position is preferable. In general, the conduit as installed may deviate as much as 10°-15° from the vertical and still be substantially vertical for the purposes of the invention. The vertical conduit projects for a substantial distance along the axis of the combustion chamber and preferably extends through either the upper end wall of the containing vessel and/or the lower end wall thereof, being also mechanically supported by such end wall as by welded or flanged connection. The thermocouple housing conduit is desirably centered on a line parallel to and radially displaced from the central longitudinal axis of the vessel, and is preferably formed such that one wall of the combustion chamber itself forms a portion of the wall of the enclosing conduit for the thermocouple means.

In the preferred embodiment of this invention, the thermocouple sensing device is placed directly and physically within the combustion chamber and is exposed directly to the flame front within the combustion chamber. By operating with the thermocouple sensing means within the combustion chamber, it is possible for even greater sensitivity to be built into the apparatus for accurately placing the physical location of the stabilized cool flame within the combustion chamber.

In either event; that is, in the event the thermocouple sensing means is placed within the combustion chamber

or placed without the combustion chamber, the drive means for traversing by raising and lowering the thermocouple means may comprise, for example, a pair of wire cables, tapes or chains connected to the thermocouple sensing device and driven by reversible electric motor or air motor through a system of sheaves, drums, sprockets, weights and/or spring-loaded, or the like. The thermocouple detecting means may ride on a single cable, tape, or chain arranged in a triple sheaf, double-looped system, with one sheaf being driven by reversible prime mover and the other two sheaves idling. Alternatively, when the required vertical displacement is not too great, the thermocouple sensing means may be positioned by means of reciprocal rods or shafts activated by pneumatic or hydraulic systems. Other equivalent drive systems will be apparent to those skilled in the art.

The output signal from the thermocouple sensing means is fed through signal leads to a suitable readout device, such as a strip chart or x-y recorder. The readout device may be mounted locally near the vessel or remotely in a control house. During a given traverse of the combustion chamber by the thermocouple sensing device, the location of the stabilized cool flame is indicated by relatively sharp step change or transition from one signal level to another. The recorder chart drive may be manually synchronized with the source-detector drive means or may be positively activated thereby through a position servo so that the location of the cool flame front may be directly observed from the chart in terms of combustion chamber dimensions.

The invention may be more fully understood with reference to the accompanying drawings in which:

FIG. 1 is a schematic representation of one embodiment of the invention wherein the thermocouple sensing device is placed externally to the combustion chamber, and,

FIG. 2 is a schematic representation of another embodiment of this invention wherein the thermocouple sensing device is placed physically within the combustion chamber.

DESCRIPTION OF THE DRAWINGS

With reference to FIG. 1, the analyzer comprises in combination combustion chamber 16 contained in outer casing or canister 13 having a closed lower end and an open upper end. Canister 13 is provided with a fluid heating medium inlet conduit 14 and a heating medium outlet conduit 15. Other heating means can be used, such as a contained fluid medium canister having external heating means, etc. The upper end of canister 13 is enclosed by suitable flange means and gasket means, not shown, those skilled in the art being familiar with appropriate ways of closing a hollow canister of this sort. If desired, the exterior of canister 13 may be encased in one or more layers of insulation, again not shown.

Canister 13 contains an elongate thin-wall combustion tube 16 having at its lower extremity a burner nozzle assembly, not shown. Appropriate conduits for the introduction of hydrocarbons to be analyzed and oxygen-containing gas are appropriately shown as conduits 10 and 11, respectively, with the proper fuel-air ratio being injected into combustion chamber 16 via inlet conduit 12. Other specific details as to the construction of the apparatus may be found in said copending application, supra.

Vent gases comprising the partial oxidation products of the stabilized cool flame are removed from combustion tube 16 through line 17 which includes a back pressure regulator or controller 23. Appropriate pressure indicating device, such as a pressure recorder, is indicated at 27 being connected through appropriate lead 26 to the vent gas outlet conduit 17.

The front of the stabilized cool flame is a relatively narrow well-defined transverse section spaced a predetermined distance above the nozzle assembly. In the present

embodiment, the detection of the physical position of the flame within the combustion chamber is effected by a continual or periodic traverse of thermocouple sensing means 18 containing thermocouples 20 and 21 contained therein at an exterior location of combustion chamber 16. The thermocouple sensing device is contained within elongated conduit 19, the operation of which has been previously discussed. Appropriate windup means including suitable cycle timer means for making the thermocouple sensing device 18 traverse up and down the combustion chamber is shown as item 24 and is connected by suitable leads to a temperature responsive indicating device 22. Thus, thermocouple sensing device 18 comprises, for example, a pair of axially spaced thermocouples, 20 and 21, which are inserted into a suitable casing and which have actual contact with the exterior of the wall of combustion chamber 16. Thermocouples 20 and 21 may be iron-constantan couples, for example and are connected to n-voltage opposite. Temperature controller indicator 22 may be a conventional self-balancing potentiometer in combination with pneumatic control means activating through lead 25 pressure controller 23 in a preferred embodiment of the invention.

In the operation of the inventive apparatus, when the flame front is exactly positioned between thermocouples 20 and 21, both couples will be at about the same temperature and the voltage appearing at the input of differential temperature controller 22 will be approximately zero. However, another equally satisfactory manner of operation is to operate the apparatus with a small net voltage difference, either positive or negative, corresponding to a temperature differential in the order of 10°-40° F. This means that the flame front is then slightly asymmetrical with respect to couples 20 and 21. While this mode achieves greater sensitivity, it is not a critical requirement and one may still realize good results if the apparatus is operated at zero temperature differential.

As previously mentioned, the operation of the apparatus in its preferred embodiment will utilize differential temperature controller 22 to adjust one of the combustion parameters, such as pressure, operating with pressure control valve 23 in order to move the flame front into a fixed predetermined location, the degree of change necessary to reposition the flame front being directly correlatable with the desired composition parameter of the sample charged into the system. For ease of operation, the output from temperature controller 22 is connected by appropriate lead 28 to temperature recorder 29 wherein a visual indication of the flame front location may be recorded.

With reference to FIG. 2, the preferred arrangement of the apparatus is shown and comprises outer casing or canister 114 having as previously disclosed a closed lower end and an open upper end which can be suitably enclosed by flange and gasket means, not shown. Canister 114 has fluid heating medium inlet conduit 116 and heating medium fluid outlet conduit 115. The combustion chamber is shown as 117 having connected to it suitable inlet conduits for hydrocarbon and air as 110 and 111, respectively, with the proper fuel-air ratio being introduced into combustion chamber 117 via inlet conduit 113 and burner assembly, not shown. The exhaust gases are removed from combustion chamber 117 via conduit 121 having located therein suitable back pressure control means 124 also which is connected through lead 122 to pressure recorder 123.

In this preferred embodiment of the invention, the thermocouple sensing device 118 is placed physically within combustion chamber 117 and comprises, preferably, two thermocouple leads indicated as 119. Device 118 is suitably attached via cable 125 to appropriate windup means 120 including cycle timer means, also having connection via lead 126 to differential temperature recorder 127. Again, in the preferred embodiment of the apparatus, differential temperature recorder 127 is connected via lead 129 to pressure controller 124 so that changes in ΔT

reflected by controller 127 activate and is responsive to pressure controller 124. By appropriate lead 128 the differential temperature measured by device 118 and picked up by 127 is indicated visually in temperature recorder 130.

As a preferred example, utilizing the configuration of apparatus in FIG. 2, a gasoline fraction is introduced via line 110, admixed with air from 111, and introduced into the system via line 113. Generally, combustion chamber 117 is a one inch diameter tube which is maintained under a pressure of 16 to 50 p.s.i.a., utilizing pressure controller 124, more fully discussed hereinafter. The temperature of the induction zone is about 630° F. In the region of the flame front the temperature climbs rapidly, peaking at about 750° F., then falling off rapidly to about 640° F. When the flame front is stabilized thermocouple sensing device 118 makes a continual traverse over the lengthwise direction of combustion chamber 117 until the temperature of both couples 119 are at about the same temperature thereby being indicated as the net voltage appearing at the input of differential temperature controller 127 being zero. Preferably, differential temperature controller 127 activates pressure controller 124 so as to move the flame front to a predetermined location within combustion chamber 117. In other words, an increase in pressure will cause the flame front to recede towards the burner end of the combustion chamber and a decrease in pressure will cause the flame front to advance away from the burner. Therefore, if the hydrocarbon composition changes in a manner such that the front attempts to move back toward the burner, thermocouples 119 will reflect a temperature rise and the differential temperature controller 118 will act through controller 127 to decrease combustion pressure until the front is restored to its predetermined original position. Conversely, if the hydrocarbon composition changes in a manner such that the front attempts to move away from the burner, device 118 is movably traversed through the combustion chamber until differential temperature controller 127 indicates a substantially zero net voltage. At this point differential temperature controller 127 will increase combustion pressure until the front is restored to its original position, again being determined by the continual traverse of thermocouple sensing device 118. In any event, the change in combustion pressure required to immobilize the flame front at its original predetermined location following a composition change is a correlatable function with such composition change.

Alternatively, as mentioned previously, the cool flame is allowed to locate itself within the combustion chamber according to the confines of temperature and pressure therein and such location is determined by means of a traversing thermocouple. The determined location is recorded and correlated with the combustion parameter, such as octane number.

PREFERRED EMBODIMENT

Therefore, from the above description, the preferred embodiment of this invention comprises an analyzer for hydrocarbon composition, which comprises, in combination, a combustion chamber; means for generating a stabilized cool flame within said combustion chamber, said generating means comprising in further combination burner means, hydrocarbon inlet means communicating with said burner means, and means for varying the pressure in said combustion chamber; means for sensing the physical position of said flame relative to said burner means, said sensing means comprising traversing thermocouple means positioned internally and movably axially to said combustion chamber; control means cooperating with said sensing means and with said pressure varying means sufficient to vary combustion chamber pressure responsive to movement of said flame, thereby substantially immobilizing the position of said flame; and, readout means developing a signal responsive to combustion chamber

pressure and correlatable to hydrocarbon composition.

According to the preferred embodiment of this invention, there is provided a method for monitoring changes in hydrocarbon composition which comprises introducing a sample of hydrocarbon mixture into an elongated combustion chamber maintained under combustion conditions sufficient to generate therein a stabilized cool flame; traversing the combustion chamber in a substantially lengthwise direction thereby sensing the position of the flame; developing a control signal relating to said sensed position; utilizing said control signal to vary at least one of said combustion conditions responsive to movement of said flame, thereby maintaining the position of said flame at a selected plane; sensing said varied condition; and, developing from said varied condition an output signal correlatable to changes in the composition of said sample.

A distinctly preferred embodiment of the method aspects of this invention include the method hereinabove wherein said varied combustion condition is pressure.

The invention claimed:

1. Analyzer for hydrocarbon composition which comprises, in combination, a combustion chamber; means for generating a stabilized cool flame within said chamber, said generating means using only the hydrocarbons to be analyzed as fuel therefor; means for sensing the physical position of said flame, said sensing means comprising traversing thermocouple means; and, readout means developing a signal responsive to said sensed flame position and correlatable to said hydrocarbon fuel composition.

2. Analyzer according to claim 1 wherein said sensing means is located within said combustion chamber.

3. Analyzer for hydrocarbon composition which comprises, in combination, a combustion chamber; means for generating a stabilized cool flame within said chamber, said generating means using only the hydrocarbon to be analyzed as fuel therefor; means for sensing the physical position of said flame, said sensing means comprising traversing thermocouple means; control means coupled to said sensing means and to said generating means sufficient to vary at least one combustion condition responsive to movement of said flame position thereby maintaining the position of said flame at a selected plane; and, readout means developing a signal responsive to said varied condition and correlatable to hydrocarbon composition.

4. Analyzer for hydrocarbon composition which comprises, in combination, a combustion chamber; means for generating a stabilized cool flame within said combustion chamber, said generating means comprising in further combination burner means, hydrocarbon inlet means communicating with said burner means, and means for varying the pressure in said combustion chamber; means for sensing the physical position of said flame relative to said burner means, said sensing means comprising traversing thermocouple means positioned interiorly and movably axially to said combustion chamber; control means cooperating with said sensing means and with said pressure varying means sufficient to vary combustion chamber pressure responsive to movement of said flame thereby substantially immobilizing the position of said flame; and, readout means developing a signal responsive to combustion chamber pressure and correlatable to hydrocarbon composition.

5. Method for monitoring changes in hydrocarbon composition which comprises introducing a sample of hydrocarbon mixture into an elongated combustion chamber maintained under combustion conditions sufficient to generate therein a stabilized cool flame; traversing the combustion chamber with traversing temperature sensing means in a substantially lengthwise direction thereby to determine the position of the flame; and, developing from said determined position an output signal correlatable to changes in the composition of said sample.

6. Method for monitoring changes in hydrocarbon composition which comprises introducing a sample of hydrocarbon mixture into an elongated combustion cham-

ber maintained under combustion conditions sufficient to generate therein a stabilized cool flame; traversing the combustion chamber in a substantially length-wise direction thereby sensing the position of the flame; developing a control signal relating the said sensed position; utilizing said control signal to vary at least one of said combustion conditions responsive to movement of said flame thereby maintaining the position of said flame at a selected plane; sensing said varied condition; and, developing from said varied condition an output signal correlatable to changes in the composition of said sample.

7. Method according to claim 6 wherein said varied combustion condition is pressure.

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