PROCESS AND APPARATUS FOR TREATMENT OF HYDROCARBONS

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Filed May 18, 1959, Ser. No. 813,772

Claims priority, application Belgium Sept. 8, 1958 8 Claims. (Cl. 260—679)

This invention relates to a process for the thermal treatment of hydrocarbons and to apparatus therefor.

Unsaturated hydrocarbons, particularly acetylene, can be produced in a very pure state by pyrolysis of gaseous hydrocarbons having fewer unsaturations. Advantageously, the pyrolysis uses hot gases, preferably free of oxygen, originating from a flame produced by the combustion of a liquid or gaseous fuel with a combustion supporting gas such as oxygen.

The furnaces used in the process advantageously essentially comprise:

1. A combustion chamber in which the fuel and combustion supporting gas, fed separately into the chamber, are mixed and form a flame at a burner outlet of the chamber;
2. A pyrolysis chamber connected directly with the combustion chamber, at the junction of which the hydrocarbon to be pyrolyzed is injected into the hot gases from the combustion chamber;
3. A device for quenching the pyrolysis gases.

The principle of the method lies in very rapidly heating the hydrocarbon to be pyrolyzed to a high temperature in the substantial absence of oxygen. Consequently, a high concentration of heat is to be attained in the combustion chamber under conditions as adiabatic as possible; and the combustion gases, into which the hydrocarbon to be pyrolyzed is injected, are to be at very high temperature and to contain substantially no free oxygen.

In the present invention, the combustion zone defined by the flame jets is of such small volume that only the initial combustion phase can occur therein before mixing of the gases with steam occurs. During this initial combustion phase, which is of very short duration because of the use of very pure fuel and oxygen, the temperature attained can produce only an insignificant number of free radicals. After this initial phase, the reacting components are immediately and homogeneously mixed with steam, and the presence of this steam in the final phase leads to a completion of the reaction with substantially complete removal of free oxygen. When the fuel and oxygen are used in stoichiometric proportions, the combustion gases contain neither free oxygen nor unburned fuel in substantial amounts. This facilitates subsequent steps for separating and concentrating the unsaturated hydrocarbons formed by the pyrolysis and reduces to a minimum oxidation of the hydrocarbon to be pyrolyzed.

It has also been observed that the introduction of steam mixed with fuel gas and/or oxygen does not offer the same advantages as a separate injection of steam in the form of a ring surrounding the flame ring. To carry out the combustion reaction in a zone of very small volume—that is, to carry out the reaction at very high rate—substantially pure components must be used in the first phase of combustion. The dilution of the reagents with steam reduces the reaction rate, resulting in an increase in the volume of the combustion zone and, consequently, a less intense concentration of heat.

The nature and advantages of the invention will be more clearly understood by reference to the accompanying drawings, in which a preferred embodiment of a furnace for the pyrolysis of hydrocarbons is given by way of example.

FIGURE 1 is a front view, in section, of a circular furnace which can advantageously be used for producing unsaturated hydrocarbons by injection of the hydrocarbon to be pyrolyzed into hot combustion gases;
FIGURE 2 is a plan sectional view of the furnace at 2–2 of FIGURE 1;
FIGURE 3 is a front view, in section, of a portion of
the furnace of FIGURE 1, showing in detail a configuration for the injection of steam, fuel and oxygen; and FIG. 4 is a plot of combustion temperature as a function of the length of the combustion chamber, both for processes known to the art and for a furnace such as is shown in FIG. 1.

In FIGURE 1, the embodiment shown comprises distributor manifold 11, combustion chamber 12, and pyrolysis chamber 13. Conduits 14 and 15, respectively feed fuel and combustion-supporting gas such as oxygen to distributor 11. Conduit 16 feeds a pyrolyzable hydrocarbon such as naphtha to pyrolysis chamber 13. A device such as sprayer ring 17 for the injection of cold water is provided for quenching the pyrolysis gases.

That side of distributor 11 which faces combustion chamber 12 comprises circular notch 18, of trapezoidal cross section, the axis of which is also the longitudinal axis of the pyrolysis furnace. A perforated ring 19 connected with conduit 14 and a second concentric perforated ring 20 connected with conduit 15 feed fuel gas and oxygen, respectively, to chamber 12. Rings 19 and 20 abut the inclined side walls of notch 18 and are inclined perpendicularly to said walls. The side walls form an angle of 45° with the longitudinal axis of the furnace. The perforations in rings 19 and 20 are symmetrically distributed around the circumference of the rings and are advantageously of a suitable diameter to give a high nozzle velocity of 500 m./second for, for example, to escape from fluids. The momenta of fluids leaving corresponding perforations in rings 19 and 20 per unit time are preferably substantially equal.

Distributor manifold 11 is also provided with a central steam chamber 21 connected with steam conduit 22. Steam from chamber 21 is introduced into combustion chamber 12 through annular slit 23, inclined at an angle of from about 35° to 50° to the longitudinal furnace axis. A second annular slit 24, also inclined at an angle from about 35° to 50° with the furnace axis injects another steam jet so that two jets or envelopes of steam are present. The two steam jets meet, advantageously inclining an angle of about 70° to 100° between them. The steam jets meet approximately on the same line, parallel to the furnace axis, as the meeting of the jets of fuel and oxygen. The relative width of slits 23 and 24 is such that substantially equal amounts of steam pass throughout in unit time.

FIGURE 2 and FIGURE 3 show in detail the configuration of rings 19 and 20 and slits 23 and 24.

In operation, hydrogen, or a hydrogen rich fuel gas, and oxygen are introduced into combustion chamber 12 through conduit 14 and ring 19 and through conduit 15 and ring 20, respectively. The gaseous reagents, which may be preheated, meet at an angle of approximately 90° on issuing from rings 19 and 20 with high linear velocity and at substantially equal flow rates. This results in an efficient and rapid local mixing, with the formation of a ring of short flames extending generally in a direction parallel to the axis of the combustion chamber 12.

Steam fed through conduit 22 passes through chamber 21 of distributor 11, protecting the latter against overheating, and is then injected into combustion chamber 12 through slit 23. Additional steam passes into chamber 12 from slit 24. The steam jets meet at an angle between about 70° to 100° and surround the ring of flames completely, outlining a combustion zone within which only a primary combustion phase occurs. The steam jets form a thermal screen protecting the walls of combustion chamber 12 against radiant heat. The fuel and oxygen react in the combustion zone, which is of small volume, outlined by the steam jackets. As only the first combustion phase occurs therein, a minimum of free radicals are formed. At the completion of the first combustion phase, the steam jackets and combustion gases meet rapidly and with a homogeneous distribution as regards both heat and composition. After this initial phase, the products of the combustion are mixed with steam. The final combustion phase, or completion of the reaction, then occurs, during which phase substantially all free oxygen is consumed and the fuel is completely burned.

At the outlet of chamber 12, the mixture of steam and combustion gases passes into pyrolysis chamber 13. The hydrocarbon to be pyrolyzed is injected through conduit 16 and apertures 25. It is decomposed at high temperatures to yield principally acetylene and ethylene. The pyrolysis gases are quenched by transverse injection of cold water through sprayer ring 17.

A particularly advantageous embodiment of a furnace of the kind shown in FIGURE 1 is described in Example 1 below.

Example

A furnace of the type shown in FIGURE 1 has been used for the simultaneous production of acetylene and ethylene at rates as high as 1922 kilograms/day and 4282 kilograms/day, respectively.

Such a furnace is advantageously constructed with a combustion chamber 12 defined by a distributor manifold 11 conveniently of steel and side walls conveniently of refractory brick. The wall of pyrolysis chamber 13 is conveniently made of steel. The walls of both chambers are advantageously cooled externally by circulation of cold water through sprayer ring 17 in FIGURE 1. Combustion chamber 12 has an internal diameter of 140 mm. and a height of 168 mm. Distributor 11 comprises notch 18, the sides of which are each inclined at 45° with the vertical. Perforated ring 20 comprises 24 apertures of 7 mm. diameter distributed symmetrically on a circle having a diameter of 104 mm. Ring 19 comprises 24 holes of 4.5 mm. diameter on a circle having a diameter of 66 mm. Annular slit 23 in distributor 11 has a diameter of 52 mm. (measured on the lower face of the distributor), a width of 5.5 mm., and is inclined at an angle of 37° from the vertical. Slit 24 has a diameter of 116 mm., a width of 3 mm., and is inclined at 37° with the vertical axis of the furnace.

A coke oven gas of the following composition was fed through conduit 14 and ring 19 into combustion chamber 12 at a throughput of 260 Nm³/hour:

Percent by volume

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>59.8</td>
</tr>
<tr>
<td>Methane</td>
<td>26.8</td>
</tr>
<tr>
<td>C₃ hydrocarbons</td>
<td>2.1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>5.6</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.4</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Oxygen of 93.5 percent purity was introduced into chamber 12 through conduit 15 and ring 20 at a throughput of 250 Nm³/hour. On entering the combustion chamber, the gaseous reactants were interpenetrated at an angle of 90° and ignited very rapidly to form a flame ring extending in a direction parallel to the axis of chamber 12.

The flame was completely surrounded by a screen of steam obtained by injecting steam through slits 23 and 24. The total throughput of steam, at 600°C, was 500 kilograms/hour, under a pressure (before passing through a preheater not shown in FIGURE 1) of 2 kg./cm². The steam throughput and velocities were substantially the same at each slit, and the steam jackets met at an angle of 74° and on a vertical line beneath the meeting point of the combustion reagents. 524 kg./hour of naphtha were injected into the mixture of combustion gases and steam. The temperature of the naphtha was about 580°C. at the inlet of the
pyrolysis furnace. The naphtha had the following characteristics:

Initial boiling point: 41°C.
End boiling point: 130°C.
Aromatic hydrocarbons: 10 percent by weight.
Naphthenic hydrocarbons: 10.5 percent by weight.

As mentioned earlier, the steam jackets preferably meet to include an angle between 70° and 100°. This selection of the angle value and of the distance between the injection slits depends mainly on the nature of the fuel used in producing the hot combustion gases. For each fuel, the combustion zone outlined by the steam jackets advantageously has a volume such that the first combustion phase proceeds normally and such that the temperature attained in this phase is in the same range as the temperature reached on completion of combustion after mixture with the steam of the screen has occurred.

This condition is shown in FIGURE 4 of the accompanying drawings. In FIGURE 4, temperature is plotted in arbitrary units on the ordinate, and the length of a combustion chamber such as that shown as 12 in FIGURE 1 is plotted on the abscissa in millimeters. According to the process of this invention (curve 26), the temperature within the chamber increases rapidly during the primary combustion phase (portion OA). Then, after the mixing in of steam with the combustion gases, the temperature remains substantially constant, the cooling effect of the steam (curve 27) being compensated by the exothermicity of the reaction completing the combustion (curve 28). A combustion chamber 165 mm. long (as in Example 1) is thus sufficient to give a mixture of steam and combustion gases which is both thermally and compositionally homogeneous.

By way of contrast, curve 30 shows the temperature pattern in a combustion chamber when a fuel gas and combustion supporting gas containing steam admixed prior to any combustion are used. The combustion, since carried out with impure reagents, proceeds more slowly. A long combustion chamber is necessary, resulting in significant heat losses.

Curve 29 is descriptive of a process in which steam is introduced after complete combustion. The temperature increases steeply during the combustion (portion OB of curve 29), and then decreases due to the introduction of relatively colder steam. In this case, a long combustion chamber, at least 300 mm. long, must be provided to get a thermally and compositionally homogeneous mixture of combustion gases and steam. In comparison with the process of the present invention, the introduction of steam after complete combustion results in heat losses due to:

1. The higher temperature in the combustion chamber (i.e., OB greater than OA); and
2. The greater volume required for the combustion chamber and the resultant larger exchange surface of the walls thereof.

In addition, because of the elevated temperature, there is significant formation of free radicals during the combustion.

Comparative measurements have been made with the steam screen of the present invention in the form of two jackets surrounding the flame ring and including an angle of about 74°, and with a steam. Then, simply directed along the side walls of combustion chamber 12. Under the same conditions of nature and throughput of reagents and ethylene/acylene ratio in the pyrolysis gas, the measurements show that with the steam screen of the present invention:

1. The length of the combustion chamber can be substantially reduced (e.g., from 300 mm. to 165 mm.), resulting in a reduction of the heat losses by over 50 percent; and
2. The oxidation of the hydrocarbon to be pyrolyzed by oxygen and free radicals in the combustion gases can be reduced from 9 percent to 4.5 percent.

The process of the present invention may also be used when several flame rings are formed, each of which is then surrounded by two steam jackets. Such a configuration is particularly suitable for the large-scale production of unsaturated hydrocarbons.

Although specific embodiments have been shown and described, it is to be understood that they are illustrative and are not to be construed as limiting on the scope and spirit of the invention.

What is claimed is:

1. A process for the preparation of unsaturated hydrocarbons by pyrolysis of hydrocarbons with hot combustion gases comprising forming a ring of flames in a combustion chamber by the combustion of a fluid fuel and a combustible gas introduced into said chamber through perforations distributed on a plurality of concentric rings, injecting the hydrocarbon to be pyrolyzed into the hot combustion gases originating from said ring of flames, to obtain pyrolysis products, and quenching the pyrolysis products, the steps comprising surrounding said ring of flames with a plurality of steam screens formed by pairs of opposing steam jets meeting to define a combustion zone of small volume wherein said combustion is first partially effected, mixing said steam and said hot combustion gases rapidly and homogeneously prior to completion of said combustion whereby said combustion is completed in the presence of steam, and thereafter injecting the hydrocarbon to be pyrolyzed into the hot gases originating from the completion of the combustion reaction in the presence of steam.

2. A process as in claim 1 wherein said steam jets meet to include an angle between about 50° and 120°.

3. A process as in claim 1 wherein said steam jets meet to include an angle between about 70° to 100°.

4. A process as in claim 1 wherein said steam jets meet on a line parallel to the longitudinal axis of the combustion chamber and substantially directly below said ring of flames.

5. A process for the preparation of unsaturated hydrocarbons by pyrolysis of hydrocarbons with hot combustion gases, the steps comprising mixing steam with hot gases formed by partial combustion of a fluid fuel and a combustible gas prior to complete combustion thereof, and injecting the hydrocarbons to be pyrolyzed into the hot gases after completion of the combustion reaction in the presence of steam.

6. A process for the preparation of unsaturated hydrocarbons by pyrolysis of hydrocarbons with hot combustion gases, the steps comprising cooling the reagents in an exothermal combustion reaction by mixing steam with said reagents after combustion has begun but before it is completed, whereby a constant temperature gaseous mixture of steam and combustion gases is produced, and thereafter injecting the hydrocarbons to be pyrolyzed into said constant temperature gaseous mixture.

7. A furnace for the preparation of unsaturated hydrocarbons by pyrolysis of more saturated hydrocarbons with hot combustion gases, which apparatus comprises concentric annular conduits for feeding, respectively, fuel gases, combustible gases, and steam, a distributor for said gases, a combustion chamber and a pyrolysis chamber, said combustion chamber having a small volume, said distributor provided, on its side facing the combustion chamber, with an annular groove concentric with said combustion chamber and with the annular conduits for feeding the gaseous reagents and the steam, the sides of said groove diverging at an angle not greater than 90° and having small perforations connecting said groove with the annular conduits for the fuel and combustible gases, the perforations connected to the conduit for introducing one of the gases being paired with corresponding perforations for introducing the other reactive gas, said groove also
having in the sides thereof annular slits connecting said groove with the annular conduits for the steam, said annular slits being disposed pairwise on either side of each set of paired perforations for fuel and comburent gases and opposed to define an acute angle therebetween, whereby to inject paired steam jets which meet to define a reaction zone of small volume surrounding said paired perforations.

8. A furnace as in claim 7 wherein said steam jets meet to include an angle between about 50° and 120°.

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