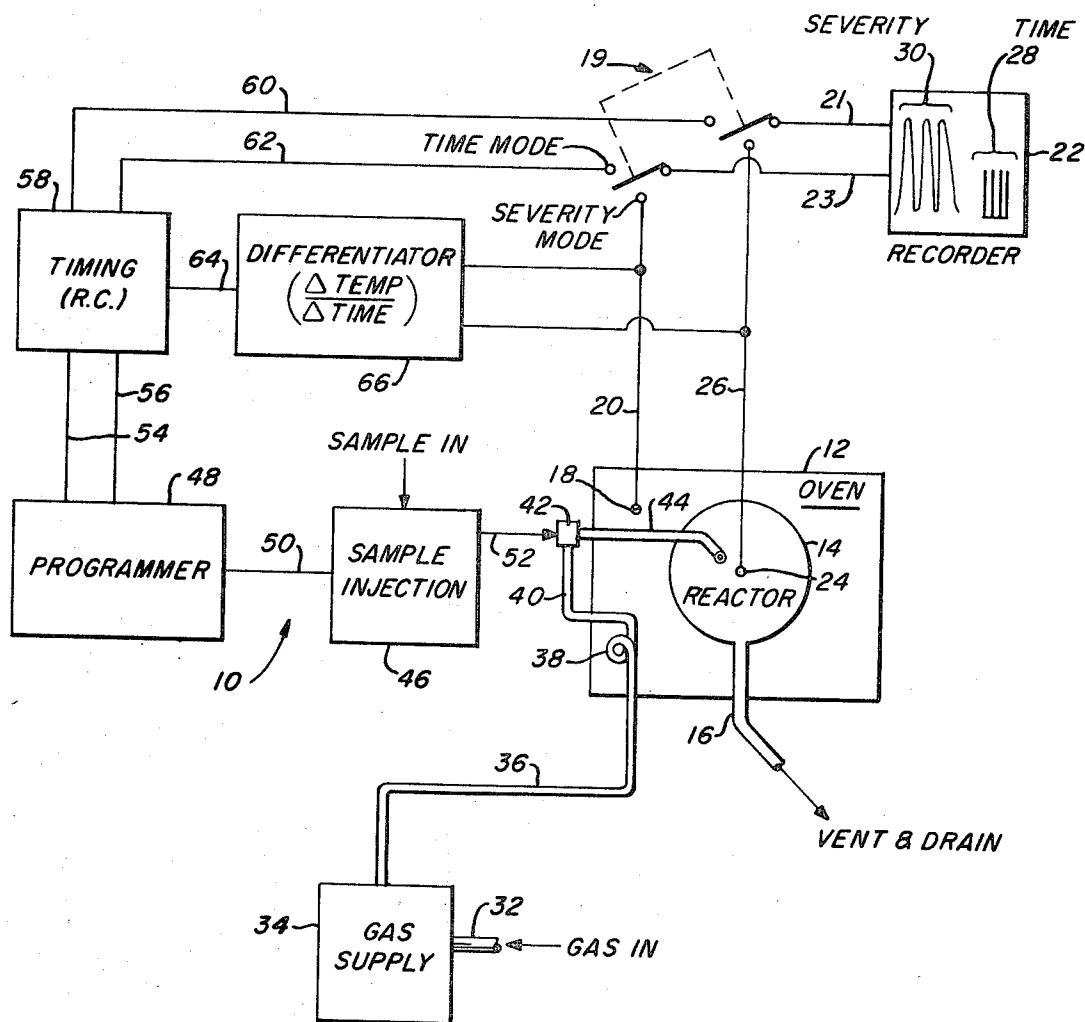


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OCTANE ANALYZER

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27 Claims

ABSTRACT OF THE DISCLOSURE

Means to determine a characteristic of a hydrocarbon, such as the octane rating of gasoline, by reacting a sample of the hydrocarbon with an oxygen containing gas, such as air, under certain conditions to maintain a mild reaction less vigorous than an explosion. The time elapsed between injection of the hydrocarbon into the gas stream and reaction of the hydrocarbon with the oxygen in the gas, and/or some facet of the severity of the reaction, are correlatable to the value of the characteristic of interest of that hydrocarbon.

This invention pertains to the analysis of hydrocarbons, and in particular it pertains to such analysis by means of mildly chemically reacting individual samples of such substances with an oxygen containing gas so as to maintain reaction conditions less violent than an explosion. The invention comprises the use of a mild oxidation reaction which emits no apparent light and which appears to be homogenous in time and space, thus apparently not having a flame front. Therefore, such a reaction may be thought of as less vigorous than a combustion, and hence the word "combustion" as used in the specification and claims herein shall be understood to mean reactions at and more vigorous than a reaction at the non-inclusive upper limit of the mild oxidation reactions used in the invention. The invention comprises correlating one or more parameters of this mild reaction to some characteristic of the hydrocarbon sample. Specifically, when measuring octane rating, correlations have been found to pressure pulse produced, temperature pulse produced, rate of reaction or slope of the temperature or pressure curve, and elapsed time between sample injection and the beginning of the reaction. The first three items above, pressure, temperature, and rate of reaction, may be thought of together as the severity of the reaction. Further, as will appear below, it may be desirable to handle combinations of these parameters to possibly make an additional analysis of the sample. The correlation, of whichever type or combination, can be performed with the use of calibration curves, or by direct comparisons with similar type results obtained from similar standardized substances having known values of the characteristic of interest, or in other ways which may suggest themselves to those skilled in the art.

It is an object of the invention to provide method and apparatus of the character described particularly adapted to determine the octane rating of gasoline. In the following description the invention is described in terms of an octane monitor for gasoline. It is anticipated that octane rating determination of gasoline will be the most important use of the invention, however, it is thought that the invention may be operable to determine other characteristics of other hydrocarbon substances. For example, the invention could possibly be used in determining the cetane rating of diesel fuel, or with other refinery processes, in blending operations, or the like, involving a hydrocarbon substance.

Heretofore, there was not a completely satisfactory method of measuring the octane rating of gasoline. It is tremendously important to the refiner to accurately know

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the octane rating of his gasoline. In order to assure minimum ratings, and to accommodate inaccuracies in existing techniques, the refiner usually blended the final gasoline so that its octane rating exceeded the minimum specification. This practice costs refiners a great deal of money. For example, as an indication of orders of magnitude only, this excess octane rating can cost as much as \$0.25 per barrel of blended gasoline.

There are presently available two basic types or general classes of methods of measuring octane rating. The first and more basic method is, generally, to burn the gasoline in a special engine, and to then detect the sound of knocking. This system is very slow, expensive in that it requires a skilled operator, not readily adaptable to on-stream operation, requires frequent and expensive maintenance, experiences difficulty in holding engine conditions constant between the tests due to "drifting" of the engine, and is subject to the objection that sound per se is a difficult characteristic to handle scientifically. However, the industry accepted standard is an engine method, and the standardized fuels used in the method of the invention and in the second general class of analytical techniques, are standardized by this accepted system. Still within this first class of octane determination methods and apparatuses are those devices which built up from an engine by automating it, in various ways, thus removing or diminishing the disadvantage of having to have an operator present. However, most of the other disadvantages of the basic engine method still apply to automated engines, perhaps the most important one of which is the difficulty of on-stream application.

The second broad class of octane determination techniques do not use an engine, but rather operate on the gasoline itself in various different manners. The present invention is of this general class. At present, the most popular such technique reacts gasoline with air in a specific type of chamber under controlled and variable flow, temperature, and pressure conditions so as to produce a "cool flame" in the chamber. A cool flame is a chemical reaction less violent than an explosion, but more violent than the mild reactions used in the present invention, and is characterized by the production of a characteristic luminosity, i.e., a certain kind of light production, and therefore may be considered a combustion. The principle of operation is to detect this light or the heat accompanying it, and to then adjust flow rate, pressure, and/or temperature to physically hold the area of luminosity or "cool flame" at a constant location within the chamber. The amount of adjustment of these control influences needed to hold the cool flame steady, in response to compositional changes in the gasoline being analyzed which reflect as factors tending to move the cool flame region in the chamber, is correlated to the octane rating or changes in the octane rating of the substance under analysis.

These cool flame based systems suffer from many problems. First, a cool flame is inherently an unstable phenomenon. Thus, operation of such methods and apparatus is at all times critical and extremely sensitive. The apparatus itself must be vertically oriented so as to eliminate any gravity effects on the cool flame region which has a different density than the remainder of the substances in the reactor. Another disadvantage of cool flame based techniques is that they are one step further removed from the reaction than is the present invention. That is, in the present invention the time for the sample to react and/or the severity of the reaction is correlated to the final characteristic of interest. In these prior methods it is some outside influence, which has some effect on the reaction, which is correlated to the final characteristic of interest. Thus, the advantages of the present invention over the prior art of its general type include that it pro-

vides methods and apparatus which operate in a broad reaction region as opposed to the narrow and unstable cool flame region and is therefore not highly critical in operation, easier to use, and more "forgiving" of minor errors. The reactor used in the present invention is insensitive to and unaffected by orientation. The method of the invention is closely and directly related to the chemical reaction which occurs.

The underlying basis of the present invention is the discovery that when a gasoline or other hydrocarbon is mildly reacted with an oxygen containing gas under certain conditions selected to keep the reaction less vigorous than either an explosion or a cool flame, the time elapsed between injection of the hydrocarbon into the gas stream and reaction of the hydrocarbon with the oxygen in the gas, and/or the severity of the reaction, is directly correlatable to the octane rating of that gasoline, or to some other characteristic of interest of some other hydrocarbon. The apparatus embodying the invention includes a pen and chart type recorder for charting or trending reaction times and/or severity. Initial testing of the invention, in the severity mode, has shown that different gasolines produce characteristically shaped output curves, and that therefore the invention may be useful as both a qualitatively and quantitatively analytical device.

The quality of a gasoline is determined by a large number of factors which affect the performance of that gasoline in an engine. However, the word "quality" as used in the specification and claims herein shall be understood to refer primarily to the mix of particular types of compounds in that gasoline, as is known to those skilled in the art. For example, a reformate is high in aromatics, other quality gasolines such as alkylates may contain varying quantities of branch chain paraffins, and the like. Tests of the capabilities of the invention have shown that octane rating correlated to both elapsed time between sample injection and the start of the reaction, and to some one or some combination of the various facets of the severity of the reaction. Tests with the pressure pulse produced by the reaction have not been run, but it is excepted that these results will parallel the temperature rise results because both are indicative of reaction severity, and also because the results of the correlation to slope of the reaction curve paralleled the temperature results. Thus, the term "severity" shall refer to temperature rise and/or pressure pulse, and/or slope of the reaction curve, and shall be understood to have that meaning in the specification and claims herein. This testing has also shown that the severity correlations are more sensitive to octane rating than the elapsed injection time correlation, but that severity is also more sensitive to quality of the sample. Thus, when an unknown quality sample is being analyzed, the elapsed time octane correlation would be preferred since it is not as sensitive to quality. Conversely, where known quality samples are being analyzed, then some severity correlation would be preferred because the sensitivity to octane is better and the increased sensitivity to quality is not disruptive because quality is either constant or else, since it is known, can be accommodated in the data handling.

The apparatus of the invention permits both kinds of correlations, i.e., elapsed time or at least one of the various kinds of severity, with only the movement of a switch. An interesting future capability of the invention would be to run both severity and elapsed time types of analyses, and to then use statistical methods and a computer to analyze the relatively large amount of data generated to determine both the quality of and the octane of the unknown sample. This sort of additional determination may be made possible by the different sensitivities of the various correlations as mentioned above, combined with suitable mathematical analytical techniques.

While air has been used in testing the invention, and it is anticipated that air will be used generally because of its easy availability, generally adequate service with the

invention, and low price, it is of course within the scope of the invention to use any other oxygen containing gas. In any case, the amount of oxygen in the gas will be a known percent of the gas. It is presently thought that there is some optimum oxygen percentage for maximum accuracy, probably less than the amount of oxygen in ordinary air, but this facet of the invention has not yet been fully researched.

Thus, there is provided method and apparatus of the character described which is simple in use and concept, economical, and includes no moving parts inherent to the analysis performed.

The above and other advantages of the invention will be pointed out or will become evident in the following detailed description and claims, and in the accompanying drawing also forming a part of the disclosure, in which the sole figure is a schematic diagram of an apparatus which has been built in successfully testing the invention.

Referring now in detail to the drawing, 10 generally designates apparatus which embodies the invention and comprises an oven 12 in which is positioned a reactor 14 having an atmospheric vent 16 which extends through the wall of the oven and is suitably sealed therein. Means not shown will be provided to very accurately control the temperature of the oven 12 and hence of the reactor 14. Preferably, a high quality proportional type of precision temperature controller will be used. Air, products of combustion, water, and the like exit from the reactor via vent 16. Further, the vent 16 serves to provide atmospheric pressure in the reactor 14. For safety purposes, a flash back arrestor, not shown, is provided in vent 16.

The reactor 14 is preferably made of glass, preferably, Pyrex. In the experiment work which has been done, it was found that a metal reactor, grade 316 stainless steel was tried, may interfere with the reaction, perhaps by having a catalytic effect on the reaction. However, further work will be done in this area since a metal vessel is preferred simply because it would be more durable than glass, which durability is desirable in an industrial environment.

The single preferred reaction temperature, for gasoline, is approximately 315° C., with an operative range of 275° C. to 350° C., and a preferred range of 300° C. to 320° C. Tests have shown that above 350° C. the reaction becomes unstable, and it probably enters the combustion or even the explosion zone. At temperatures less than 275° C. the reaction is not sufficiently vigorous to yield meaningful results, or else does not occur at all. Of course, different temperatures and ranges will be needed for different hydrocarbons. The reaction is carried out at or near atmospheric pressure via the vented reactor.

Means are provided to sense the temperature increase in the reactor as it occurs when the gasoline and oxygen react therein. To this end, a micro-thermocouple 18 is connected by a line 20 to a two position mode selector switch 19, and a second thermocouple 24 is connected by a line 26 to said switch; a recorder 22 is connected by a pair of lines 21 and 23 to the common terminals on switch 19. Because the reaction occurs quickly, it is preferred that thermocouple 24 be as small as possible, and be located centrally within the reactor 14. It is thought that a micro-iron/constantan thermocouple would be best used at 24. The two thermocouples are connected into the recorder 22, when the selector switch 19 is so positioned, in a differential or so-called "bucking" mode, which results in no output on the recorder until there is some reaction, which reactions produce an output, such as the set of spikes 28 shown in the drawing. The curves 28 represent the elapsed time mode of operation of the invention. The length of each of the lines 28 is proportional to the elapsed time between injection of the sample and the beginning of the reaction. The chart paper would be traveling horizontally in the drawing. How the spikes 28 and the second set of curves

30 representing the severity mode are produced will be explained further below. The signals on the lines 21 and 23 may also be connected into a read-out device, not shown, which would automatically change elapsed time between injection and reaction into octane number. Such a device, in effect, would comprise a wired version of the calibration curve, could be used with or without recorder 22, is a simple matter for one skilled in the art to fabricate, and is optional. Further, as will be clear to those skilled in the art, an output device other than or in addition to recorder 22, such as a CR tube display, could be used.

Means are provided to supply air or other oxygen containing gas to react with the gasoline supplied to the reactor 14. A conduit 32 supplies the gas to supply means 34 from any conventional source, such as a tank, bottle, or the service air readily available in industry. The supply means 34 includes several standard components, such as a throttling device if needed, a flow controller or needle valve to control the quantity, and a rotometer to measure flow, all arranged in the usual manner. Thus, the air supply means 34 provide a constant mass flow of air or other oxygen containing gas for combustion, which constant flow is required in order to keep the reaction constant.

A conduit 36 delivers the gas from supply means 34 to a preheater coil 38 located within the precision oven 12. After preheater coil 38 the gas supply system comprises a loop conduit 40 which provides an access point 42 for sample injection. After injection point 42 a conduit 44 delivers the sample laden air or gas through the wall of the oven and through the wall of the reactor and into the middle of the reactor, suitable sealing means, not shown, being provided where conduits pass through walls. The gas and sample do not react in conduit 44 for several reasons. The conduit 44 is small with respect to the relatively large reactor 14. Further, the conduit 44 is preferably smaller than the other conduits 36 and 40, all to the end that a relatively high flow rate and thus a short residence time of the gasoline and oxygen containing gas in the conduit 44 is achieved. In the constructed embodiment used in successfully testing the invention, conduit 44 was approximately 3 inches in length, and the flow rate was such that residence time was less than $\frac{1}{10}$ of a second. Since the quickest reaction tested required a wait for an elapsed time of about two seconds, and ranged up to 15 or 20 seconds for other gasolines, it appears certain that the gasoline just barely has time to vaporize in passing through conduit 44, and that no reaction occurs therein.

Injection point 42 could be part of an automatic injection valve or other such means tapped into some flowing stream which is to be periodically sampled, whereby the invention can be used in an on-stream application. Such arrangements and the sampling components required are well known to those skilled in the art. In a laboratory version, injection means 42 could comprise simply a rubber septum at the end of conduit 44.

Means are provided to determine the time at which the sample is injected into conduit 44 and the reactor 14, and to measure the elapsed time between the moment of injection and the time when the reaction occurs as determined by the differential thermocouples 18 and 24. It is this elapsed time upon which the invention depends for one of its correlations to octane number. Because this elapsed time differs for different substances, it can be seen that it is a parameter of the sample.

Block 46 represents means to control sample injection. In a laboratory version using a syringe and septum type of arrangement, block 46 could represent a solenoid to automatically operate the syringe, or the syringe itself where the system is operated manually. In an on-stream application, block 46 would represent the control portion of the automatic sampling valve. In any case, sample injection occurs under the control of a program-

mer 48 which provides a signal on a line 50 to injection control means 46, which in turn controls the physical injection of sample, which physical injection is represented by the arrow 52 on the drawing. A pair of lines 54 and 56 interconnect programmer 48 with timing means 58. A pair of lines 60 and 62 interconnect circuit 58 to the second position of the selector switch 19. A line 64 interconnects timing means 58 with a differentiator circuit 66. Differentiator 66 receives signals from the two thermocouples 18 and 24 via branching lines off of the thermocouple lines 20 and 26. Programmer 48 may comprise a motor driven multi-cam and switch array type of device, or any other suitable programming means. Timing means 58 may comprise an RC circuit, a digital timer, or the like. The function of these components will be described as this specification continues.

With regard to amount of sample hydrocarbon substance, it is desired to use the smallest quantity which will yield good results. The electronics, especially the thermocouples, are a source of electronic noise, and the amount of hydrocarbon substance reacted must be large enough to overcome this instrument noise. In tests run to prove the invention, samples in the range of about 25 to about 50 microliters were used. Another advantage of using small samples is that they react quickly, clean-up quickly with just the normal flow of air or oxygen containing gas, and thereby permit running successive samples rapidly. Overly large samples produced sufficient heat to upset the thermal balance of the apparatus. Going to extremes, an excessively large sample, with respect to the size of the reactor, could cause an explosion.

Tests of the invention have shown a reproducibility of within less than half an octane number, which is greater than the accuracy of more than half an octane number which is obtainable by engine methods. Thus, the invention octane determination methods and apparatus have a greater reproducibility than the standard against which they are calibrated. In use, the calibration curve has been found to be substantially a straight line with a slope equal to about $\frac{1}{2}$ of a second per octane number. The calibration curve is obtained by repeatedly running samples of known octane rating through the invention apparatus. It is thought that the elapsed time for reaction to initiate is greater with higher octane fuels because such fuels produce a low temperature oxidation less readily.

An important operating condition in all modes is that a relatively small sample be reacted with a relatively large quantity of air in a relatively large volume. As an example of these conditions, in tests which were run to test the invention, elapsed time mode, about 25 microliters of unleaded gasoline were injected into a flowing air stream moving at about 300 cm.³ per minute into a glass reactor having a volume of about 500 cm.³. The oven was accurately held at a temperature of 315° C. For this particular gasoline which had a known octane number of 92, the elapsed time was 11.8 seconds. A similar gasoline but of 88 octane required an elapsed time of 9.8 seconds when tested under the same conditions. Similar results were obtained with the invention's severity mode of operation. Generally, the higher the octane the less severe the reaction.

When switch 19 is in the upper position or "time mode," then the components 58 and 66 come into play. Ideally, in this mode, the apparatus should measure the elapsed time between the moment of injection and the beginning of the mild oxidation reaction of the sample gasoline. It is a simple matter to locate the moment of injection in time, but it is more difficult to fix the beginning of the reaction. The differentiator circuit 66 can be used to measure the time rate of change, analogous to acceleration, of the temperature to thereby detect and trigger other components upon the first positive indication that the reaction has initiated. Alternatively, a recorder could be in block 66, and some arbitrary amount

of pen motion used to activate a switch, in lieu of a differentiator circuit, to thereby fix a time for the beginning of the reaction. The timing means 58 serves to convert the actual elapsed time into an analog signal for driving the recorder 22 and may comprise a digital timer or simply an ordinary tuned resistance/capacitance circuit, with the charge on the capacitor being proportional to the elapsed time. The two lines 54 and 56 between components 48 and 58 serve to start the timing means and to reset the timing means. The two lines 60 and 62 are needed for plus and minus or ground millivolt output to drive recorder 22. The sequence of events is (1) programmer 48 via line 50 operates means 46 to cause a sample to be injected and simultaneously starts timing means 58. (2) Device 66 via line 64 stops timer 58 at the start of the reaction. (3) The programmer 48 sends a signal to the timer 58 to cause the stored signal proportional to elapsed time to be recorded on recorder 22. (4) The programmer resets the timing means.

The set of curves 28 on the drawing are the time spikes produced by a series of reactions, their heights being proportional to each elapsed time. As mentioned above, this elapsed time mode of operation of the invention is less sensitive to octane rating than the severity mode, but has the advantage that it is also less sensitive to varying quality in the sample. Thus, the heights of the lines 28 correlate to octane rating, and so correlate substantially regardless of sample quality.

When switch 19 is moved, either manually or with suitable automatic means, to the lower or "severity mode," then the recorder 22 or other display means is driven directly by the thermocouples 18 and 24 to produce curves such as 30. In this case, the height of each curve above the base line correlates to octane rating of the sample. Also, we have found that the slope of the reaction curve correlates to octane rating, and, as defined above, this slope is included in "severity." Further, we have found that the shape of each of the curves 30 can be helpful in identifying an unknown or an unknown quality of a sample. That is, certain qualities produce characteristically shaped curves. Since the severity modes of the invention are more sensitive to both octane and quality, it is not preferred when analyzing a sample of unknown quality. A possible future capability of the invention, however, is to combine the respective strengths of the various modes of operation of the invention in order to permit determination of both octane rating and quality of an unknown sample.

The drawing is a schematic of a laboratory or "bread-board" embodiment of the invention, but it does prove the principle and does operate. As is well known, a great deal of polishing and refinement could and would be done in building an industrial or commercial quality apparatus. As examples of such improvements, the operative parts of the invention including reactor 14, the oven's operative parts, and the thermocouples, may all be housed in an efficient temperature shield such as a dewar flask, and then the entire apparatus, except for the display and the controls, placed in an explosion proof housing. Further refinements might include the ability to analyze several streams at the same time, computer read-out, or a tie-in to an automatic blending operation. An increased chart speed in recorder 22 would be needed for the slope of the reaction curve type of severity correlation.

While the invention has been described in detail above, it is to be understood that this detailed description is by way of example only, and the protection granted is to be limited only within the spirit of the invention and the scope of the following claims.

We claim:

1. A method of determining the value of a selected characteristic of a hydrocarbon substance, comprising the steps of injecting an individual sample of a predetermined amount of the hydrocarbon substance into a stream of an

oxygen-containing gas, whereby the sample is carried into a reactor, mildly reacting the sample with the oxygen-containing gas at selected conditions in said reactor to keep the kinetics of the reaction slower than that associated with an explosion; detecting either the reaction parameter of the elapsed time between the injection of said sample and the beginning of said reaction, or a reaction parameter of the severity of said mild reaction; and correlating a value for said hydrocarbon substance characteristic to said detected parameter resultant of said mild reaction.

2. The method of claim 1, wherein the temperature rise produced by said mild reaction is correlated to said selected characteristic of said hydrocarbon substance.

3. The method of claim 1, wherein the slope of the reaction curve produced by said mild reaction is correlated to said selected characteristic of said hydrocarbon substance.

4. The method of claim 1, wherein said correlation is made to both the elapsed time between the injection of said hydrocarbon substance into said gas stream and the beginning of said mild reaction, and at least one of the temperature rise and the slope of reaction curve produced by said mild reaction.

5. The method of claim 1, wherein said hydrocarbon substance is gasoline and said selected characteristic is octane rating.

6. The method of claim 1, wherein said sample comprises a relatively small quantity of said hydrocarbon substance and said stream comprises a relatively large quantity of said oxygen containing gas, whereby successive samples may be rapidly analyzed in said reactor.

7. The method of claim 1, wherein said oxygen containing gas comprises air, and wherein the air is supplied at a constant flow per unit time.

8. The method of claim 1, wherein said reaction is carried out at about atmospheric pressure.

9. The method of claim 1, wherein said reaction is carried out at a temperature ranging from about 275° C. to about 350° C.

10. The method of claim 1, and the step of pre-heating said oxygen containing gas before said step of injecting hydrocarbon substance.

11. The method of claim 1, wherein said reactor is housed within an oven, and wherein said step of detecting the beginning of the reaction is accomplished by the steps of constantly measuring the temperature within the oven and continuously measuring the temperature within said reactor, and differentiating the temperature rise in said reactor with respect to time.

12. The method of claim 1, wherein the quantity of said sample is selected from the range of about 25 to about 50 microliters.

13. The method of claim 1, wherein said reaction is carried out at a preferred temperature ranging from about 300° C. to about 320° C.

14. The method of claim 13, wherein said reaction is carried out at about 315° C.

15. In combination, a reactor, means for holding said reactor at a selected predetermined temperature, means for flowing an oxygen-containing gas through said reactor, means for injecting a sample of a hydrocarbon substance into said flowing gas stream whereby said sample is carried into said reactor, said injecting means comprising a hypodermic syringe and a rubber septum in a conduit carrying said gas stream or an automatic sample injection valve, whereby a continuously flowing stream of said hydrocarbon substance may be periodically and regularly sampled, means for detecting the reaction of said hydrocarbon substance with said oxygen-containing gas in said reactor, said detecting means comprising at least a part thereof located within said reactor whereby said at least a part of said detecting means is directly exposed to said reaction in said reactor, and means for correlating the value of either the reaction parameter of the elapsed time

between the injection of said sample and the beginning of said mild reaction or the reaction parameter of the severity of said mild reaction to a value of a selected characteristic of said hydrocarbon substance.

16. The combination of claim 15, said detecting means comprising means for measuring the time elapsed between the injection of said hydrocarbon substance and the occurrence of said reaction.

17. The combination of claim 15, wherein the oxygen containing gas comprises air, and means to supply a constant mass of air per unit time.

18. The combination of claim 15, and vent means in said reactor, whereby said reaction is carried out at about atmospheric pressure.

19. The combination of claim 15, wherein said hydrocarbon substance is gasoline and said selected characteristic is octane rating.

20. The combination of claim 15, and means for preheating said gas stream before said stream encounters said injecting means.

21. The combination of claim 15, said temperature holding means comprising an oven in which said reactor is housed, said reaction detecting means comprising a differential thermocouple array, said thermocouple array comprising one thermocouple in said oven and said at least a part of said detecting means located within said reactor comprising a second thermocouple of said thermocouple array.

22. The combination of claim 15, said means for correlating at least one parameter including a selector switch for selectively connecting said reaction detecting means to display means in one of two manners:

(1) directly, or

(2) via means for detecting the beginning of said reaction.

23. The combination of claim 22, said display means comprising a pen and chart type recorder.

24. The combination of claim 22, said temperature holding means comprising an oven in which said reactor is housed, said reaction detecting means comprising a differential thermocouple array, said thermocouple array comprising one thermocouple in said oven, and said at least a part of said detecting means located within said reactor comprising a second thermocouple of said thermocouple array.

25. The combination of claim 22, said means for detecting the beginning of said reaction comprising a temperature to time differentiator circuit.

26. The combination of claim 25, said display means comprising a pen and chart type recorder, and an RC timing circuit for converting elapsed time between injection and the beginning of said reaction into an analog signal for driving said recorder.

27. The combination of claim 25, said display means comprising a pen and chart type recorder, and a digital timer for converting elapsed time between injection and the beginning of said reaction into a signal for driving said recorder.

References Cited

UNITED STATES PATENTS

3,527,567	9/1970	Philyaw	23—230 PC
3,533,745	10/1970	Fenske	23—253 PC

MORRIS O. WOLK, Primary Examiner

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