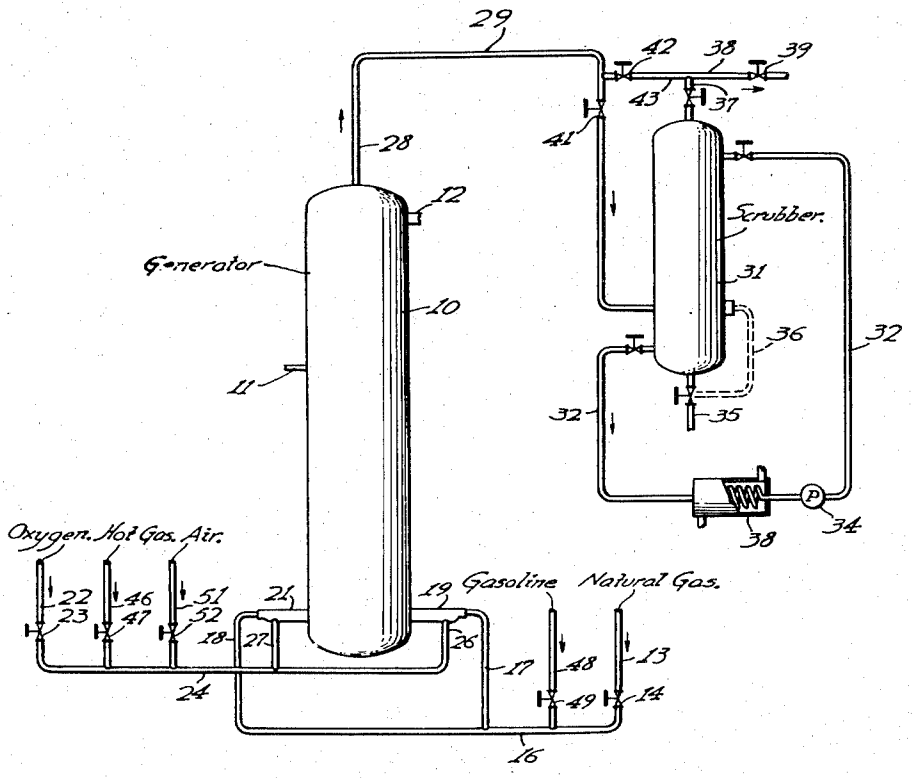
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METHOD OF STARTING A UNIT FOR HIGH-TEMPERATURE REACTIONS

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METHOD OF STARTING A UNIT FOR HIGH-TEMPERATURE REACTIONS

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This invention relates to a method of starting up units employed in carrying out high temperature and especially high pressure exothermic reactions. More particularly, the invention relates to a method of starting up apparatus used in carrying out a reaction between natural gas and oxygen to form a synthesis gas adapted to be used in the Fischer-Tropsch synthesis of hydrocarbons.

The starting up of any unit or equipment in which a high temperature exothermic reaction, especially a vapor phase reaction, is carried out, presents difficulties which frequently are greater than the problems encountered once the unit is on-stream. These starting-up difficulties are increased when the reaction must be carried out at elevated pressures.

An example of such a reaction is that between natural gas and oxygen to produce reaction or combustion products comprising carbon monoxide and hydrogen adapted for use in the synthesis of hydrocarbons. This reaction is advantageously carried out at a temperature of about 1800° to 2800° F. and a pressure of the order of 150 to 650 pounds per square inch in an elongated combustion tube having heat retentive walls. The reaction temperature is a function of the temperatures to which the reactants are heated. Accordingly, the plant for this process includes suitable furnaces for heating either or both the natural gas and oxygen to selected elevated temperatures. Since the reaction in the combustion tube is exothermic and the walls retain heat, once started the reaction goes smoothly as the mixture being introduced is brought quickly to ignition temperature by the heat produced in the reaction of a previous increment of the charge mixture and by the heat radiated from the walls. The pressure may be easily controlled by the adjustment of a suitable valve in the plant down-stream from the combustion tube. The present invention is concerned with the problem of starting up units in which processes of this type are carried out.

In accordance with the invention, a unit employed in carrying out a high temperature exothermic reaction which is initiated at an elevated temperature is started up by a process in which the unit is first heated to an intermediate temperature substantially below the reaction initiation temperature of the charge mixture (this temperature being the ignition temperature in the case of a charge mixture comprising a hydrocarbon and an oxygen-containing gas) but above the ignition temperature of a mixture of an oxygen-containing gas and a hydrocarbon or

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mixture of hydrocarbons ignitible at low temperatures. When the unit has been brought to this intermediate temperature, a mixture of the oxygen-containing gas such as air and an easily ignitible hydrocarbon or mixture of hydrocarbons such as casing head gasoline, light straight run gasoline, pentane, and hexane, is passed into the unit. Because the temperature of the unit is above the ignition temperature of the introduced hydrocarbon, this term being employed to refer to a single hydrocarbon or a mixture of hydrocarbons unless otherwise indicated, the combustion reaction involving this hydrocarbon takes place and heat is evolved which acts to increase the temperature of the unit. The introduction of the easily ignitible hydrocarbon and air is continued until the temperature of the unit is brought to a temperature above that at which the final charge mixture ignites, at which time the introduction of the charge mixture is begun. Since the reaction taking place in the charge mixture is exothermic, continued rise in temperature of the unit may be accomplished if necessary to attain the desired reaction temperature.

The process of the invention is particularly valuable in cases where the reaction is one that is carried out under pressure. To bring the unit to the desired reaction pressure, it is only necessary at a stage in the starting-up procedure to adjust the valve which controls the pressure in the unit. This adjustment is preferably made during the initial period of introduction of the final charge mixture.

In cases where the reaction carried out in the unit is a combustion reaction between hydrocarbons and oxygen, it is usually desirable when first introducing the hydrocarbons to employ air rather than oxygen itself as the source of oxygen. As the heating of the unit is continued, air may be replaced with substantially pure oxygen.

The present process is of special interest when employed for starting up a unit used for carrying out the reaction between natural gas and oxygen to produce synthesis gas. Accordingly, the following description will be concerned with starting up such a unit. In order that this description may be understood more fully, reference should be had to the accompanying drawing, hereby made a part of this specification, in which the single figure is a diagrammatic illustration of a system for producing synthesis gas.

Referring to the drawing, there is shown a synthesis gas generator 10 which comprises in its lower portion a combustion tube having heat retentive walls, not shown, and in its upper portion

a suitable cooling section, also not shown. The cooling medium, preferably water, is introduced into the cooling section through an inlet pipe 11 and the hot medium such as steam is removed through an outlet pipe 12. When the generator is being employed for the preparation of synthesis gas by the reaction between natural gas and oxygen, the temperature in the combustion tube is maintained within the range of about 1800° to about 2800° F. and the pressure is maintained at from about 150 to about 650 pounds per square inch.

The natural gas employed in this reaction is introduced from any suitable source through a line 13 provided with a valve 14 and is passed into a manifold line 16. Line 16 has two branches 17 and 18 leading to mixing nozzles 19 and 21 adapted to mix gases and pass the mixture into the interior of the generator 10. Oxygen is supplied to the system through a line 22 provided with a valve 23 and enters a manifold line 24 having branches 26 and 27 leading to the mixing nozzles. Prior to being introduced into the system, the oxygen and natural gas are preferably heated separately in suitable furnaces, not shown, so that on admixture a temperature of about 100° to about 1000° F. results. The oxygen and natural gas are mixed in the mixing nozzles and enter the generator as a combustible mixture ignitible at a temperature below the temperature maintained in the combustion tube. As a result, combustion of this charge mixture is initiated and the desired reaction takes place. The resulting mixture comprising carbon monoxide and hydrogen and other products of combustion is cooled in the cooling section of the generator 10 and passes from the generator through an exit line 28 leading to a line 29 which is connected with a direct contact scrubber 31. In this scrubber the gases are intimately contacted with a spray of water which is effective to remove carbon and condense steam from the combustion products. The scrubbing water collects in the bottom of the scrubber and is removed continuously through line 32, cooled in cooler 33, and is pumped by means of pump 34 to the top of scrubber 31. A valved line 35 is provided for the purpose of preventing excessive build-up of water in this unit by removing liquid continuously. The operation of the valve in line 35 is controlled by liquid level controller 36.

The scrubbed gases are passed overhead from scrubber 31 through a valved line 37 and thence into a line 38 leading to a suitable synthesis unit or to storage. Line 38 is provided with a pressure control valve 39 which is effective to maintain the pressure in the system at the selected pressure within the range of about 150 to about 650 pounds per square inch. It is sometimes desirable to by-pass the scrubber 31, and this may be accomplished by shutting valve 41 in line 29 and opening a valve 42 in by-pass line 43, the valve in line 37 of course being closed.

The process of the invention is employed in starting up a unit such as that illustrated in the drawing in the following manner. Any suitable heated gas under pressure sufficient to overcome the substantial pressure drop through the mixing nozzles 19 and 21 is introduced into the system through a line 46 provided with a valve 47. This gas may be air or it may be flue gas. The gas is preferably at a temperature of the order of 1000° to 1200° F. and is caused to flow through manifold line 24 and branches 26 and 27 to the mixing nozzles. The introduction of this hot gas

is continued until the temperature in the unit has been raised to a temperature above the ignition point of the combustible mixture which is later introduced. Preferably the unit is raised to a temperature in the neighborhood of 800° F. While passing the hot gas through the unit, the pressure is preferably maintained at about atmospheric by control of the valve 39, and the scrubber 31 is cut out of the system.

When the desired temperature has been reached, the flow of the heated gas is shut off and the introduction of air and an easily ignitible hydrocarbon, such as a light straight run gasoline having an end boiling point at atmospheric pressure of about 200° to about 300° F. or a light gasoline fraction of the hydrocarbons produced in the synthesis reaction between carbon monoxide and hydrogen having a similar end point, is begun. The light gasoline at a convenient temperature such as atmospheric temperature is introduced through line 48 provided with valve 49 and is passed through line 16, branches 17 and 18, to mixing nozzles 19 and 21. Air, preferably at a temperature of about 400° to about 500° F. is introduced through line 51 provided with valve 52 and is passed through line 24, branches 26 and 27, to the mixing nozzles. The gasoline and the air are intimately mixed in the mixing nozzles and are introduced into the generator 10. The light gasoline and air are employed in proportions such that a combustible mixture in vapor form is produced. These proportions may be, for example, such as to produce an air-gasoline ratio of the order of 14:1. Because the ignition temperature of a mixture of air and light straight run gasoline is of the order of 450 to 600° F., the mixture formed in the mixing nozzles ignites soon after it enters the combustion tube of generator 10 which, as stated previously, is at a temperature of about 800° F. The combustion of the gasoline produces considerable heat and the introduction of this combustible mixture is continued until the unit has been heated to a temperature substantially above 1200° F.; for example, a temperature of about 1400° F. During this period the pressure in the unit is also maintained at about atmospheric and the scrubber 31 is by-passed.

The introduction of gasoline is then discontinued by shutting off valve 49 and the introduction of natural gas is begun. The ignition temperature of a mixture of natural gas and air is in the neighborhood of 1000° to 1200° F. and therefore the 1400° F. temperature existing in the generator is sufficient to cause ignition of this mixture. The mixture of natural gas and air is introduced into the generator and burned therein until the temperature in the generator is approaching the desired reaction temperature. Prior to reaching this temperature, the introduction of air is discontinued by shutting valve 52 and this air is replaced by substantially pure oxygen from line 22.

The reaction between natural gas and oxygen is also exothermic and produces additional heat to continue raising the temperature of the unit until the desired reaction temperature between about 1800° and 2800° F. is attained. Shortly after beginning the introduction of the natural gas-oxygen mixture, the pressure is gradually increased by control of valve 39 until the unit is brought to the desired elevated pressure. When the reaction conditions of temperature and pressure have been attained, valve 41, which previously had been partially opened to permit the scrub-

ber 31 to come up to pressure, and the valve in line 37 are opened wide, valve 42 is closed, scrubber 31 is in operation and the unit is on-stream.

When operating as described above in bringing the unit up to the reaction temperature and utilizing a mixture of natural gas and air, the composition of this mixture is controlled so as to cause a hightly exothermic reaction and yield combustion products containing a relatively high proportion of carbon dioxide and steam. Moreover, the composition of the natural gas-air mixture may be varied during the introduction. Thus the mixture initially introduced may be one that is most easily ignitible at the temperature to which the unit has been heated by the gasoline-air mixture, whereas the natural gas-air mixture introduced in the latter stages is preferably one that produces the maximum amount of heat of combustion.

In the interest of simplicity of description, the furnaces or other heating units forming a part of the overall plant employed in carrying out the present process have been omitted from the drawing. As previously stated, when the unit is on-stream, it is frequently desirable to heat the natural gas and oxygen separately to selected temperatures in order to attain in the generator the desired reaction temperature. The furnaces for heating the natural gas and oxygen can be employed for heating the materials used in the starting-up procedure. For example, by the use of conventional piping arrangements, the oxygen furnace can be employed for heating both the gas used in the initial heating of the generator and the air used in admixture with the light gasoline and the natural gas in the intermediate heating periods. Similarly, the light gasoline can be heated, if desired, by the furnace used for heating the natural gas during on-stream operation. Thus, the starting-up process requires little more equipment than is necessary for the normal operation of the unit.

While the invention includes in its broader aspects a procedure involving heating the unit with the mixture of gasoline and air until the ultimate reaction temperature is reached, this procedure is less economical than that described above.

In the foregoing description the use of hydrocarbons in forming the intermediate combustible mixture has been stressed. This is because the use of hydrocarbons, particularly mixtures of hydrocarbons such as casing head gasoline and light straight run gasoline, is entirely satisfactory and is more economical than the use of other fuels. It will be understood, however, that other organic compounds or mixtures of compounds easily ignitible at relatively low temperatures, especially temperatures below 800° F., may also be used. Examples of such compounds are n-amyl alcohol, n-butyl alcohol, diethyl ether, and methyl ethyl ether. Organic compounds having the desirable low temperature ignition characteristics and easily ignitible hydrocarbons are referred to herein as easily ignitible fuels.

The ignition temperature of the intermediate fuel-air mixture has been referred to in the preceding description. As is well known, in the ignition of a combustible mixture two factors play parts: the temperature and the time during which the mixture is maintained at the temperature. Thus, if a fuel-air mixture is maintained at just a little above the minimum ignition temperature, the time required to ignite the mixture may be relatively long. Accordingly, it is generally preferred to heat the unit substantially above the minimum ignition temperature of the fuel-air mixture employed in order to reduce to a minimum the induction period required to cause ignition. In general, it is preferred to heat the unit with the heating gas to a temperature such that the ignition induction period of the fuel-air mixture employed is less than 0.1 second.

It will be obvious that in place of the natural gas-air mixture employed after the gasoline-air mixture or mixture of other fuel with air has heated the unit to above 1200° F., a mixture of natural gas and oxygen may be used. However, since the primary purpose of the combustion at this stage is to produce heat rather than to produce synthesis gas, it is preferable for reasons of economy to employ air rather than oxygen for admixture with the natural gas.

It will be seen that the process described is simple and efficient and has important advantages. It is desirable that a unit operated under these very severe temperature and pressure conditions should contain no more apertures than are absolutely necessary for operation of the process. This is particularly important in the combustion tube section of the device as any breaks or openings in the heat retentive insulating walls of the tube might permit the escape of hot gases to the steel shell and cause buckling. The present process has the important advantage that the gases and combustible mixtures used during the starting-up procedure may be introduced through the nozzles employed for introducing the final charge mixture and the resulting hot gases may be removed from the unit through the exit employed for removing the desired reaction products.

The process also has the additional advantage that the unit being started up may be pressure tested, the pressure may be released, and the unit may be started up and placed on-stream without losing the pressure test because it is not necessary to open any flanges to start the unit by this process.

Obviously many modifications and variations of the invention as hereinabove set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for starting a unit employed in carrying out a high temperature exothermic reaction initiated at an elevated temperature above 1000° F. without requiring the use of ignition devices, which comprises heating the unit to a temperature substantially below the reaction initiation temperature of the charge mixture to be employed in said reaction but above the ignition temperature of a mixture of an oxygen-containing gas and a fuel ignitible at a low temperature by passing hot gas heated externally of the unit through said unit, introducing said mixture of an oxygen-containing gas and a fuel into the unit and automatically igniting said last-mentioned mixture within the unit by means of the heat contained therein, continuing the introduction and combustion of said last-mentioned mixture until the unit is heated at least to the reaction initiation temperature of a mixture comprising the charge mixture, and introducing said charge mixture, automatically initiating reaction therein by the heat contained in the unit, and removing desired reaction products from the unit.

2. A process for starting a unit employed in

carrying out a high temperature exothermic reaction between a hydrocarbon and oxygen initiated at an elevated temperature above 1000° F. without requiring the use of ignition devices, which comprises heating the unit to a temperature substantially below the ignition temperature of the charge mixture to be employed in said reaction but above the ignition temperature of a mixture of an oxygen-containing gas and a hydrocarbon ignitible at a low temperature by passing hot gas heated externally of the unit through said unit, introducing said mixture of an oxygen-containing gas and a hydrocarbon into the unit and automatically igniting said last-mentioned mixture within the unit by means of the heat contained therein, continuing the introduction and combustion of said last-mentioned mixture until the unit is heated at least to the ignition temperature of a mixture comprising the charge mixture, and introducing said charge mixture, automatically igniting said charge mixture within the unit by the heat contained therein, and removing desired reaction products from the unit.

3. A process for starting a unit employed in carrying out at a superatmospheric reaction pressure a high temperature exothermic reaction between a hydrocarbon and oxygen initiated at an elevated temperature above 1000° F. without requiring the use of ignition devices, which comprises first heating the unit to a temperature substantially below the ignition temperature of the charge mixture consisting essentially of said hydrocarbon and oxygen to be employed in said reaction but above the ignition temperature of a mixture of an oxygen-containing gas and a fuel ignitible at a low temperature by passing hot gas heated externally of the unit through said unit, introducing the said mixture of an oxygen-containing gas and fuel into the unit and automatically igniting said last-mentioned mixture within the unit by means of the heat contained therein, continuing the introduction and combustion of said last-mentioned mixture until the unit is heated at least to the ignition temperature of a mixture comprising the charge mixture, and introducing said charge mixture, automatically igniting said charge mixture within the unit by the heat contained therein and removing desired reaction products from the unit, and at a stage in said process after said first heating step raising the pressure in said unit to said superatmospheric reaction pressure.

4. A process for starting a unit employed in carrying out at a superatmospheric reaction pressure a high temperature exothermic reaction between a hydrocarbon and oxygen initiated at a temperature above 1000° F. without requiring the use of ignition devices, which comprises first heating the unit to an elevated temperature below 1000° F. and substantially below the ignition temperature of the charge mixture consisting essentially of said hydrocarbon and oxygen to be employed in said reaction but above the ignition temperature of a mixture of an oxygen-containing gas and a fuel ignitible below 800° F. by passing hot gas heated externally of the unit through said unit, introducing said mixture of an oxygen-containing gas and fuel into the unit and automatically igniting said last-mentioned mixture within the unit by means of the heat contained therein, continuing the introduction and combustion of said last-mentioned mixture until the unit is heated at least to the ignition temperature of a mixture comprising the charge mixture, then introducing into said unit such a mixture comprising said charge mixture and another ingredient and automatically igniting said mixture comprising said charge mixtures and another ingredient within said unit by means of the heat contained therein, and introducing said charge mixture, automatically igniting said charge mixture within the unit by the heat contained therein, and removing desired reaction products from the unit, and at a stage in said process after said first heating step raising the pressure in said unit to said superatmospheric reaction pressure.

5. A process for starting a unit employed in carrying out at a superatmospheric reaction pressure a high temperature exothermic reaction between natural gas and oxygen initiated at a temperature above 1000° F. without requiring the use of ignition devices, which comprises first heating the unit to an elevated temperature above 800° F. by passing a hot gas heated externally of the unit through said unit, said elevated temperature being substantially below the ignition temperature of the charge mixture consisting essentially of said natural gas and oxygen to be employed in said reaction but above the ignition temperature of a mixture of an oxygen-containing gas and a hydrocarbon mixture ignitible below 800° F., introducing the said mixture of an oxygen-containing gas and a hydrocarbon mixture into the unit and automatically igniting said last-mentioned mixture within the unit by means of the heat contained therein, continuing the introduction and combustion of said last-mentioned mixture until the unit is heated at least to the ignition temperature of a mixture comprising the charge mixture, then introducing into said unit such a mixture comprising said charge mixture and another ingredient and automatically igniting said mixture comprising said charge mixture and another ingredient within said unit by means of the heat contained therein, and introducing said charge mixture, automatically igniting said charge mixture within the unit by the heat contained therein, and removing desired reaction products from said unit, and after beinning introduction of said charge mixture raising the pressure in said unit to said superatmospheric reaction pressure.

6. A process as defined in claim 5 wherein the hydrocarbon ignitible below 800° F. is a light gasoline having an end boiling point at atmospheric pressure of about 200° to about 300° F.

7. A process for starting a unit employed in carrying out at a superatmospheric reaction pressure a high temperature exothermic reaction between natural gas and oxygen initiated at a temperature above 1200° F. without requiring the use of ignition devices, which comprises first heating the unit to an elevated temperature below 1000° F. and substantially below the ignition temperature of the charge mixture consisting essentially of said natural gas and oxygen to be employed in said reaction but above the ignition temperature of a mixture of air and a hydrocarbon ignitible below 800° F. by passing hot gas heated externally of the unit through said unit, introducing the said mixture of air and a hydrocarbon into the unit and automatically igniting said last-mentioned mixture within the unit by means of the heat contained therein, continuing the introduction and combustion of said last-mentioned mixture until the unit is heated at least to the ignition temperature of a mixture comprising the charge mixture, then introducing into said unit a mixture of natural gas and

air and automatically igniting said mixture of natural gas and air within said unit by means of the heat contained therein, continuing the introduction and combustion of said mixture of natural gas and air to heat the unit additionally, and introducing said charge mixture, automatically igniting said charge mixture within the unit by the heat contained therein, and removing desired reaction products from said unit, and after beginning introduction of said charge mixture raising the pressure in said unit to said superatmospheric reaction pressure.

8. A process for starting a unit employed in carrying out, at a superatmospheric reaction pressure of from about 150 to about 600 pounds per square inch, an exothermic reaction at a temperature of about 1800° to 2800° F. between a charge mixture of natural gas and oxygen to produce a synthesis gas comprising carbon monoxide and hydrogen without requiring the use of ignition devices, which comprises first heating the unit to an elevated temperature below 1000° F. and substantially below the ignition temperature of a mixture consisting essentially of natural gas and air but above the ignition temperature of a mixture of air and light gasoline ignitible below 800° F. by passing hot gas heated externally of the unit through said unit, introducing a mixture of hot air and said light gasoline into the unit and automatically igniting said last-mentioned mixture within the unit by means of the heat contained therein, continuing the introduction and combustion of said last-mentioned mixture until the unit is heated at least to the ignition temperature of a mixture of natural gas and air, said ignition temperature being in the range of about 1000° to 1200° F., then introducing said mixture of natural gas and air and automatically igniting said mixture of natural gas and air within said unit by means of the heat contained therein, continuing the introduction and combustion of said mixture of natural gas and air to heat the unit additionally, introducing said charge mixture comprising natural gas and oxygen into said unit and automatically igniting said charge mixture within the unit by the heat contained therein, and removing synthesis gas from said unit, and after beginning introduction of said charge mixture, raising the pressure in said unit to said superatmospheric reaction pressure.

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