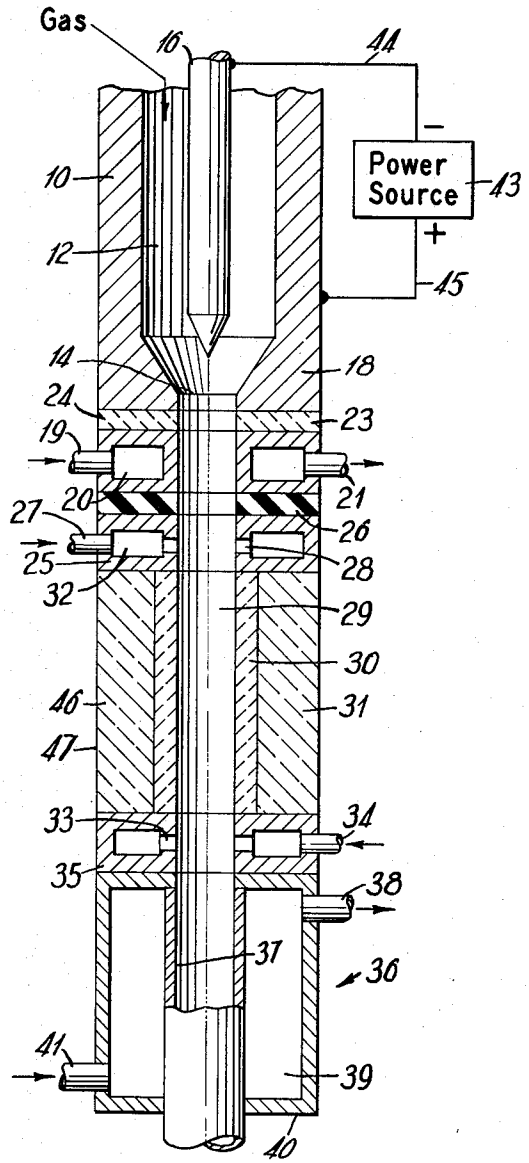
Feb. 18, 1964 L. E. CASE 3,121,675

ARC PROMOTED CHEMICAL REACTIONS

Filed Nov. 30, 1960



INVENTOR.
LAURA E. CASE

BY William F. Mesinger
ATTORNEY

United States Patent Office 3,121,675 Patented Feb. 18, 1964

3,121,675

ARC PROMOTED CHEMICAL REACTIONS

Laura E. Case, Lafayette, Ind., assignor to Union Carbide Corporation, a corporation of New York

Filed Nov. 30, 1960, Ser. No. 72,638
11 Claims. (Cl. 204—171)

This invention relates to a method of producing acetylene and more particularly to a method of increasing the efficiency of conversion of hydrocarbon feed to acetylene product in a hydrocarbon pyrolysis process for acetylene production.

Acetylene can be obtained by the pyrolysis of various hydrocarbons. Saturated hydrocarbons, such as methane, are preferred but aromatic hydrocarbons, such as benzene, could also be used in some cases. It is reasonably well-known that such pyrolysis reactions must be conducted at relatively high temperatures in order to crack and reform the hydrocarbons and then rapidly quenched in order to prevent decomposition of the acetylene formed during pyrolysis. High velocity combustion processes are intended to carry out the pyrolysis and subsequent quench in a short enough time to retain a large amount of acetylene. Slower acting pyrolysis reactions, such as a regenerative cracking process require a diluent, such as steam or nitrogen, to be added to the pyrolysis reactants in order to lower the partial pressure of any acetylene formed and thus reduce its rate of decomposition until the reaction products can be properly quenched.

It has now been discovered that reduced carbon formation and increased acetylene efficiency (percent of hydrocarbon reacted which forms acetylene) can be obtained when the hot pyrolysis products are partially quenched by contact with hydrogen prior to final complete quenching. Efficiencies as high as 93% can be easily attained as contrasted with efficiencies as low as 32% when hydrogen partial quench is not employed under otherwise comparable reaction condition. While minor additions of hydrogen in the order of about 10 volume percent based on the hydrocarbon reactant feed are useful, the preferred hydrogen partial quench feed rate is about 20–70 volume percent. The hydrogen apparently combines with some of the unreacted carbon from the hydrocarbon feed stock to form additional acetylene.

This particular process is especially unique when compared to the teachings of the prior art. The present invention allows acetylene efficiency of about 90% to be easily attained with a hydrogen partial quench amounting to about 30–40 vol. percent of the reactant feed. If an inert gas, such as helium or argon, is used as partial quench in a hydrocarbon pyrolysis reaction it would require quenching gas in an amount about 80–90 vol. percent of the reactant feed to achieve 90% acetylene efficiency. If hydrogen is added the reactant feed in a pyrolysis reaction under conditions substantially the same as those used with hydrogen partial quench, it would require about 150 vol. percent hydrogen mixed with the reactant feed in order to achieve about 90% acetylene efficiency. This less-efficient process not only requires more process materials but also produces a more dilute product gas mixture from which it is more difficult to separate the desired acetylene.

The introduction of hydrogen into the hot reaction gases prior to their being completely quenched is useful not only where acetylene alone is the desired product but also when acetylene is mixed with other desired products. For example, hydrogen partial quench can be employed when acetylene and hydrogen cyanide are produced concurrently as described in my copending U.S. patent application Serial No. 37,197 filed June 20, 1960, this application being a continuation-in-part thereof. In this latter case hydrogen partial quench can be used to increase acetylene yield without affecting hydrogen cyanide production.

While the invention in its broadest aspects relates to any hydrocarbon pyrolysis process for acetylene production, the inventive concept will be described with reference to a preferred electric arc promoted process.

Accordingly it is a main object of the present invention to provide an improved hydrocarbon pyrolysis process for the production of acetylene whereby the efficiency of conversion of hydrocarbon feed to acetylene product is increased.

Another object is to provide an improved, electric arc process for the pyrolysis of a fluid hydrocarbon wherein increased yields of acetylene are obtained.

Another object is to provide an improved collimated arc promoted process for converting hydrocarbon reactant material to acetylene product.

Other objects and advantages will be pointed out or become apparent from the following description and drawings found herein.

According to the present invention an improved hydrocarbon pyrolysis process for the production of acetylene is obtained by partially quenching the hot pyrolysis reaction product by contact with hydrogen gas prior to further complete quenching.

More specifically according to the invention there is provided a process for the production of acetylene by the pyrolysis of fluid hydrocarbons which includes energizing a high pressure arc of predetermined arc intensity, flowing an arc gas at a controllable rate through said high pressure arc, discharging the resultant hot arc gas stream, intimately mixing the effluent stream of hot arc gas with a supply of fluid hydrocarbon stock to pyrolyze said stock and produce acetylene as a reaction product; partially quenching the acetylene reaction product by contact with hydrogen, and then further cooling and quenching said acetylene reaction product.

The invention will be described more in detail in referring to the drawings in which:

The sole figure is a sectional view of a piece of apparatus for carrying out the invention.

Referring to the figure, 10 is a cylindrical copper body member which contains a cylindrical bore 12. The bore 12 tapers to a cylindrical nozzle passage 14 in the anode section 18 of body 10. A cathode 16 is axially aligned within bore 12 and is spaced from the walls of body member 10. Cathode 16 is preferably in the form of a rod or pencil and is conveniently constructed of thoriated tungsten. Anode 18 and body member 10 may conveniently be made of copper.

In order to prevent melting due to arc heat, the torch body 10 and anode section 18 are cooled by passing water or other cooling fluid from inlet 19 through annular cooling passage 20 and out through outlet 21. Even under these conditions the anode 18 is subject to severe arc erosion and pitting. It has been found that anode erosion can be practically eliminated by incorporating preferential electrode inserts in the anode nozzle wall. The preferential electrode is shown with inserts 23 and 24, each of which is in the shape of a small rod. These inserts could be of any desired shape as long as a surface is exposed to the nozzle passage. The preferential electrode may be of tungsten, tantalum or other material resistant to erosion by the high intensity electric arc. It is important that the insert be mounted so as to be partially thermally insulated from the adjacent cool anode material in order that the insert will operate at a higher temperature than the adjacent anode material. The exposed insert surface inside the nozzle passage thereby operates "hot" and the arc thus tends to strike the hot insert rather than the adjacent cool copper anode. This

poor heat exchange relationship is conveniently obtained by loosely fitting the insert in the anode wall and making electrical connection by soldering only at the outer surface. The use of these tungsten inserts is especially effective in reducing anode erosion when an active diatomic gas, such as hydrogen or nitrogen is used as the arc gas. This torch modification using preferential electrode inserts is disclosed in U.S. 2,951,143.

A feed stock inlet means 25 is positioned substantially adjacent to nozzle anode 18 and is separated therefrom by electrical insulator 26. Feed stock inlet means 25 has an inlet conduit 27 and inlet passage 32 through which desired hydrocarbon feed stock passes for contact with the arc gas effluent from nozzle passage 14.

Reaction zone 29 wherein substantially complete mixing takes place between the injected feed stock and the arc gas effluent can be contained within any suitable surrounding means that can stand up to the operating temperatures. A water-cooled copper tube could be used, but the heat loss through the cooled walls is highly undesirable. It is preferred that a refractory liner 30 be used surrounding the reaction zone 29. Such liner can be fabricated, for example, from carbon, zirconia or tungsten. It is further desired that the liner 30 be surrounded by an additional insulating layer 31 conveniently of thermatomic carbon. This reactor combination reduces heat loss from the reaction zone and maintains a high thermal efficiency for the process. In the apparatus shown in FIG. 1, the reaction zone is contained in a longitudinal member 46 having a centrally located passage forming reaction zone 29 therethrough, a refractory liner 30 forming the walls of said passage and an insulating layer 31 between said liner 30 and the outside wall 47 of said longitudinal member 46.

A second inlet means 35 similar to 25 is preferably positioned adjacent first reaction zone 29 and is axially aligned therewith. A quench zone member 36 is positioned downstream with respect to the second inlet means 35 and comprises a quenching surface 37 which is cooled by passing cooling fluid such as water from inlet 41 through the annular space 39 between quench surface 37 and outer wall 40 then out through outlet 38.

Cathode 16 and anode 18 are connected to a suitable source of electric power 43 by leads 44 and 45 for energizing a high-pressure arc across such electrodes. Typical arc circuits are shown in U.S. Patent 2,858,411, issued October 28, 1958.

An arc gas such as hydrogen, argon, nitrogen or other suitable gas or gas mixture, is introduced through inlet means (not shown) into the annular space between bore 12 and cathode 16. The gas flows around cathode 16 and into nozzle passage 14. The arc between the electrodes is forced into the nozzle 14 by the flow of such gas, and the arc and gas are thereby stabilized and collimated by the walls of the nozzle and laterally constrained to conform to the dimensions of the nozzle. The arc gas is heated by the arc in the nozzle 14, is collimated to conform to the cross-sectional shape of the nozzle; and is discharged as a hot, high-velocity gas stream.

The fluid hydrocarbon stock, preferably methane, to be treated enters feed inlet means 25 through hydrocarbon inlet carbon 27 and is injected through the openings 28 into the hot, high-velocity gas stream discharged from nozzle 14.

Then the combined gas stream containing hot arc gas effluent and reactant material passes into a reaction chamber 29 wherein complete mixing occurs. Hydrogen quench gas is then added through a second annular member 35 through inlet conduit 34 and is injected through openings 33 into the hot reaction products.

The hot reaction gases then pass to quench zone member 36 wherein they are cooled to a temperature at which there is substantially no decomposition of acetylene. Various quench means can be used, such as heat exchange with a liquid spray or with a gas stream. In order to prevent diluting the reaction product gases with quench material, it is preferable that a cold surface be used to quench the reaction gases. The product collected is then ready for further processing.

The following examples describe the present invention in actual practice.

Example I

The apparatus used was substantially the same as shown in FIG. 1 with the second inlet means located about ½ inch downstream of the first feed inlet means. A nitrogen gas stream of 132 gram moles/hr. (49.3 liters/min.) containing 14.13 kw. of thermal energy contacted a methane stream of 89 gram moles/hr. (33.2 liters/min.) to provide an energy input of 136.6 kilocalories/gram moles of carbon. The hot reaction gases then contacted the hydrogen stream of 56 gram moles/hr. (20.9 liters/min.) followed by complete quenching through contact with a cold heat exchange surface. The hydrogen quench flow was 63 vol. percent of the methane flow. The quenched product gases contained 7.8 vol. percent acetylene and 4.2 vol. percent hydrogen cyanide. Calculations indicated that 63.9% of the reacted methane formed acetylene. This is a substantial improvement over the acetylene conversion of only 43% obtained at comparable energy input without hydrogen partial quench.

Example II

The apparatus used was substantially the same as that described in Example I except that the second inlet means was positioned about 2 inches downstream of the first inlet means and additional inlet means for hydrogen quench gas was positioned about 1 inch downstream of the second feed inlet. Nitrogen at 99.3 gram moles/hr. (37.1 liters/min.) containing 13.14 kw. of thermal energy contacted first methane stream of 56.2 gram moles/hr. (21 liters/min.) and a second ethane stream of 58.2 gram moles/hr. (21.7 liters/min.) to provide an overall energy input to the feed stock of 65.5 kilocalories/gram moles of carbon. The hot reaction gases were then contacted with a hydrogen stream of 59.4 gram moles/hr. (22.2 liters/min.) followed by a complete quenching through contact with a cold heat exchange surface. The hydrogen quench flow was 52 vol. percent of the methane plus ethane flow. The quenched product gases contained 9.4 vol. percent acetylene and 3.6 vol. percent hydrogen cyanide. Calculations indicated that about 89% of the feed stock reacted and that 60.9% of the reacted feed stock was converted to acetylene and hydrogen cyanide.

The following examples describe a process for producing acetylene only where hydrogen gas is used as a partial quench.

Example III

Hydrogen gas at 87.2 gram moles/hr. (32.6 liters/min. N.T.P.) passed through an arc device where it was heated by 18 kw. of total electrical power. This hot hydrogen stream then contacted a stream of 136.5 gram moles/hr. methane (51.0 liters/min. N.T.P.) The reaction gases were then rapidly contacted with and partially quenched by 89.8 gram moles/hr. hydrogen (33.5 liters/min. N.T.P.) followed by complete quenching with water. The hydrogen quench flow was 66 vol. percent of the methane flow. Calculations based on analysis of product gas indicated that 90.3% of the reacted methane was converted to acetylene. A similar run which did not use hydrogen partial quench had a conversion of only about 75% of the reacted methane to acetylene.

The above run was accomplished with laboratory scale equipment. As the process conditions are scaled-up to commercial size equipment, the use of hydrogen partial quench becomes even more important as shown by the following example.

Example IV

Hydrogen gas at 730 ft.^{3}/hr. passed through an arc

device where it was heated by 90 kw. of total electrical power. This hot hydrogen stream then contacted a stream of 1485 ft.^{3}/hr. methane. The reaction gases were then rapidly contacted and partially quenched by 630 ft.^{3}/hr. hydrogen followed by complete quenching through contact with a cold heat exchanger surface. The hydrogen quench flow was 42.4 vol. percent of the methane flow. Calculations based on analysis of the product gas indicated that 92.3% of the reacted methane was converted to acetylene. A similar run which did not use hydrogen partial quench had a conversion of only about 32.1% of the reacted methane to acetylene.

All the above examples employed direct current straight polarity power. It should be understood that while this type of electrical power is preferred, direct current, reverse polarity and alternating current are also useful.

It is to be understood that modifications may be made to the specific embodiments of the invention disclosed herein without departing from the spirit and scope thereof and that such disclosure merely describes the preferred forms of the invention without limiting the inventive concept herein disclosed. For example, while the above disclosure has been limited primarily to the preferred use of collimated arc apparatus for providing the high thermal content gas effluent for chemical reaction promotion, other arc devices can be employed as long as the thermal content requirements of the hot gas effluent are met.

The above description has also been directed primarily at production of acetylene wherein an electric arc is the heat source. It should be understood that the hydrogen partial quench process step disclosed herein is also useful with other hydrocarbon pyrolysis processes, such as regenerative cracking processes or high velocity burner reactions.

What is claimed is:

1. In a process for the production of acetylene by the pyrolysis of a hydrocarbon reactant material the improvement which comprises partially quenching the hot pyrolysis reaction products by contact with hydrogen gas prior to further complete quenching.

2. In a process for the production of acetylene by the pyrolysis of methane the improvement which comprises partially quenching the hot acetylene containing reaction product by contact with hydrogen gas prior to further complete quenching.

3. A process for the production of acetylene by the pyrolysis of fluid hydrocarbons which comprises energizing a high pressure arc of predetermined arc intensity, flowing an arc gas at a controllable rate through said high pressure arc, discharging the resultant hot arc gas stream, intimately mixing the effluent stream of hot arc gas with a supply of fluid hydrocarbon stock to pyrolyze said stock and produce acetylene as a reaction product correlating the arc intensity and the arc gas flow rate with the supply of said fluid hydrocarbon stock; partially quenching the acetylene reaction product by contact with hydrogen, and then further cooling and quenching said acetylene reaction product.

4. A process for the production of acetylene by the pyrolysis of fluid hydrocarbons which comprises energizing a high pressure arc of predetermined arc intensity, flowing an arc gas at a controllable rate through said high pressure arc, collimating and stabilizing such arc and gas stream by surrounding such stream with a cool surface, discharging the resultant collimated hot arc gas stream, intimately mixing the effluent stream of hot arc gas with supply of fluid hydrocarbon stock to pyrolyze said stock and produce acetylene as a reaction product; correlating the arc intensity and the arc gas flow rate with the supply of said fluid hydrocarbon stock; partially quenching the acetylene reaction product by contact with hydrogen, and then further cooling and quenching said acetylene reaction product.

5. A process according to claim 1 wherein the hydrogen partial quench feed rate is at least about 10 volume percent of the hydrocarbon reactant feed.

6. A process according to claim 1 where the hydrogen partial quench feed rate is from about 20 to about 70 volume percent of the hydrocarbon reactant feed.

7. A process according to claim 1 wherein the hydrogen partial quench feed rate is from about 30 to about 40 volume percent of the hydrocarbon reactant feed.

8. In a process for the production of acetylene wherein a hydrocarbon reactant material is contacted with a high temperature heat source to convert the hydrocarbon to acetylene in a pyrolysis reaction and then the pyrolysis products are quenched prior to decomposition of the acetylene so formed, the improvement which comprises partially quenching the hot pyrolysis reaction products by contact with hydrogen gas prior to further complete quenching, such improvement thereby resulting in increased acetylene efficiency and reduced carbon formation.

9. In a process for the production of acetylene wherein a hydrocarbon reactant material is contacted with hot gases from a combustion process to convert the hydrocarbon to acetylene in a pyrolysis reaction and then the pyrolysis products are quenched prior to decomposition of the acetylene so formed, the improvement which comprises partially quenching the hot pyrolysis reaction products by contact with hydrogen gas prior to further complete quenching, such improvement thereby resulting in increased acetylene efficiency and reduced carbon formation.

10. In a process for the production of acetylene wherein a hydrocarbon reactant material is contacted with the hot surfaces of a regenerative cracking furnace to convert the hydrocarbon to acetylene in a pyrolysis reaction and then the pyrolysis products are quenched prior to decomposition of the acetylene so formed, the improvement which comprises partially quenching the hot pyrolysis reaction products by contact with hydrogen gas prior to further complete quenching, such improvement thereby resulting in increased acetylene efficiency and reduced carbon formation.

11. Process for the concurrent production of acetylene and hydrogen cyanide which comprises energizing a high-pressure arc of predetermined arc intensity, flowing at least one arc gas taken from the class consisting of nitrogen, hydrogen and argon at a controllable rate through said high-pressure arc, discharging the resultant hot arc gas stream at a pre-selected thermal energy content into a reaction zone, controllably feeding to said reaction zone reactant material taken from the class consisting of hydrocarbons and mixtures of such hydrocarbons with at least one material taken from the class consisting of nitrogen, hydrogen and dissociable nitrogen-containing compounds with the proviso that nitrogen be present in said reaction zone, correlating the arc intensity and the arc gas flow rate with the feed of said reactant material to provide a predetermined thermal energy to said reactant material ratio, intimately mixing said hot arc gas stream with said reactant material to produce acetylene and hydrogen cyanide as reaction products, partially quenching the reaction products by contacting them with hydrogen, and then cooling and quenching said reaction products.

References Cited in the file of this patent

UNITED STATES PATENTS

2,013,996	Baumann et al.	Sept. 10, 1935
2,860,094	Ishizuka	Nov. 11, 1958
2,916,534	Schallus et al.	Dec. 8, 1959
2,951,143	Anderson et al.	Aug. 30, 1960
3,051,639	Anderson	Aug. 28, 1962