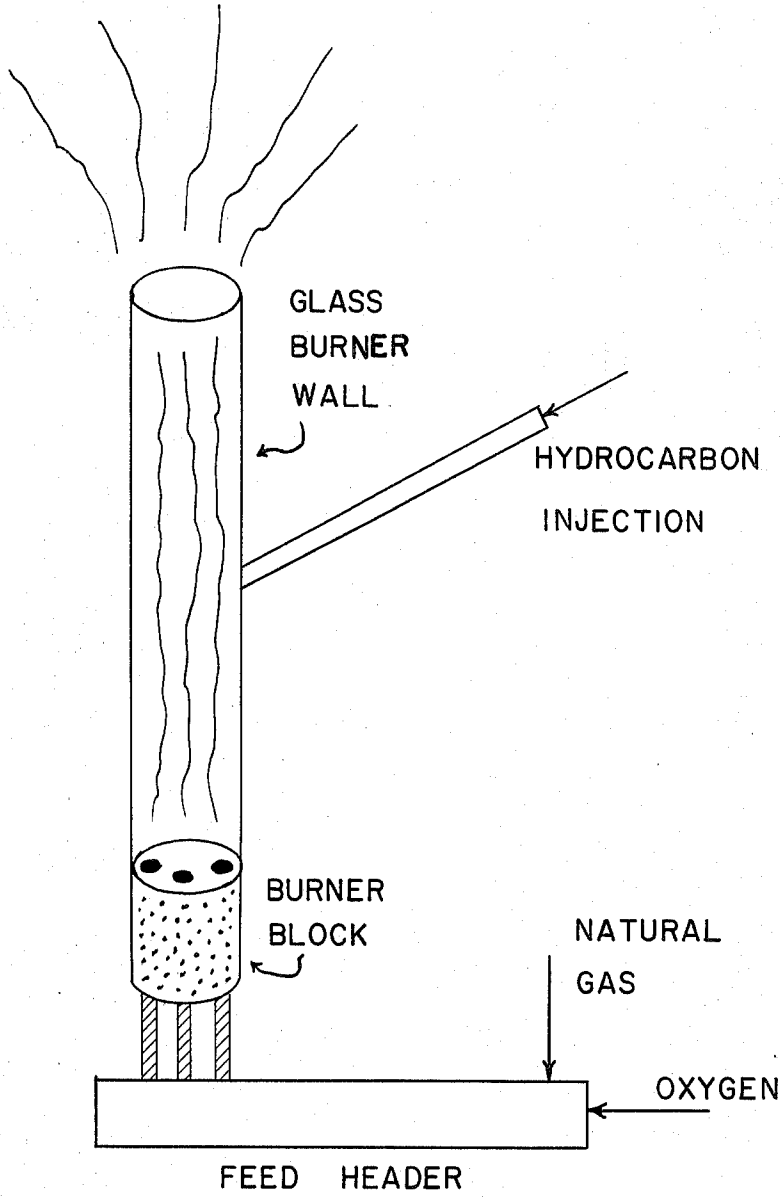
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PRODUCTION OF ACETYLENE

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PRODUCTION OF ACETYLENE

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This application is a continuation-in-part of application Serial No. 17,386 filed March 24, 1960 now abandoned.

This invention relates to improvements in the process for the production of acetylene. In particular, it relates to the production of acetylene from hydrocarbons by the partial combustion process.

There are four commonly used processes for the commercial production of acetylene from hydrocarbon gases. They are usually referred to as the electric arc, one-stage burner, two-stage burner, and the regenerative furnace. To produce acetylene from hydrocarbons, energy must be supplied in large amounts at high temperatures. The heating must be done quickly, and it must be followed by a rapid quench. These four processes mentioned above differ primarily in the means of supplying the energy and accomplishing the quenching.

The one-stage burner process is commonly called the partial combustion of methane. This process can be considered as occurring in two steps, the combustion step and the cracking step. In the combustion step, part of the natural gas or methane is burned with a quantity of oxygen, insufficient for complete combustion, to furnish heat in the range of 1200 to 1800° C. and preferably from about 1300° C. to about 1700° C. Since the combustion is incomplete, there still remains a portion of the methane which is the reaction component in the second step. In the cracking step, most of the remaining methane is cracked to acetylene, utilizing the heat available from the combustion step. After the formation of the acetylene in the cracking reaction, it is rapidly cooled to prevent any further reaction. These reactions occur almost simultaneously and probably with some interaction but certainly the combustion step must begin first. The net effects of the two steps can be separated. The cracked gas from the partial combustion process is subsequently separated so that substantially pure acetylene is the final result.

The drawing shows a conventional block burner modified to provide an inlet tube, for the admission of higher hydrocarbon, in the burner wall at, or slightly beyond the point of maximum acetylene formation.

Unlike the two-stage process where some suitable fuel undergoes complete combustion to furnish heat which cracks a separate hydrocarbon to acetylene, the partial combustion process must use the same component for fuel and cracking stock. This makes the use of higher hydrocarbons uneconomical in the partial combustion process, as a general rule, even though the higher hydrocarbons produce higher concentrations of acetylene in the off-gas.

The partial combustion process has another technical disadvantage which is not immediately apparent. At the necessary operating conditions of flame temperature and methane-oxygen ratio, the products of the combustion of methane do not consist of the most desirable products. Instead of reacting with oxygen to form primarily carbon dioxide and water, the combustion reaction forms principally carbon monoxide, hydrogen and water.

There are thus two bad effects. One is the dilution of cracked gas by noncondensable hydrogen above that formed by the cracking reaction. The other is less combustion heat per pound of methane burned. The result is still more cracked gas dilution from the additional combustion required over what would be required if optimum combustion could be obtained. Because of this, the maximum acetylene in the cracked gas is in the range of 8 to 9 mol percent.

It is an object of the present invention to provide an improved method of converting a hydrocarbon feed to acetylene in a partial combustion process. Another object of the invention is to provide a means of utilizing more of the heat energy produced in a partial combustion process. A further object is to provide a process which will increase the conversion of hydrocarbon to acetylene above the usual amount realized in the partial oxidation of methane to acetylene in a one-stage burner. These and other objects of the invention will become apparent from the following description of the invention.

According to this invention, higher hydrocarbons are injected into the combustion chamber of a partial combustion process in the vicinity of the point, that is, at or just past the point, where the acetylene concentration resulting from the cracking of primary feed hydrocarbon to acetylene in the partial combustion reaction is at a peak and where the temperature of the gas mixture in the combustion chamber is in the range of 1300 to 1700° C. These higher hydrocarbon can be cracked to acetylene at temperatures lower than that required to crack methane to acetylene. The amount of higher hydrocarbon injected is such that its sensible heat and the endothermic heat of cracking will not cool the resulting gas mixture to below 1200° C. Temperatures down to 1200° C. are sufficient to crack the injected higher hydrocarbons, but being below the temperature for peak acetylene production resulting from cracking of the primary feed hydrocarbon, for instance methane, are lower than that required to crack additional methane to acetylene. This results in substantially greater amounts of acetylene in the cracked gas.

An important feature involved in this invention is the use of the turbulent interaction between the main hydrocarbon feed and the secondarily injected higher hydrocarbon feed. This turbulence pattern provides for rapid and thorough mixing of the injected material with its surroundings. After intimate mixing of the injected material with the partial combustion products the heat available quickly cracks the injected hydrocarbon to acetylene thus adding to the amount of acetylene already present from the precedent cracking of methane.

An advantage of this scheme is that partial combustion of the primary feed, cracking of the primary feed, mixing of the secondary injected feed, with the partial combustion products, cracking of the secondary injected feed, and quenching of the products, all occur consecutively almost instantaneously and in a single chamber. Another advantage is that no additional heat need be added by any means to crack the secondary injected higher hydrocarbons to acetylene. The heat required for this cracking is already present from the partial combustion of methane and ordinarily wasted as the cracked gas is quenched and separated. Another advantage of this invention is that additional acetylene is produced without use of additional oxygen, an expensive constituent in the production of acetylene by the partial combustion process.

The following examples are given as illustration, but should not be construed as limiting the scope of the invention in any manner whatsoever.

Example I

In the usual and standard method for the production of acetylene by the partial combustion of methane, 38 pounds per hour of a feed gas containing oxygen and methane in a weight ratio of 1.4/1 were fed through a burner block into a 1¾ inch diameter quartz tube at approximately 30° C. The partial combustion took place primarily in the zone from the face of the burner block to a distance about 6 inches from the burner block. The methane cracking began in this same region but was not complete until the gas had passed to a distance of 8 inches from the burner block. This was determined

by suitably samplying the gas along the length of the quartz tube. The cracked gas was exhausted from the top of the tube and in the ordinary production of acetylene would have been quenched and recovered at this point. Temperatures in the burner during the cracking of methane were in the range of 1300° C. to 1700° C. Peak acetylene content in the cracked gas measured 6.3 mol percent.

Example II

As one means of practicing this invention, for instance, using ethane as the higher hydrocarbon which is secondarily injected, 38 pounds per hour of a feed gas containing oxygen and methane in a weight ratio of 1.4/1 were fed through a burner block into a 1¾ inch diameter quartz tube at approximately 30° C. as shown in the drawing. The partial combustion took place primarily in the zone from the face of the burner block to a distance about 6 inches from the burner block. The methane cracking began in this same region but was not complete until the gas had passed to a distance of 8 inches from the burner block. This was determined by suitably sampling the gas along the length of the quartz tube. A hydrocarbon stream approximately 1.6 weight percent of the total primary feedstream and composed of substantially pure ethane was injected into the quartz tube across the main flow of gas at a point from 0 to ½ inch past the point of peak acetylene concentration from the methane partial combustion, that is, from about 8 to 8½ inches from the face of the burner block. The temperature at this point in the tube was approximately 1400° C. to 1600° C. The ethane stream and the combustion products in the tube were intimately mixed and the cracking of the ethane to acetylene followed quickly. The cracked gas was exhausted from the top of the tube at which point it ordinarily would be quenched and recovered. Downstream of the ethane injection location the acetylene concentration was found to reach a peak of 7.5 mol percent. The temperature during the cracking of the ethane in the tube was in the range of 1200° C. to 1400° C. and was substantially lower than the temperature required for cracking of methane.

Example III

Another exemplification of the present invention, as an example, was demonstrated by the use of propane as the secondarily injected higher hydrocarbon stream. Thirty-eight pounds per hour of a feed gas containing oxygen and methane in a weight ratio of 1.4/1 were fed through a burner block into a quartz tube identical to that shown in the drawing. The partial combustion took place primarily in the zone from the face of the burner block to a distance about 6 inches from the burner block. The machine cracking began in this same region but was not complete until the gas had passed to a distance of 8 inches from the burner block. This was determined by suitably sampling the gas along the length of the quartz tube. The secondarily injected higher hydrocarbon stream composed of substantially pure propane and amounting to approximately 1.6 weight percent of the total primary feedstream was injected into the quartz tube across the main flow of gas at a point from 0 to ½ inch past the point of peak acetylene concentration from the methane partial combustion, that is, from about 8 to about 8½ inches from the face of the burner block. The temperature at this point in the tube was approximately 1400° C. to 1600° C. The secondarily injected stream and the cracked gas in the tube were intimately mixed and cracking of the propane took place thereupon. Temperatures during the cracking of propane in the tube were in the range of 1200° C. to 1400° C. and were lower than those required for methane cracking. Acetylene content in the exhaust gases from the tube was measured to be 7.0 mol percent.

Likewise, as in Examples II and III, various other hydrocarbons may be injected into the burner tube to accomplish the results above. For example, any other straight-chain, branched-chain or cyclic paraffinic hydrocarbon, preferably, those having from 4 to 12 carbon atoms, such as butane, isobutane, pentane, hexane, heptane, and octane, and cyclopentane, cyclohexane, etc., may be injected as secondary feed in this invention. In addition, any olefinic hydrocarbon, either straight-chain, branched-chain or cyclic, preferably those having from 2 to 12 carbon atoms, such as ethylene, propylene, butylene, cyclopentadiene, methylcyclopentadiene, etc., may be used.

Pressure is not critical in this invention. The burner operates at essentially atmospheric pressure, but pressures as high as 25 p.s.i.g. or as low as 5 p.s.i.a. may be satisfactorily used.

Temperature is quite important. The combustion reaction develops temperatures in the range of 1300° C. to 1700° C. to furnish sufficient heat to crack the primary methane feed remaining from the combustion. However, the secondary higher hydrocarbon is cracked to acetylene over a temperature range below that necessary for the acetylene formation from methane. The cracking of the secondarily injected feed takes place from 1200° C. to about 1500° C.

It is critical in the practice of this invention, from the standpoint of maximum energy and feed utilization, to inject the higher hydrocarbon at or immediately past the point where the cracking of the primary feed hydrocarbon to acetylene results in peak acetylene concentration. The proper area for injection can be determined by developing a composition profile of the partial combustion burner. In this area heat from the combustion of the primary feed and oxygen is adequate to crack the higher hydrocarbon to acetylene, but the reaction has not progressed to a point where carbonization products begin forming. By trial and error the proper area for injection can be determined. For instance, in the quartz tube used in the examples, the point of injection must be from 0 to about one inch past the point of peak acetylene concentration. The following examples are presented to illustrate the criticality of the point at which the higher hydrocarbon must be injected into the acetylene converter to enjoy maximum conversion to acetylene.

Example IV

Approximately 15.3 pounds per hour of natural gas and approximately 21.5 pounds per hour of oxygen were fed into a vertical quartz tube through a burner block and burned. The combustion products left the top of the tube and were vented to the atmosphere. Samples of the combustion products were taken at different heights from the burner block and it was determined that the optimum cracking of methane to acetylene, as determined by maximum acetylene concentration, occurred at a distance of 8 inches from the burner block and the acetylene content at that point was 6.5 mol percent. In another run, the identical feed was used but 0.575 pound per hour of ethane was injected into the combustion stream at a distance of 7 inches from the burner block. Samples of the combustion products were again taken at various heights from the burner block and it was found that the maximum acetylene concentration in the cracked gas had increased to only 6.8 mol percent and occurred at about 9 to 10 inches from the burner block.

Example V

Approximately 15.7 pounds per hour of natural gas and approximately 22.2 pounds per hour of oxygen were fed into a vertical quartz tube through a burner block and burned. Again it was determined that the optimum cracking of methane to acetylene, as determined by maximum acetylene concentration of the combustion gases occurred at eight inches above the burner block and the acetylene concentration at that point was 6.5 mol percent. In another run under the identical conditions, 0.592 pound per hour of ethane was injected into the

tube at a distance of 8½ inches from the burner block and at a temperature in the tube from about 1300° C. to about 1700° C. Samples of the combustion products were taken at various heights from the burner block and the maximum acetylene concentration in the cracked gas was found to be 7.6 mol percent and the ethylene concentration was about 1.0 mol percent.

Example VI

Natural gas and oxygen were again fed through a burner block into a quartz tube at rates of 15.9 pounds per hour for natural gas and 22.4 pounds per hour for oxygen and were burned and cracked to form acetylene and other combustion products. In this run it was determined that the optimum cracking of methane to acetylene, as determined by maximum acetylene concentration in the combustion products, was at a distance of 9 inches from the burner block and the peak acetylene concentration was found to be 6.85 mol percent. In a subsequent run under the same conditions of feed, 0.626 pound per hour of ethane were injected into the combustion products at a distance of 9¼ inches from the burner block at a temperature in the tube from about 1300° C. to about 1700° C. After injection of the ethane, samples of the combustion products were taken at different heights and it was found that the maximum acetylene concentration in the cracked gas was 7.75 mol percent and the ethylene concentration was about 1.0 mol percent.

Example VII

Natural gas and oxygen were again fed through a burner block into a quartz tube at rates of about 15.7 pounds per hour for natural gas and 22.2 pounds per hour for oxygen and were burned and cracked to form acetylene and other combustion products. It was again determined that the maximum acetylene concentration in the combustion products was at a distance of about 8 inches from the burner block and the peak acetylene concentration was found to be about 6.5 mol percent. In a subsequent run under the same conditions of feed, about 1.2 pounds per hour of ethane were injected into the combustion products just past the point of peak acetylene concentration. However, the excess ethane injected resulted in a mixed gas temperature below 1200° C. after injection and as a result the peak acetylene concentration in the cracked gas leaving the tube was only 7.0 mol percent and the ethylene concentration had increased to 1.9 mol percent.

The amount of higher hydrocarbons injected to give the maximum percentage of acetylene in the cracked gas must be determined experimentally for each style of burner used and for the particular higher hydrocarbon employed. Ordinarily, the amount of higher hydrocarbons injected will be the maximum amount possible limited by the lowest temperature permitted for the gas mixture after injection, that is, a temperature not lower than about 1200° C. Secondarily injected hydrocarbon quantities in the range from 1 to 20 weight percent of the total primary feed of hydrocarbon to the burner can be used in practicing the invention. However, for efficiency of cracking to acetylene and economics of the process, the preferred quantity of injected hydrocarbon is from 1 to 10 weight percent of the total hydrocarbon feed.

Although any paraffinic or olefinic hydrocarbon having from 2 to 12 carbon atoms can successfully be employed as the secondarily injected hydrocarbon and subsequently cracked to acetylene, the preferred components are normally hydrocarbons having 2 to 8 carbon atoms such as ethane, propane, butane, pentane, hexane, heptane and octane; ethylene, propylene, butylene, pentene, hexene, heptene and octene; cyclohexane, methylcyclohexane, cyclopentadiene and methylcyclopentadiene because of the economy of the process.

What is claimed is:

1. In a process for the production of acetylene by the partial combustion of a primary feed hydrocarbon selected from the group consisting of methane and natural gas in an acetylene converter, the improvement which comprises injecting a higher hydrocarbon having from 2–12 carbon atoms chosen from the group consisting of paraffinic and olefinic hydrocarbons into the combustion chamber of said acetylene converter in the vicinity of the point where the acetylene concentration resulting from the cracking of primary feed hydrocarbon to acetylene is a maximum, in an amount such that the temperature of the resulting gas mixture does not fall below 1200° C. and cracking said higher hydrocarbon primarily to acetylene by the heat energy supplied by the partial combustion of said primary feed hydrocarbon and remaining from the cracking of a portion of said primary feed hydrocarbon to acetylene, said improvement yielding higher acetylene content in the reaction gases leaving said acetylene converter.

2. In a process for the production of acetylene by the partial combustion of methane in an acetylene converter, the improvement which comprises injecting a higher hydrocarbon having from 2–12 carbon atoms chosen from the group consisting of paraffinic and olefinic hydrocarbons into the combustion chamber of said acetylene converter at a point where the acetylene concentration resulting from the cracking of primary feed hydrocarbon to acetylene is a maximum, in an amount such that the temperature of the resulting gas mixture does not fall below 1200° C. and cracking said higher hydrocarbon primarily to acetylene by the heat energy supplied by the partial combustion of methane which remains from the cracking of a portion of the methane to acetylene, said improvement yielding higher acetylene content in the reaction gases leaving said acetylene converter.

3. In a process for the production of acetylene by the partial combustion of a primary feed hydrocarbon selected from the group consisting of methane and natural gas in an acetylene converter, the improvement which comprises injecting a higher hydrocarbon having from 2–12 carbon atoms chosen from the group consisting of paraffinic and olefinic hydrocarbons into the combustion chamber of said acetylene converter at a point immediately past the point where the acetylene concentration resulting from the cracking of primary feed hydrocarbon to acetylene is a maximum, in an amount such that the temperature of the resulting gas mixture does not fall below 1200° C. and cracking said higher hydrocarbon primarily to acetylene by the heat energy supplied by the partial combustion of said primary feed hydrocarbon which remains from the cracking of a portion of said primary feed hydrocarbon to acetylene, said improvement yielding higher acetylene content in the reaction gases leaving said acetylene converter.

4. The process of claim 1 wherein the primary feed hydrocarbon is natural gas.

5. The process of claim 1 wherein the higher hydrocarbon to be injected into the combustion chamber at a secondary inlet is a saturated straight-chain hydrocarbon chosen from the group consisting of ethane, propane, butane, pentane, hexane, heptane, octane, cyclohexane and methylcyclohexane.

6. The process of claim 1 wherein the higher hydrocarbon to be injected into the combustion chamber at a secondary inlet is an olefinic hydrocarbon chosen from the group consisting of ethylene, propylene, butylene, pentene, hexene, heptene, octene, cyclopentadiene and methylcyclopentadiene.

7. The process of claim 1 wherein the pressure in said acetylene converter is from 5 to 40 p.s.i.a.

8. The process of claim 1 wherein the higher hydrocarbon injected into said acetylene converter is in the range of 1 to 20 weight percent of the primary feed hydrocarbon.

9. The process of claim 1 wherein the temperature of the partial combustion in said acetylene converter is in the range of 1300° C. to 1700° C. and the amount of secondarily injected higher hydrocarbon is in the range of 1 to 10 weight percent of the primary feed hydrocarbon.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*