

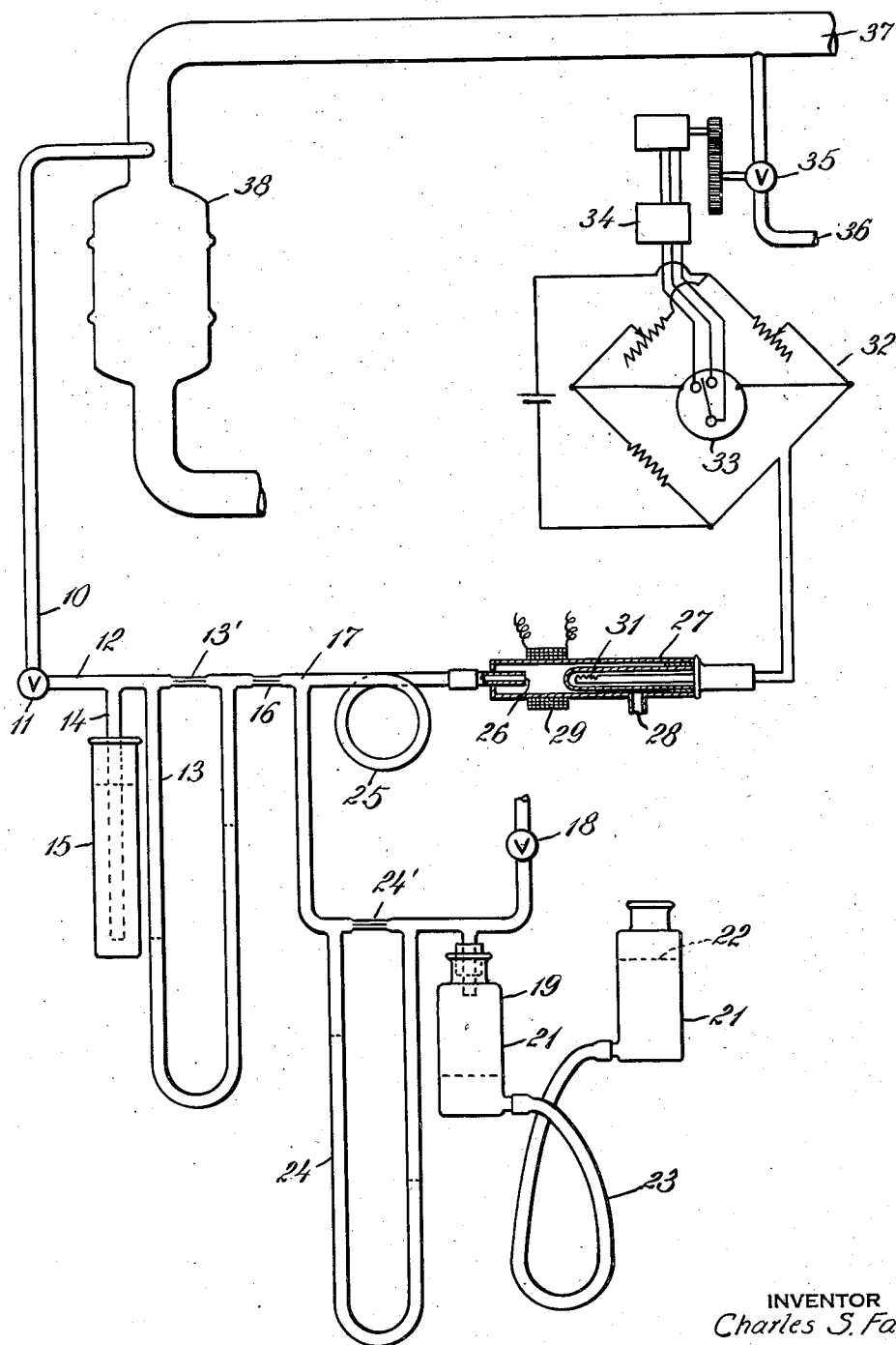
Sept. 24, 1940.

C. S. FAZEL

2,215,498

PROCESS FOR CONTROLLING VAPOR PHASE HYDROCARBON REACTIONS

Filed June 8, 1938



INVENTOR

Charles S. Fazel

BY

Benjamin Sweedler

ATTORNEY

## UNITED STATES PATENT OFFICE

2,215,498

PROCESS FOR CONTROLLING VAPOR PHASE  
HYDROCARBON REACTIONSCharles S. Fazel, Petersburg, Va., assignor to The  
Solvay Process Company, New York, N. Y., a  
corporation of New York

Application June 8, 1938, Serial No. 212,603

10 Claims. (Cl. 260—342)

The present invention relates to a process for controlling vapor phase hydrocarbon reactions such as the catalytic oxidation of naphthalene to phthalic anhydride and of benzene to maleic anhydride.

In catalytic oxidation processes such as the vapor phase oxidation of naphthalene or benzene to produce phthalic anhydride and maleic anhydride respectively, a mixture of naphthalene and air or benzene and air, as the case may be, in which the proportion of naphthalene or benzene is so low that the mixture is not capable of self-sustained combustion or burning to produce a visible flame is continuously fed to a catalytic converter. In the operation of the converter it is necessary to regulate the gas composition to prevent formation of an explosive mixture in the converter as well as mixtures which would cause burning and sintering of the catalyst.

Determination of the composition of the gas stream fed to the converter by the calorimetric measurement of the heat evolved in the combustion of carefully measured quantities of the gas is not feasible because of the relatively long time required for the calorimetric measuring device to respond to changes in gas composition. It will be appreciated the control for the continuous flowing gas stream must be quick acting so that changes in hydrocarbon concentration will be determined quickly and desired regulation of the concentration of the hydrocarbon content of the gas stream fed to the converter effected in response to such determination without a substantial time lag after the occurrence of the changes in order to prevent formation of a mixture which would react in the catalytic converter with explosive violence.

It has been proposed to effect the control in accordance with temperature changes taking place when a gas sample bled from the main gas stream fed to the converter is oxidized catalytically or is burned by passage over a hot wire, the temperature thus generated being proportional to the hydrocarbon content of the gas stream fed to the converter. These methods have been found to give insufficiently rapid temperature changes with changes in the hydrocarbon content of the gas stream fed to the con-

verter, thereby rendering them unsatisfactory for use. Moreover, the method involving combustion of the gas sample by passage over a hot wire has the added disadvantage of requiring excessively high temperatures with certain hydrocarbon gas streams, near the melting point of platinum in the case of an air-naphthalene gas stream containing .75 mol per cent naphthalene, for effecting complete combustion of the hydrocarbon content of the dilute gas stream fed to the converter.

It has also been proposed to bleed a small portion of the gas stream and pass the same through a combustion furnace where the hydrocarbon is completely oxidized to carbon dioxide and water, after which the products of combustion are passed through suitable drying agents for removal of water and water vapor, then through a carbon dioxide measuring and recording instrument for the continuous measurement and recording of the carbon dioxide contents of the gas stream, and affect the control in accordance with the carbon dioxide measurements. This method has been found to be objectionable in that it is not sufficiently quick acting.

It is an object of this invention to provide a rapid, accurate, and continuous method of analyzing and controlling the hydrocarbon gaseous mixture entering the converter, in which the content of hydrocarbon is insufficient to render the mixture combustible, i. e., the content of hydrocarbon is insufficient for the mixture to burn with a visible flame, so as to maintain the hydrocarbon content of the gas stream substantially constant and below the proportion at which explosions are apt to occur under conditions of the reactions in which the mixture is to be employed. Other objects and advantages of this invention will be apparent from the following detailed description thereof.

In accordance with my invention, a small portion of the hydrocarbon-gas mixture fed to the converter is continuously bled from the mixture and passed into a mixing chamber, and a substantially uniform amount of a combustible gas is also continuously fed into the mixing chamber, the amount of added combustible gas being sufficient to produce a mixture capable of sustaining combustion of the combustible constituents

once the combustion is initiated. The resulting mixture in which the total content of original and added combustibles is not in excess of that capable of complete combustion with the oxidizing gases of the original gas mixture is then passed to a combustion chamber and the combustibles in the enriched gas mixture are completely burned, the flame temperature being measured by a heat-responsive element such as a resistance thermometer. I have found that this temperature bears a definite ratio to the hydrocarbon in the original mixture, as hereinafter more fully pointed out, and therefore furnishes a simple method of measuring the proportion of hydrocarbon present in the mixture fed to the converter or other reaction zone. The resistance thermometer is connected to the valve controlling the supply of hydrocarbon mixed with the air or other oxygen-containing gas to regulate the concentration of hydrocarbon in the gas mixture fed to the reaction zone to maintain a substantially constant proportion of hydrocarbon in the gas mixture. The resistance thermometer or other heat-responsive device may be connected to a suitable electric instrument for indicating and recording the hydrocarbon concentration.

In the drawing, in which is shown for purposes of exemplification a preferred form of apparatus for practicing the process of this invention, reference character 10 indicates a conduit having a valve 11 therein through which conduit and valve is bled continuously a small portion of the mixture of hydrocarbon and oxygen-containing gas such as air to be reacted in the catalytic converter or other reaction zone. The conduit system, or any desired portion thereof, through which the gas flows may be heated in any suitable manner so that the temperature of the gas flowing therethrough will be maintained above its dew point to prevent condensation in the system. From the valve 11 the gas mixture flows through tube 12 to a flow-meter 13 comprising a capillary tube 13', the flow-meter being of a conventional type for indicating the rate of gas flow. Leading from tube 12 between valve 11 and flow-meter 13 is a vent tube 14 extending into an excess flow-trap 15 having a liquid bath through which excess gas may bubble to the atmosphere, the excess flow-trap serving to insure a uniform hydrocarbon gas flow to a mixing chamber 25.

From flow-meter 13 the gas is conducted through a capillary tube 16 slightly smaller in diameter than that of the capillary tube 13' to a junction 17 where a combustible fluid, such as hydrogen, methane or alcohol, is introduced for enriching the hydrocarbon gas stream to render the resultant mixture capable of self-sustained combustion. The hydrogen may be supplied from a commercial cylinder (not shown) by bleeding the gas through a reducing valve 18 into a small constant pressure gas holder 19 which may comprise a pair of bottles 21 containing a liquid bath 22 and connected by a flexible tube 23. The holder serves to insure a uniform flow of hydrogen to the mixing chamber 25. The hydrogen is conducted from the gas holder through a conventional flow-meter 24 comprising a capillary tube 24' for measuring the rate of gas flow to the junction 17 where it meets the hydrocarbon gas stream, the resultant mixture flowing into and through mixing chamber 25 to a quartz burner tip 26 located in a combustion

chamber comprising a cylindrical quartz tube 27 which may be integral at one end thereof with the burner tip and provided with an outlet 28 for the products of combustion.

The amount of hydrogen supplied to any one combustion unit will vary, depending upon the size of the burner tip in the unit, the hydrocarbon concentration of the gas being fed thereto, etc. In one example of the practice of this invention, in the oxidation of naphthalene to phthalic anhydride, utilizing a burner tip having an internal diameter of 3.8 mm., 2.1 liters of the naphthalene-air mixture and 0.3 liter of hydrogen per minute was found to give excellent results.

Surrounding the combustion chamber adjacent the burner tip is an electric heating coil 29 for igniting the gas mixture within the combustion chamber to initiate combustion. Sealed within the other end of the combustion chamber is a resistance thermometer 31, the tip of which extends to within about one and one-half centimeters of the burner tip, for measuring the flame temperature of the combustion. Resistance thermometer 31 is connected by suitable conductors to a Wheatstone bridge circuit 32, of a commonly employed type, containing a galvanometer 33 or other suitable current-indicating device which may be provided with electrical contacts for actuation of a relay 34. Relay 34 controls current to a reversible motor-driven valve 35 or any similarly controlled valve, which in turn regulates the flow of hydrocarbon vapor through the line 36 to the air stream in line 37. The resulting hydrocarbon-air mixture, whose composition is thus controlled, is then conveyed to the catalyst contained in converter 38.

Preferably the combustion chamber 27 is not insulated because it has been found the insulation of this chamber results in a decrease of the sensitiveness of the resistance thermometer to indicate promptly changes in the hydrocarbon concentration. For example, in the case of the oxidation of naphthalene to phthalic anhydride, it was found that changes in temperature are indicated almost instantaneously with increase of naphthalene concentration, and require about one to two seconds for indication when a decrease of naphthalene concentration takes place using an uninsulated combustion chamber.

Due to radiation, flame characteristics, and other variable factors peculiar to each combustion unit, the apparent flame temperature is measured, which temperature, I have found, bears a definite ratio to the concentration of hydrocarbon in the gas stream fed to the converter. For example, in the control of the oxidation of naphthalene to phthalic anhydride in which the inlet gas stream to the combustion chamber flowed at the rate of 2.1 liters per minute, to which was added hydrogen in the proportion of about 0.12 liter per liter of inlet gas, the flame temperatures indicated by various quantities of naphthalene in the inlet gas were as follows:

| Mol percent naphthalene in inlet gas | 0.4 | 0.6 | 0.8  | 1.0  |
|--------------------------------------|-----|-----|------|------|
| Apparent flame temperature, ° C..... | 790 | 903 | 1020 | 1135 |

In another example of the practice of the invention involving the control of the oxidation of benzene to maleic anhydride in which 0.14 volume of hydrogen per volume of inlet gas was

added to the combustion chamber into which flowed the inlet gas at the rate of 2.1 liters per minute and the resultant mixture burned, the flame temperatures indicated by the various quantities of benzene in the inlet gas were as follows:

| Mol percent benzene in inlet gas     | 0.4 | 0.8 | 1.20 | 1.60 |
|--------------------------------------|-----|-----|------|------|
| Apparent flame temperature, ° C..... | 655 | 865 | 990  | 1093 |

Since an apparatus rather than an absolute flame temperature is measured by each combustion unit, and since with each unit the temperatures produced by burning the hydrocarbon-gas mixture are constant and reproducible, each combustion unit should be calibrated by burning two or more mixtures of hydrocarbon and oxygen-containing gas of known composition of the type involved in the reaction it is desired to control.

If desired there may be operably connected with or used in lieu of galvanometer suitable devices for indicating and recording the concentration of hydrocarbon in the gas mixture fed to the converter, whereby both an instantaneous and permanent showing of the hydrocarbon concentration is provided. A calibration curve or chart for use in the indicating and recording instrument could be made from the results obtained in calibrating the resistance thermometer, which chart, if desired, could be calibrated to give a direct reading of the concentration of hydrocarbon in the gas stream.

Although actuation of valve 35 to maintain a constant concentration of hydrocarbon in the gas mixture fed to the converter has been described as automatically effected by resistance thermometer 31, it is to be understood that valve 35 may be manually operated, if desired, in which case resistance thermometer 31 may be connected with suitable devices for indicating to the operator when such manual adjustment of the valve is necessary. Also, if desired, valve 35 may be manually or automatically closed to shut off completely the flow of hydrocarbon gas admixed with air in case the concentration of the hydrocarbon gas in the gas mixture fed to the converter rises above a predetermined point.

It is to be further understood that resistance thermometer 31 may be replaced by other suitable devices. For example, a thermocouple may be alternatively employed and may be connected in a suitable electrical circuit for operating devices to indicate hydrocarbon concentration or for directly operating valve 35 which controls the flow of hydrocarbon.

In operation, the control hereinabove described has been found quick acting, accurate and efficient, giving an almost instantaneous indication and record of the gas composition. For example, in the case of the oxidation of naphthalene to phthalic anhydride with an inlet gas containing .75 mol per cent naphthalene and a hydrogen addition of 12.4 mols per 100 mols of inlet gas, the apparent flame temperature varied about 60° C. for a variation in the naphthalene concentration of 0.1%. When the mol per cent naphthalene was suddenly increased from .75 to 0.8, the response in temperature rise was noted within one second.

Since certain changes may be made in the described embodiment of the invention without departing from the spirit of the invention, it will

be understood that the invention is not intended to be limited to the foregoing description thereof.

What is claimed is:

1. A method for controlling the reaction of a hydrocarbon gas mixture, in which the amount of hydrocarbon is insufficient to render the mixture capable of self-sustaining combustion, which comprises continuously feeding a stream of said gas mixture to the reaction zone, continuously bleeding off from said stream a small portion of the gas mixture, continuously adding a uniform amount of a combustible fluid to the gas stream thus bled off, the amount of added combustible fluid being such that the gas stream thus enriched is capable of self-sustaining combustion and the total content of original and added combustibles contained therein is not in excess of that capable of complete combustion with the oxidizing gases present in the gas stream thus bled off, continuously burning the resultant gas mixture containing the added combustible fluid to burn completely the combustibles in said resultant gas mixture, and effecting said control in accordance with the temperatures generated by the said burning of the said gas stream containing the added combustible fluid.

2. A method for controlling the concentration of hydrocarbon in a gas stream fed to a reaction zone, in which gas stream the amount of hydrocarbon is insufficient to render the gas stream capable of self-sustaining combustion, which comprises continuously feeding said gas stream to the reaction zone, continuously bleeding off from said stream a small portion of the hydrocarbon gas mixture, continuously adding a uniform amount of a combustible fluid to the gas stream thus bled off, the amount of added combustible fluid being such that the gas stream thus enriched is capable of self-sustaining combustion and the total content of original and added combustibles contained therein is not in excess of that capable of complete combustion with the oxidizing gases present in the gas stream thus bled off, continuously burning the resultant gas mixture containing the added combustible fluid to burn completely the combustibles in said resultant gas mixture, and effecting the control of the hydrocarbon concentration in accordance with the temperatures thus generated.

3. A method for controlling oxidation of a gaseous hydrocarbon which comprises continuously feeding to a converter a stream of gaseous hydrocarbon and oxygen-containing gas in which the amount of hydrocarbon is insufficient to render the gas stream capable of self-sustaining combustion, continuously bleeding off from said stream a small portion of the hydrocarbon gas mixture, continuously adding a uniform amount of a combustible gas to the gas stream thus bled off, the amount of added combustible gas being such that the gas stream thus enriched is capable of self-sustaining combustion and the total content of original and added combustibles contained therein is not in excess of that capable of complete combustion with the oxygen-containing gas present in the gas stream thus bled off, continuously burning the resultant gas mixture containing the added combustible gas to burn completely the combustibles in said resultant gas mixture, and maintaining the concentration of the hydrocarbon in the gas stream fed to the converter substantially constant by regulating the amount of hydrocarbon admixed with the oxy-

gen-containing gas in accordance with temperatures generated by the said burning of the said gas mixture.

4. A method for controlling the oxidation of naphthalene to phthalic anhydride which comprises continuously feeding to a catalytic converter a gaseous stream of naphthalene and air in which the concentration of naphthalene is insufficient to render the mixture capable of self-sustaining combustion, continuously bleeding off from said stream a small portion of the naphthalene-air mixture, continuously adding a uniform amount of a combustible gas to the naphthalene-air mixture thus bled off, the amount of added combustible gas being such that the resultant enriched gas mixture is capable of self-sustaining combustion and the total content of original and added combustibles contained therein is not in excess of that capable of complete combustion with the air present in the naphthalene-air mixture thus bled off, continuously burning the resultant gas mixture containing the added combustible gas to burn completely the combustibles in said resultant gas mixture, and maintaining the concentration of naphthalene in the gas stream fed to the converter substantially constant by regulating the amount of naphthalene admixed with the air to form said gas stream fed to the converter in accordance with temperatures generated by the said burning of the said gas mixture.

5. A method for controlling the oxidation of naphthalene to phthalic anhydride which comprises continuously feeding to a catalytic converter a gaseous stream of naphthalene and air in which the concentration of naphthalene is insufficient to render the mixture capable of self-sustaining combustion, continuously bleeding off from said stream a small portion of the naphthalene-air mixture, continuously adding a uniform amount of hydrogen to the naphthalene-air mixture thus bled off, the amount of added hydrogen being such that the resultant enriched gas mixture is capable of self-sustaining combustion and the total content of naphthalene and hydrogen contained therein is not in excess of that capable of complete combustion with the air present in the naphthalene-air mixture thus bled off, continuously burning the resultant gas mixture containing the added hydrogen to burn completely the naphthalene and hydrogen therein contained, and maintaining the concentration of the naphthalene in the gas stream fed to the converter substantially constant by regulating the amount of naphthalene admixed with the air to form said gas stream in accordance with temperatures generated by the said burning of the said gas mixture.

6. A method for controlling the oxidation of benzene to maleic anhydride which comprises continuously feeding to a catalytic converter a gaseous stream of benzene and air in which the concentration of benzene is insufficient to render the mixture capable of self-sustaining combustion, continuously bleeding off from said stream a small portion of the benzene-air mixture, continuously adding a uniform amount of hydrogen to the benzene-air mixture thus bled off, the amount of added hydrogen being such that the resultant enriched gas mixture is capable of self-sustaining combustion and the total content of benzene and hydrogen contained therein is not in excess of that capable of complete combustion with the air present in the benzene-air mixture thus bled off, continuously burning the resultant

gas mixture containing the added hydrogen to burn completely the benzene and hydrogen therein contained, and maintaining the concentration of the benzene in the gas stream fed to the converter substantially constant by regulating the amount of benzene admixed with the air to form said gas stream in accordance with temperatures generated by the said burning of the said gas mixture.

7. A method for controlling the reaction of a naphthalene gas mixture, in which the amount of naphthalene is insufficient to render the mixture capable of self-sustaining combustion, which comprises continuously feeding a stream of said naphthalene gas mixture to a reaction zone, continuously bleeding off from said stream a small portion of the naphthalene gas mixture, continuously adding a uniform amount of hydrogen to the naphthalene gas mixture thus bled off, the amount of added hydrogen being such that the resultant enriched gas mixture is capable of self-sustaining combustion and the total content of naphthalene and hydrogen contained therein is not in excess of that capable of complete combustion with the oxidizing gases present in the naphthalene gas mixture thus bled off, continuously burning the resultant gas mixture containing the added hydrogen to burn completely the naphthalene and hydrogen therein contained, and effecting said control in accordance with the temperatures generated by said burning of said gas stream containing the added hydrogen.

8. A method for determining the concentration of hydrocarbon in a gas mixture in which the amount of hydrocarbon is insufficient to render the mixture capable of self-sustaining combustion, which comprises continuously bleeding off a small portion of said gas mixture, continuously adding a uniform amount of a combustible fluid to the gas mixture thus bled off, the amount of added combustible fluid being such that the resultant enriched gas mixture is capable of self-sustaining combustion and the total content of original and added combustibles contained therein is not in excess of that capable of complete combustion with the oxidizing gases present in the gas mixture thus bled off, continuously burning the resultant gas mixture containing the added combustible fluid to burn completely the combustibles in said resultant gas mixture and thereby generate a flame temperature dependent upon the hydrocarbon concentration in said first-mentioned gas mixture.

9. A method for controlling the concentration of naphthalene in a naphthalene-air gas mixture in which the amount of naphthalene is insufficient to render the mixture capable of self-sustaining combustion, which comprises continuously withdrawing a small portion of said gas mixture, continuously adding a uniform amount of hydrogen to the gas mixture thus withdrawn, the amount of added hydrogen being such that the resultant enriched gas mixture is capable of self-sustaining combustion and the total content of naphthalene and hydrogen contained therein is not in excess of that capable of complete combustion with the air present in the gas mixture thus withdrawn, continuously burning the resultant gas mixture containing the added hydrogen to burn completely the naphthalene and hydrogen therein contained and thus form a combustion zone having a temperature dependent upon the naphthalene concentration in the first-mentioned gas mixture, and effecting control of

the naphthalene concentration in said first-mentioned gas mixture in accordance with the temperature thus attained.

5 10. A method for controlling the concentration of benzene in a benzene-air gas mixture in which the amount of benzene is insufficient to render the mixture capable of self-sustaining combustion, which comprises continuously withdrawing a small portion of said gas mixture,  
10 continuously adding a uniform amount of hydrogen to the gas mixture thus withdrawn, the amount of added hydrogen being such that the resultant enriched gas mixture is capable of self-sustaining combustion and the total content of

benzene and hydrogen contained therein is not in excess of that capable of complete combustion with the air present in the gas mixture thus withdrawn, continuously burning the resultant gas mixture containing the added hydrogen to burn  
5 completely the benzene and hydrogen therein contained and thus form a combustion zone having a temperature dependent upon the benzene concentration in the first-mentioned gas mixture, and effecting control of the benzene concentration in said first-mentioned gas mixture in  
10 accordance with the temperature thus attained.

CHARLES S. FAZEL.