Dec. 24, 1957 W. E. LOBO 2,817,690

CONVERSION OF HYDROCARBONS

Filed July 14, 1954

FIG. 1

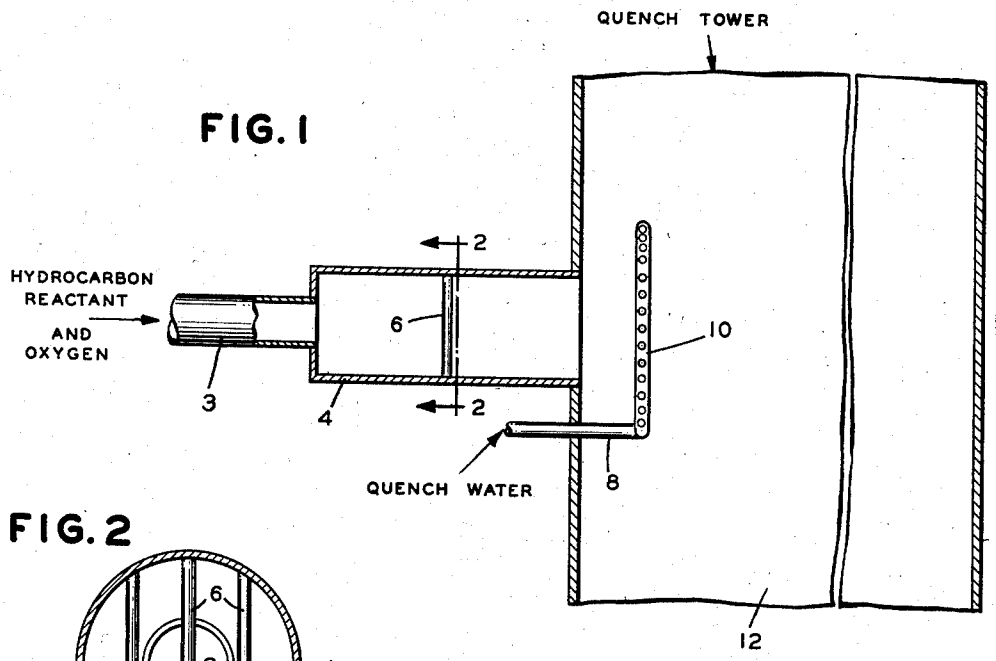


FIG. 2

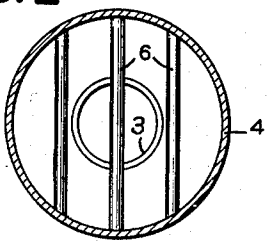


FIG. 3

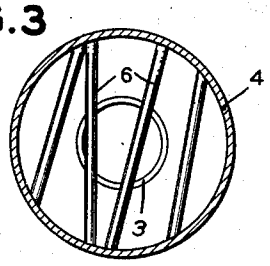


FIG. 4

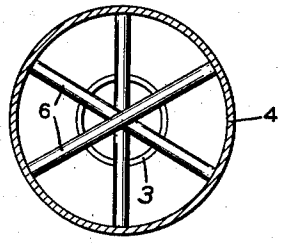


FIG. 5

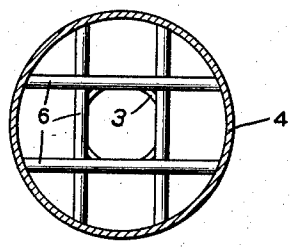


FIG. 6

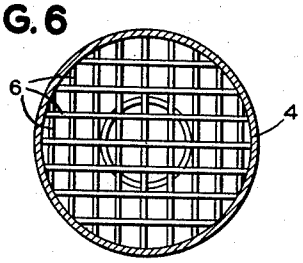


FIG. 7

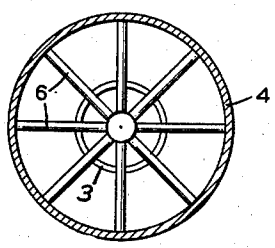
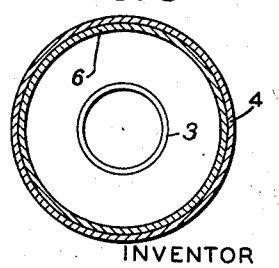


FIG. 8



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CONVERSION OF HYDROCARBONS

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4 Claims. (Cl. 260—679)

This invention relates to the partial combustion and pyrolysis of hydrocarbons and more particularly to method and means for producing hydrocarbons having a high carbon content. Still more particularly it relates to method and means for stabilizing the flame partial combustion of hydrocarbons to acetylene.

In general the production from hydrocarbons of hydrocarbons having a higher carbon content requires high temperatures and large quantities of thermal energy. The reactions which occur in the preparation of acetylene from methane, for example, are endothermic in nature and take place at temperatures from about 2000° F. to about 3000° F. Part of the sensible and reaction heat required for the pyrolysis of methane may be obtained by preheating the hydrocarbon feed. Unfortunately, the preheat temperature is by necessity limited to a level substantially lower than the reaction temperature in order to avoid premature reaction. A preferred method of supplying the additional thermal energy required is by partial combustion of the hydrocarbon material with oxygen. This provides a combustion flame in which the temperature quickly reaches the high level required for pyrolysis, and the hydrocarbon is readily converted to more unsaturated hydrocarbons.

As a general rule, the pyrolysis reaction proceeds more quickly and with higher yields as the reaction temperature is increased. However, subjecting the reactants to high temperatures over any extended period of time tends to produce undesirable reactions, thereby decreasing the yield of unsaturated hydrocarbons. The preferred process is one in which the temperature is maintained at a high level and the reaction time is held to a minimum. The more usual method of accomplishing this and thereby obtaining the desired reaction product is to limit the size of the reaction zone and pass the reactants therethrough at a high velocity, with subsequent quenching of the reaction products. With the proper control of time, temperature and other reaction variables it is possible to reduce undesirable reactions to a minimum and obtain substantial yields of unsaturated compounds. To provide the short reaction times requires a high reactant linear velocity to be maintained in the reaction zone. Since this velocity is often greater than the flame propagation velocity of the gaseous mixture frequent extinguishment of the combustion flame is common. Various solutions to this problem have been proposed including numerous types of apparatus arrangements, both regenerative and non-regenerative, the use of low velocity pilot flames having a high oxygen content, and others.

It is an object of this invention to provide improved method and means for carrying out the partial combustion and pyrolysis of hydrocarbons to produce hydrocarbons having a higher carbon content.

It is another object of this invention to provide method and apparatus for maintaining and stabilizing a combustion flame in the partial combustion and pyrolysis of hydrocarbons to acetylene.

These and other objects of the invention will become

more apparent from the following detailed description and discussion.

In this invention a mixture of oxygen and a hydrocarbon material to be pyrolyzed is passed at a high velocity through a reaction zone maintained at a high temperature by flame partial combustion of the hydrocarbon material and the mixture is contacted therein with a refractory supported flame stabilizing material having catalytic oxidizing properties.

As mentioned before the process of converting hydrocarbons having a low carbon content to hydrocarbons having a higher carbon content requires high temperatures. Depending on the type of reactants and the product desired, temperatures from as low as about 300° F. to as high as about 5000° F. are commonly employed in carrying out the reaction. When oxygen or an oxygen containing gas such as air is utilized to supply the thermal requirements of the process, that is, by partial combustion of a portion of the hydrocarbon reactant, the required ratio of oxygen to hydrocarbon reactant is between about 0.45 and about 0.60 mol per mol, the exact quantity needed being dependent on the type of reactants and the reactant temperature. Usually pure oxygen is preferred since the use of air or a similar oxygen containing material introduces compounds which dilute the hydrocarbon feed and the effluent from the reaction zone. Pressure has two effects on the pyrolysis reaction: (1) It increases the temperature at which the reaction proceeds, and (2) it increases density of the reactant gases, thus increasing the time in the reaction zone which makes it necessary to maintain a higher gas velocity therein. It is advisable therefore to maintain as low a pressure as possible in the reaction zone. However, if desirable, pressures ranging from a few to several hundred atmospheres are used. The residence time of the reactants in the reaction zone is preferably limited to suppress the formation of carbon and undesirable hydrocarbon products. Reaction times from as low as about 0.0005 second to as high as several hours are not unusual. A degree of latitude in reaction time exists for each particular pyrolysis reaction, the optimum value in each case depending primarily on the temperature selected for carrying out the reaction and the products desired from the reaction. More usual reaction times under favored operating conditions are on the order of seconds or fractions of a second. In order to obtain such short residence times it is necessary to employ a small reaction zone and to pass the reactants therethrough at a high velocity, frequently well above the corresponding flame propagation velocity for the reactants involved. Depending again on the hydrocarbon feed material and the reaction conditions, the linear velocity of the oxygen-hydrocarbon mixture in the reaction zone varies over a wide range, from as low as 1 foot per second to about 1000 feet per second.

Many types of hydrocarbons are pyrolyzed to produce high carbon containing compounds, including paraffins, olefins, aromatics, naphthenes, etc. Because of their greater availability, particularly in petroleum refinery gases, the lower boiling aliphatic hydrocarbons such as methane, ethane, ethylene, propane, propylene, etc., find frequent use in the pyrolysis processes.

Various catalytic materials which promote oxidation reactions are useful in carrying out the invention, for example, copper, cobalt, iron, nickel, platinum, palladium, aluminum, silver, manganese, vanadium, etc., and alloys and oxides thereof. These materials can be used singly or in mixtures of one or more catalysts in varying proportions. In some cases it may be desirable to use a non-catalytic material in conjunction with the catalyst, for example, as a binder. The primary consideration in the selection of the catalyst is to choose one which promotes oxidation of the hydrocarbon material to be pyrolyzed,

The catalytic material is arranged in the reaction zone to provide a surface for contact with the reactants passing therethrough. The quantity of catalytic material is preferably limited so that the surface area presented to the reactants is relatively small, usually not more than three or four times the cross-sectional area of the reaction zone and more usually, between about 0.10 and about 2.0 times the reaction zone cross-sectional area. Limitation of contact surface is desirable for two reasons; first, the nature of the catalyst is such that it tends to promote complete oxidation of the hydrocarbon reactant and may also tend to produce undesirable side reactions, therefore it is preferred that the proportion of the hydrocarbon reactant coming in contact with the catalyst be restricted. The other reason for limiting the amount of catalytic material is to provide a minimum obstruction to flow through the reaction zone.

At the temperatures encountered in the reaction zone, highly refractory materials are required to support and impart mechanical strength to the catalyst. Fused alumina, silicon carbide, quartz, porcelain, etc., are a few of the materials which are satisfactory. The catalyst is preferably deposited on the surface of the refractory support in the form of a coating or film. This may be done by any conventional means, for example, by coating the refractory material with a solution of the salt of the catalyst and calcining in a reducing or oxidizing atmosphere, to produce either a metal or metal oxide film. Mixtures of metal or metal oxide catalysts may also be deposited in a similar manner. An effective flame stabilizing material is also prepared by mixing a metal or metal oxide catalyst with the refractory material as an integral step in the preparation of the physical form of flame stabilizer desired. Since the catalytic activity of the flame stabilizer is limited to the surface thereof the latter method of preparation is wasteful of catalyst as compared to the film or coating method, however, in the event that erosion or loss of stabilizing material due to other causes occurs to a substantial extent the latter method of preparation porvides a continuous new source of catalyst surface.

Usually, the flame stabilizing material employed is in the form of rods or bars. The oxidation reactions which normally take place in the combustion flame are greatly accelerated at the surface of the rods, heating them to incandescence and providing a high temperature source which serves to maintain the partial combustion flame and reignite it if it becomes extinguished. In practice, the incandescent catalytic material sufficiently stabilizes the combustion flame so that the danger of extinguishment is substantially eliminated. The arrangement of the flame stabilizing material in the reaction zone may take varied forms, including catalyst coated rods or bars arranged in the manner illustrated in the accompanying drawings or a mesh or lattice work arrangement, also illustrated. It is desirable that the flame stabilizing material be disposed in one section of the reaction chamber so as to localize the combustion flame and thereby provide control over the residence time of the reactants in this high temperature region. However, residence time may be controlled entirely by reactant velocity, in which case the stabilizing material may be distributed throughout the reaction zone.

Of particular interest among the pyrolysis reactions is the high temperature conversion of low boiling aliphatic hydrocarbons, for example methane, to acetylene. To provide the sensible and reaction heat necessary to sustain a reaction of this type partial combustion with oxygen is employed, as previously described. Since it is usually advantageous to minimize oxygen consumption a substantial part of the sensible heat required in the reaction is supplied by preheating the hydrocarbon and oxygen. In general a high preheat temperature gives higher conversion rates therefore maximum preheat temperatures are preferred.

In a typical process a mixture of methane and oxygen in a ratio of between about 1.7 and about 2.3 mols of hydrocarbon per mol of oxygen is preheated to between about 600° F. and about 900° F. and is passed into a reaction zone. Flame combustion within this zone increases the temperature to between about 2200° F. and about 3000° F. whereupon pyrolysis of the hydrocarbon occurs. By maintaining a high linear velocity within the reaction zone, that is, between about 60 feet per second and about 400 feet per second, the residence time therein is held at an optimum level, between about 0.001 second and about 0.05 second. Although these velocities greatly exceed the flame propagation velocity there is essentially no problem of flame extinguishment due to velocity because of the presence of a flame stabilizing material of the type previously described, which serves to maintain the combustion flame, reigniting it if, for any reason, it becomes extinguished.

To more clearly illustrate the invention and to provide a better understanding thereof, reference is had to the accompanying drawings of which:

Figure 1 is a diagrammatic illustration of a reaction zone and quenching tower suitable for the conversion of methane to acetylene in the presence of a combustion flame and,

Figures 2 through 8 are sectional views taken perpendicular to the reaction zone, at point **2**, illustrating various arrangements of catalytic flame stabilizing material.

Referring to Figure 1, methane and oxygen in a mol ratio of about 1.9 are preheated to a temperature of about 800° F. and are passed through conduit **3** into a conventional reaction chamber **4**. Contained in the reaction chamber are three silicon carbide rods **6** arranged in a plane substantially perpendicular to the longitudinal axis of the reaction zone. The rods are coated with an alumina-platinum composite catalyst and are disposed in a parallel arrangement, spaced substantially equidistant across the reaction zone. The diameter and length of the rods is such that their combined outside surface area is about 30% times the cross-sectional area of the reaction zone.

A temperature higher than the preheat temperature is required to initiate the combustion reaction. This is provided by a torch or a spark igniter (not shown). After ignition the combustion reaction proceeds, producing a flame which heats the methane to a sufficient temperature to initiate the pyrolysis reaction. The temperature in the reaction zone as a result of these reactions is about 2800° F. As the reactant gases pass through the reaction zone, at a linear velocity of about 300 feet per second, the reactions which produce the combustion flame are accelerated at the surface of the catalyst coated rods and the rods become heated to a very high temperature, thereby stabilizing the flame and supplying a reignition source in the event that the flame becomes extinguished because of a temporary interruption in reactant flow or for any other reason. Because of the high velocity in the reaction zone the combustion flame exists only at and downstream from the stabilizing rods. As a result control of the residence time of the reactants in the high temperature portion of the reaction zone is obtained by appropriately locating the stabilizing rods with respect to the quench point. This method of establishing residence time, in conjunction with control of the linear velocity of the reactants provides a process having an extremely wide range of flexibility.

On leaving the reaction zone the effluent gases pass into a quench tower **10** where they are sprayed with quench water introduced through conduit **8** into a spray ring **10**. The spray serves to quickly reduce the temperature of the effluent gases below the point at which reaction proceeds. The effluent gases are passed from the quench tower for further processing (not shown).

Figures 2 through 7 illustrate various physical arrangements of flame stabilizing material in the form of rods which may be used in carrying out this invention. It is not necessary or even desirable that this material lie sub-

stantially in a single plane perpendicular to the longitudinal axis of the conversion zone. However, such an arrangement may be used for reasons of simplicity and economy. In addition, as mentioned before localization of the stabilizing material provides an additional control over reaction time. An example of a slightly different arrangement is shown in Figure 8 in which the flame stabilizing material is circular in shape and comprises a ring or a cylinder which may vary in length.

Having thus described my invention by reference to a specific application, it should be understood that no undue limitations or restrictions are to be imposed by reason thereof, but that the scope of the invention is defined by the appended claims.

I claim:

1. In a process for pyrolyzing hydrocarbons in which hydrocarbons and oxygen are passed at a linear velocity exceeding the flame propagation velocity through a conversion zone under conditions suitable to effect flame partial combustion and conversion of the hydrocarbons to hydrocarbons having a higher carbon to hydrogen ratio, the improvement which comprises maintaining the combustion flame within the conversion zone by contacting the hydrocarbon reactants and oxygen flowing therethrough with a flame stabilizing material having strong oxidizing properties and disposed across said zone in the form of surface material on spaced elongated members between which the hydrocarbon reactants and oxygen pass, said flame stabilizing material being in the form of said surface material having a surface area between about 0.10 and about 2.0 times the cross sectional area of the reaction zone, said flame stabilizing material being selected from the group consisting of copper, cobalt, iron, nickel, platinum, palladium, aluminum, silver, manganese, and vanadium, and alloys and oxides thereof.

2. In a process for producing acetylene from methane in which methane and oxygen are passed at a velocity exceeding the flame propagation velocity through a conversion zone maintained at a temperature between about 1900° F. and about 2600° F. and at a pressure between about 0 p. s. i. g. and about 10 p. s. i. g. to effect flame partial combustion and conversion of the methane to acetylene, the improvement which comprises maintaining the combustion flame within the conversion zone by contacting the reactants flowing therethrough with a flame stabilizing material having strong catalytic oxidizing properties and disposed across said zone in the form of surface material on spaced elongated members between which the methane and oxygen pass, said material being in the form of said surface material arranged to offer a minimum obstruction to flow and having a surface area between about 0.10 and about 2.0 times the cross sectional area of the reaction zone, said flame stabilizing material consisting of platinum and said elongated members consisting of fused alumina.

3. An apparatus for producing acetylene by the partial flame combustion of a hydrocarbon with oxygen which comprises means defining an elongated confined reaction chamber, means in open communication with said reaction chamber adapted for the passage of said hydrocarbon and oxygen into said reaction chamber, flame stabilizing means having catalytic oxidation properties and having a surface area between about 10% and about 200% times the cross-sectional area of said reaction chamber disposed in said reaction chamber so as to offer a surface for contact with said hydrocarbon and oxygen and a quench means adapted for receiving the effluent gases from said reaction chamber and for quenching said gases to a temperature at which reaction substantially ceases, said flame stabilizing means being in the form of a plurality of spaced rods, said rods being formed of a refractory material and having their peripheral portions impregnated with a catalyst material having strong catalytic oxidizing properties.

4. The apparatus defined in claim 3, in which the catalyst material is platinum.

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