

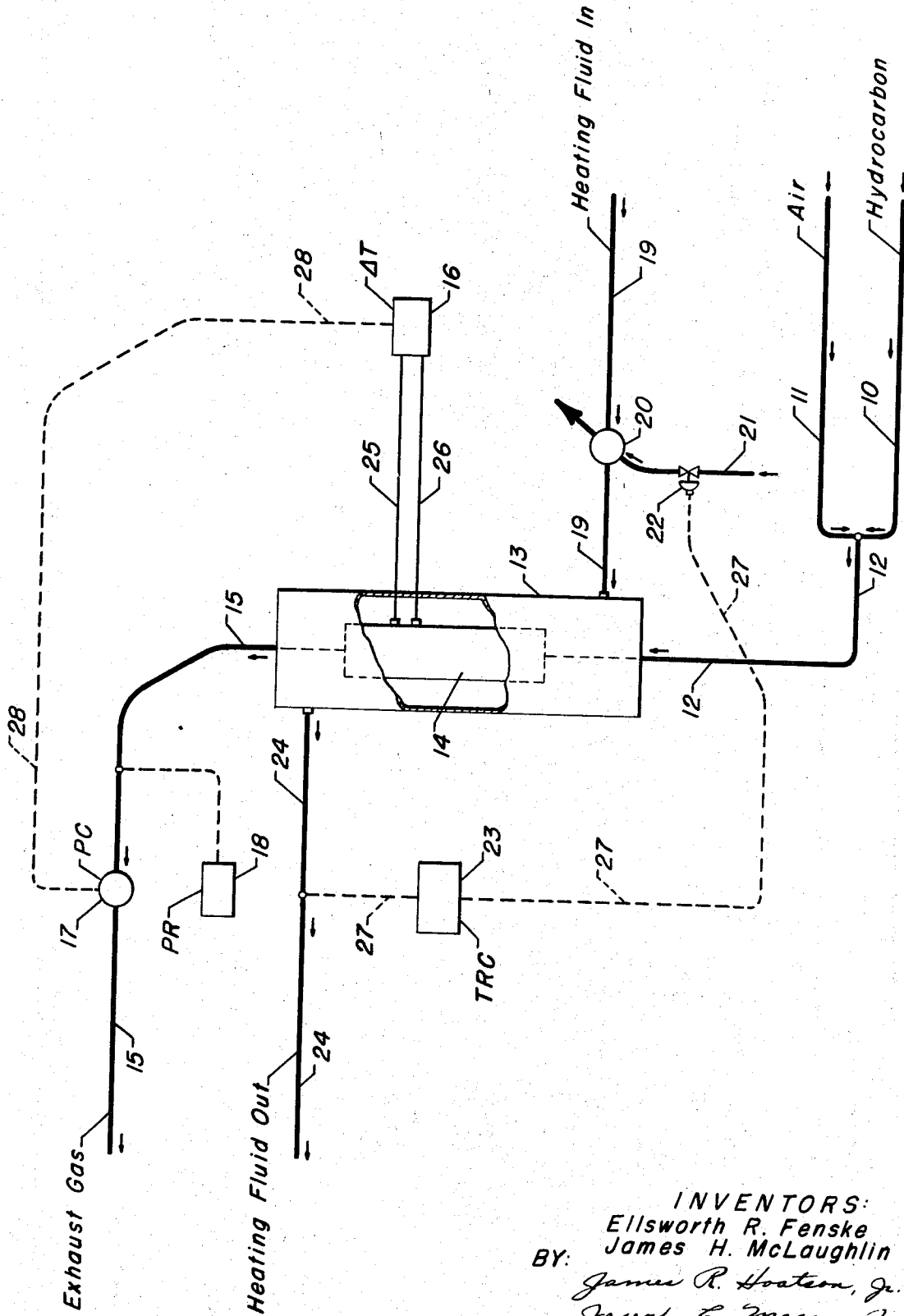
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METHOD FOR ANALYZING HYDROCARBON COMPOSITIONS

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METHOD FOR ANALYZING HYDROCARBON COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

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

BACKGROUND OF THE INVENTION

The present invention relates to a method for analyzing hydrocarbon compositions. It particularly relates to an improvement in the method for analyzing hydrocarbon mixtures which method utilizes a stabilized cool flame generator. It specifically relates to an improvement in the method 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 and said parameter.

Those skilled in the art are familiar with the phenomena of cool flame generation. 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 produces 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 minor amounts of heat. In all respects the phenomena of cool flames is short of total combustion and short of total ignition and explosion. An article by Barush and Paine in "Industrial and Engineering Chemistry," volume 43, page 2329, 1951, 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 distance of the cool flame from the end of the combustion chamber with a composition parameter, such as F-1 octane number (Research Octane Number).

A more complete explanation and description of the basic apparatus and basic method for measuring composition parameters utilizing cool flame generation is contained in our copending patent application Ser. No. 471,670, filed July 13, 1965, now U.S. Pat. No. 3,463,613 issued Aug. 26, 1969. The entire 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 de-

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tails. As will be more fully developed hereinafter, the present invention describes and claims an improvement over the basic method claimed and described in our copending application.

SUMMARY OF THE INVENTION

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

It is another object of this invention to provide an improved method for measuring a composition parameter of a hydrocarbon mixture, such as Research Octane Number, utilizing the cool flame phenomena.

Therefore, the present invention provides a method for monitoring changes in the composition of a hydrocarbon fluid mixture, which comprises (a) introducing said mixture into one end of an elongated combustion zone under conditions sufficient to produce a cool flame therein; (b) stabilizing said cool flame by surrounding said combustion zone with heat transfer means adapted to create a decreasing temperature profile within said combustion zone; (c) detecting the physical position of said flames in the combustion zone; and (d) developing from said detected position an output signal correlatable to said change in the composition of said hydrocarbon mixture.

Another embodiment of this invention includes the method hereinabove wherein said change in composition comprises a change in octane number.

A more limited embodiment of the present invention includes a method for detecting changes in composition of a fluid mixture comprising hydrocarbons which comprises the steps of (a) introducing a sample stream of said mixture into one end of an elongated combustion chamber maintained under conditions sufficient to generate therein a cool flame; (b) surrounding said combustion zone with heat transfer means adapted to create a length-wise decreasing temperature profile within said zone thereby stabilizing said flame; (c) sensing the position of said flame within said zone and developing therefrom a controlled signal; (d) utilizing said controlled 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; (e) sensing said varied condition and, (f) developing from said varied conditions an output signal correlatable to said change in composition to said sample.

A still further limited embodiment of this invention includes the method hereinabove wherein said varied condition is combustion zone pressure.

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 a paraffinic hydrocarbon mixture, for example, 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 which utilizes 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 invention will be calibrated for a particular hydrocarbon blend or charge stock and composition deviations therefrom can be accounted for by linear extrapolation. Such char-

acteristic 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 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.

Frequently, 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 as previously mentioned. 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 a temperature change (with the output signal) being used to adjust one of the combustion parameters so as to maintain the cool flame in a predetermined position within said generating means. In a preferred embodiment of this invention the output signal is used to adjust one of the combustion parameters, such as combustion zone pressure, so as to reposition the cool flame in a predetermined position. Additionally, some combination of cool-flame temperature (level, not difference) and another parameter, such as pressure, may be correlated with desired information, such as aromatic hydrocarbon content, etc.

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 vaporized 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, and in particular may contain such items as tetra-ethyl lead, tetra-methyl lead, etc. In the preferred and practical embodiment of this invention for the measurement of knock characteristics of a motor fuel, such as Research Octane Number, the feedstock 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. For example, the pressure may be in the range from about 14 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 35 p.s.i.a., together with an induction zone temperature in the range of 550° F. to 850° F. Control of induction zone temperature can be affected 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 a particular type and quantity of sample.

As previously mentioned, the detection of the physical position of the flame within the combustion chamber is preferably effected by temperature responsive thermoelectric means, although other equivalent means can be used. The thermocouple sensing device may be placed either within the combustion chamber or outside of the combustion chamber, and may either be fixed or may be movable in such a manner to completely and substantially traverse the length-wise direction of the combustion chamber in order to locate the position of the stabilized cool flame.

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. In practice, this signal is, preferably, fed directly to a controller, usually without readout means, since combustion zone pressure is read and used as an indication of cool flame position. The readout device, if any, may be mounted locally near the vessel or remotely in a control house. The location of the stabilized cool flame is generally indicated by relatively sharp step change of transition from one signal level to another. The thermocouple sensing device comprises a pair of accurately spaced thermocouple leads (e.g., one (1) inch apart) which are inserted into thin-walled, pencil-type thermowells and may be constructed of iron-constantan. The lead wires from the thermowells are connected to the terminals of a suitable differential temperature controller. Such controller may be a conventional self-balancing potentiometer in combination with pneumatic control means. A suitable input span for the controller may be minus 5 to +5 millivolts and the output signal thereof transmitted may be a conventional 3-15 p.s.i. air signal. Such control signal is used to reset the set point on a back pressure controller in the preferred embodiment of this invention. The readout means of this preferred embodiment is a pressure recorder connecting via suitable pressure taps upstream from the controller.

Therefore, from the description of the invention presented thus far, it can be seen that the present invention is an improvement over the basic method in that greater stability of the cool flame front is achieved by utilizing a decreasing temperature profile across a combustion chamber. For practical purposes, a temperature drop through the combustion zone from the inlet end to the exhaust end in the order of 25° F. or more is generally satisfactory. The control of the temperature profile is conveniently accomplished by the use of heat transfer means such as a fluid which would enter one end of an inclosing canister for the combustion zone at a relatively hot tem-

perature and exit from the other end of the same canister at a significantly lower temperature. By utilizing a flowing fluid a heat sink may be developed, which will allow the combustion zone to equilibrate at a predetermined decreasing temperature profile. Other heat transfer means and devices may be used, by those skilled in the art for accomplishing the decreasing profile as specified herein. Externally mounted cooling coils may be placed around the combustion chamber at the approximate point of the cool flame front and can be controlled either dependently or independently of the overall flowing heat transfer fluid which may also be placed around the combustion zone. Individually controlled electrical heating units can be used, whereby the upstream end of the combustion zone may be heated to a higher temperature than the lower end or downstream in order to accomplish the decreasing temperature profile down the length-wise direction of the combustion zone from the burner end of the zone to the exhaust end of the zone. Other means will be obvious to those skilled in the art.

The invention may be more fully understood with reference to the accompanying drawing which is a schematic representation of apparatus for practicing one embodiment of the invention.

DESCRIPTION OF THE DRAWINGS

With reference to the attached drawing, the analyzer comprises, in combination, combustion chamber 14 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 19 and a heating medium outlet conduit 24. 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 elongated thin-wall combustion tube 14 having at its lower extremity a burner nozzle assembly, or other mixing device, 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 14 via inlet conduit 12. 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 14 through line 15 which includes a back pressure regulator or controller 17. Appropriate pressure indicating device, such as a pressure recorder, is indicated at 18.

The front of the stabilized cool flame is relatively narrow, well-defined transverse section spaced a predetermined distance above the inlet assembly. In the present embodiment, the detection of the physical position of the flame is effected by temperature responsive thermoelectric means, other equivalent means being known by those skilled in the art. As shown with reference to the drawings, the flame position sensing means comprises a pair of axially spaced thermocouples which are inserted into thin-walled, pencil type thermowells, such thermowells preferably having a low heat capacity coupled with a relatively high thermal conductivity in the longitudinal direction. Lead wires 25 and 26 are connected to the input terminals of a suitable difference temperature of controller 16. The output signal from controller 16 may be transmitted through line 28 to reset the set point of back pressure controller 17 or may directly operate the pressure control valve.

Additionally, it is to be noted that the heating fluid inlet conduit 19 also passes through heat exchange means 20 having suitable conduit for the passage therethrough

of another heating fluid, such as hot oil, via conduit 21. The amount of heating fluid, e.g. molten salt or molten metal (or hot oil), passing through heat exchanger 20 is controlled by control valve 22 which is reset through lead 27 by temperature recorder controller (TRC) 23 (or simply a temperature controller) which is placed in outlet conduit 24 for the measurement of the temperature of the heating fluid leaving canister 13.

In the operation of the inventive apparatus, when the flame front is exactly positioned between the thermocouples placed in the combustion zone, both couples will be about the same temperature, and the voltage appearing at the input of differential temperature of controller 16 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 the thermocouples. While this mode achieves greater sensitivity, it is not a critical requirement and one may still get 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 of controller 16 to adjust one of the combustion parameters, such as pressure, operating with pressure control valve 17 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 16 is connected by appropriate lead, not shown, to for example a temperature recorder, not shown, wherein a visual indication of the flame front location may be recorded.

In the practice of the invention utilizing the apparatus shown in the drawing, a gasoline fraction is introduced via line 10, admixed with air from line 11, and the mixture is introduced into the system via line 12. Typically, combustion chamber 14 is a one-inch diameter tube which is maintained under a pressure from 16 to 50 p.s.i.a. utilizing pressure controller 17, more fully discussed hereinafter. The temperature of the induction zone is about 630° F. (in some cases a higher induction zone temperature in the range of 670°-680° F. may be desirable) and is maintained thereout by the introduction of hot molten salt via line 19. In the region of the flame front the temperature climbs rapidly peaking at about 750° F. and then falling off rapidly to about 600° F., although the level of temperature is limited by the surrounding bath temperature. When the flame front is stabilized, the thermocouple sensing devices will read approximately zero as indicated by the next voltage appearing at the input of differential temperature of controller 16. Temperature controller 16 activates pressure controller 17 so as to move the flame front to a predetermined location within combustion chamber 14. In other words, an increase in pressure will cause the flame front to recede towards the inlet end of the combustion chamber and a decrease in pressure will cause the flame front to advance away from the inlet. Therefore, if the hydrocarbon composition changes in a manner such that the flame front attempts to move back toward the inlet, the thermocouples will reflect a temperature rise, and the differential temperature controller 16 will act through controller 17 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 nozzle, controller 16 activates pressure controller 17 to increase combustion pressure until the front is restored to its original position. In any event, the changing combustion pressure required to immobilize the flame front at its predetermined loca-

tion, following a composition change is a correlatable function with such composition change.

According to the present invention, the flame front is stabilized in a facile manner by maintaining a temperature profile of decreasing magnitude length-wise down combustion tube 14. In other words, at the nozzle end of the combustion chamber there will be a relatively high temperature and at the exhaust end of the combustion zone there will be a relatively low temperature. It has been found ideally that the flame front is stabilized to its maximum extent when the temperature profile down the combustion tube 14 is characterized by being relatively high immediately upstream of the cool flame front and being relatively low downstream of the cool flame front. This decreasing temperature profile is achieved in one embodiment of the invention by sensing the temperature of the heating fluid leaving canister 13 via line 24 utilizing TRC 23. The temperature sensed by TRC 23 activates control valve 22 which will either increase or decrease the temperature of the heating fluid going into canister 13 via line 19. By operating in this manner the temperature at the nozzle end of the combustion zone is always maintained at a relatively high level and the heating fluid rising through canister 13 surrounding combustion zone 14 will slowly decrease uniformly in temperature and leave the system via line 24 at a predetermined and controllable lower temperature. It was found also by operating in this manner that the flame front was considerably more stable and more easily determinable by the thermocouple means inserted into combustion zone 14. Generally, the temperature profile will be substantially linear in its decreasing slope and will be of a magnitude of at least 25° C., more typically the temperature decrease across the combustion zone will be from 30° to 50° F. It is to be noted that the term "decreasing temperature profile" is used to embody the concept of a drop in temperature from the nozzle end of the combustion zone to the exhaust gas end of the combustion zone. It is recognized that in the neighborhood of exactly the flame front, there will be a peak in temperature which is substantially higher than the nozzle end of the combustion zone. To this extent, of course, the temperature profile will be nonlinear, although for ease of explanation, as previously mentioned, the decreasing temperature profile is a measurement of the temperature from the nozzle end of the combustion zone to the exhaust end of the combustion zone or, more preferably, refers to the temperature immediately upstream of the flame front and the temperature immediately downstream of the flame front, discounting the exact flame front temperature.

PREFERRED EMBODIMENT

Therefore, from the above description, the preferred embodiment of this invention provides a method for determining the octane rating of a gasoline fraction which comprises (a) introducing a pre-heated vaporized stream of said gasoline fraction and a pre-heated stream of air into one end of an elongated combustion zone maintained at elevated temperature; (b) partially oxidizing said fraction within said zone under conditions sufficient to generate therein a cool flame characterized by a relatively narrow well defined flame front spaced from said one end; (c) creating and maintaining a decreasing temperature profile within said zone and along the length thereof utilizing external temperature control means, said profile being further characterized by the temperature within said zone being relatively high upstream of said flame front and being relatively low downstream of said flame front; (d) sensing the position of said flame front relative to said one end and developing therefrom a control signal; (e) varying the pressure of said combustion zone responsive to said control signal in a manner to immobilize said flame front relative to said one end; and, (f) sensing said combustion zone pressure and developing

therefrom an output signal responsive to changes in the composition of said gasoline fraction and correlatable with the octane rating thereof.

A still further preferred embodiment of this invention is the method hereinabove wherein said relatively high temperature is from 550° F. to 850° F.

Another preferred embodiment of the invention is the method hereinabove wherein said relatively low temperature is at least 25° F. less than said relatively high temperature.

What is claimed is:

1. Method for monitoring changes in the composition of a hydrocarbon fluid mixture which comprises:

- (a) introducing said mixture into one end of an elongated combustion zone under conditions sufficient to produce a cool flame therein;
- (b) stabilizing said cool flame by surrounding said combustion zone with heat transfer means adapted to create a lengthwise decreasing temperature profile within said combustion zone;
- (c) detecting the physical position of said flame in the combustion zone; and,
- (d) developing from said detected position an output signal correlatable to said change in the composition of said hydrocarbon mixture.

2. Method according to claim 1 wherein said change in composition comprises a change in octane number.

3. Method for detecting changes in composition of a fluid mixture comprising hydrocarbons which comprises the steps of:

- (a) introducing a sample stream of said mixture into one end of an elongated combustion chamber maintained under conditions sufficient to generate therein a cool flame;
- (b) surrounding said combustion zone with heat transfer means adapted to create a length-wise decreasing temperature profile within said zone thereby stabilizing said flame;
- (c) sensing the position of said flame within said zone and developing therefrom a control signal;
- (d) 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;
- (e) sensing said varied condition; and,
- (f) developing from said varied condition an output signal correlatable to said change in composition of said sample.

4. Method according to claim 3 wherein said varied condition is combustion zone pressure.

5. Method according to claim 3 wherein said temperature profile is further characterized by the temperature within said zone being relatively high upstream of the cool flame front and being relatively low downstream of the cool flame front.

6. Method according to claim 5 wherein said heat transfer means comprises a mobile heat transfer fluid.

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

8. Method for determining the octane rating of a gasoline fraction which comprises:

- (a) introducing a pre-heated vaporized stream of said gasoline fraction and a pre-heated stream of air into one end of an elongated combustion zone maintained at elevated temperature;
- (b) partially oxidizing said fraction within said zone under conditions sufficient to generate therein a cool flame characterized by a relatively narrow, well defined flame front spaced from said one end;
- (c) creating and maintaining a decreasing temperature profile within said zone and along the length thereof utilizing external temperature control means, said profile being further characterized by the temperature within said zone being relatively high up-

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stream of said flame front and being relatively low downstream of said flame front;

(d) sensing the position of said flame front relative to said one end and developing therefrom a control signal;

(e) varying the pressure of said combustion zone responsive to said control signal in a manner to immobilize said flame front relative to said one end; and,

(f) sensing said combustion zone pressure and developing therefrom an output signal responsive to changes in the composition of said gasoline fraction and correlatable with the octane rating thereof.

9. Method according to claim 8 wherein said relatively high temperature is from 550° F. to 850° F.

10. Method according to claim 9 wherein said relatively

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low temperature is at least 25° F. less than said relatively high temperature.

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