PRODUCTION OF UNSATURATES BY THE NON-UNIFORM MIXING OF PARAFFIN HYDROCARBONS WITH HOT COMBUSTION GASES

OXYGEN CONTAINING GAS

FIG. 1

FIG. 2

INVENTOR.

GEORGE A. AKIN

BY

ATTORNEYS
This invention relates to a process for thermally cracking low boiling paraffinic hydrocarbons, such as propane, butane, isobutane, and the like, or mixtures thereof, to produce propylene, acetylene, and ethylene, particularly in a flame cracking process under conditions such as to produce these unsaturated hydrocarbons in commercially recoverable proportions.

The flame cracking process has been used heretofore for the production of acetylene and ethylene, but the proportions of propylene produced have been so small as to be considered only a contaminant, insufficient to justify its separation and recovery. In certain instances when commercially interesting proportions of propylene and ethylene were produced, the yield of acetylene was undesirably low. Propylene has become increasingly important as a base material in the petrochemical field as have both ethylene and acetylene. Therefore, a process which is capable of producing all three in commercial quantities is desirable.

The present invention provides a method whereby each of these compounds can be produced in economically recoverable amounts and without the production ofordinate amounts of carbon. Thus, according to the invention, for each pound of hydrocarbon feed, e.g., propane, there will be produced about 0.1 to 0.15 pound of propylene, 0.2 to 0.25 pound of ethylene, and 0.2 to 0.25 pound of acetylene. Less than 0.05 pound of carbon per pound of hydrocarbon feed is formed.

The invention will be understood by reference to the accompanying drawings of which:

FIGURE 1 is a diagrammatic representation in vertical cross section of a vessel suitable for carrying out the process of the invention;

FIGURE 2 is a horizontal cross section of the apparatus taken along lines 2-2 of FIGURE 1.

The reaction section of the vertically disposed vessel comprises a cylindrical shell enclosing bodies of isolating material 12 which surround a combustion chamber 3, a mixing zone 9, and a reaction completion chamber 14. A quench section 15 within cylindrical shell 2 is positioned below and communicates directly with the reaction section.

Combustion zone 3 is approximately cylindrical and has converging ends. A burner 4 is located in the entrance tunnel to the combustion chamber 3. Air, oxygen or other oxygen-containing gas is introduced into the burner 4 by line 7. Preferably, the amount of oxygen-containing gas is not more than the stoichiometric proportion for complete burning of the fuel. The fuel, which may be a hydrocarbon fuel such as methane, natural gas, manufactured gas, fuel oil or the like, is introduced by line 6. A diluent such as steam or flue gas may be introduced by line 8. Usually steam is employed. The charge to the burner may be preheated, say to 500° C., to 600° C. The hot products of combustion pass through the combustion chamber 3 and out of the port 5, formed by the converging lower end of the combustion chamber, into the mixing zone or venturi 9.

Around the periphery of the reaction section are hydrocarbon feed inlets 19 which discharge into an annular manifold 11. The manifold 11 communicates with radially disposed feed channels 12 which extend inwardly toward and communicate with venturi 9 near its upper end. Four inlets spaced equi-distant from each other are shown but fewer or more inlets can be employed. The manifold 11 insures even distribution of flow of hydrocarbons through channels 12, and into the hot combustion gases passing through the venturi. The drawing shows the preferred arrangement in which the axes of the feed channels are perpendicular to and coplanar with the longitudinal axis of the reaction zone. The direction of introduction of the feed into the combustion gas stream can be varied within the scope of the invention but the arrangement shown is advantageous for producing the results described herein.

Suitable cracking stocks include normally gaseous or liquid hydrocarbons, which preferably are paraffinic, but which can contain minor amounts of non-paraffinic hydrocarbons. Examples include ethane, propane, butane, pentane, natural gasoline, naphtha, etc. The feed stock should include at least one paraffin of three or more carbon atoms, i.e., propane or higher. A preferred feed is a fraction consisting predominantly of propane and butane. Liquid hydrocarbons are vaporized before charging.

The cracking feed, which may be preheated, e.g., to 500-600° C., is passed through channels 12, at a critical linear velocity which is considerably lower than the velocity of the combustion gas stream. When the venturi throat is about 7 to 11 inches in diameter, the linear velocity of the hydrocarbon feed must be in the range of about 50 to 250 feet per second. For a venturi of larger diameter the suitable range of feed gas velocity is higher. When the cracking reaction is carried out under these conditions using contact times of about 0.01 to about 0.015 seconds, the inlet velocity of the combustion gases is about 500 to 1500 feet per second or higher. At the reaction temperature, the proportion of propylene in the reaction product is about 10 to about 15% by weight of the reactant hydrocarbon charged, and from about 20% to about 25% each of acetylene and ethylene is produced.

The hot gaseous mixture passes through venturi 9 and into the generally cylindrical reaction completion chamber 14 wherein the velocity of the total mixture is reduced. The reactants then pass into quench chamber 15, defined by the cylindrical shell 2, wherein they are cooled, with liquid water which is sprayed into the reaction mixture by means of sprays 16. Only four sprays are shown, but as many as needed may be axially disposed around the shell 2. The water instantly reduces the temperature of the gaseous hydrocarbons and products emerging from quench chamber 15, to a temperature below that at which cracking takes place. By the time the gases have transversed the length of the chamber 15, the temperature is reduced to about the boiling point of water or below, at the pressure employed. Liquid water which may collect at 13 is withdrawn through valve line 19. Such liquid hydrocarbons as may be formed in the process and condensed during the quenching step will be withdrawn with the water and may be separated thereafter from by means not shown. The liquid hydrocarbons are predominantly aromatic but may also include cyclic and aliphatic hydrocarbons, unsaturated hydrocarbons such as olefins, dienes, etc.

The cooled gases and vapors, including considerable water vapor are removed from the quench chamber through line 17 and may be subjected to the usual separation treatment in suitable apparatus not shown, for the recovery of propylene, ethylene and acetylene as products. Combustion products such as carbon dioxide, carbon monoxide and water, as well as unreacted charge, if any, are removed. Hydrogen which is formed in the reaction may be recovered or may be discarded or burned. Some undescendable gases such as methane
and ethane may also be recovered or discarded as desired. I am aware that the flame process for cracking hydrocarbons is broadly old. However, in the prior art the process is carried out in a manner such that instantaneous and thorough mixing of the gaseous feed stock and the gaseous combustion products is obtained. This is done by using such feed rates for each of the gaseous streams as are designed to maintain the minimum or reaction chamber, which may include a venturi, in such a way as to obtain great turbulence at the point at which the two gas streams merge. In this way, a uniform or completely homogeneous mixture is instantaneously obtained. As a consequence, depending upon the reaction time and the reaction temperature, it is possible to control to some extent the composition of the cracked products. Thus, it is said that to produce high yields of acetylene, a reaction time of 0.0001 to 0.005 second at the cracking temperature when using the "homogeneous" method is advantageous. With a time of 0.02 to 0.3 second or longer, at a suitable cracking temperature the product is high in ethylene. From 0.1 to 1 second, or longer, at a suitable cracking temperature the product is rich in oxo process synthesis gas constituents. The cracking temperature is within the range of 2500° C. and 800° C. and preferably 2200° C. to 900° C. The pressure is generally low, say less than 100 p.s.i.g., and usually 0 to 5 p.s.i.g.

These temperature, time and pressure conditions are applicable in the present invention. The reason I am able to obtain propylene, ethylene and acetylene simultaneously in commercial yields, is because of the incomplete or non-uniform mixing of the reactant hydrocarbon feed with the hot combustion gases in the venturi and in the reaction completion zone. Because of the lower velocity of the feed gases entering through channels 12, in relation to the velocity of the gases passing through the venturi throat, only part of the feed penetrates well into the stream of hot combustion gases and is thoroughly mixed therein. This portion is subjected to high temperature and short time conversion and is converted to acetylene and ethylene in proportions similar to those previously obtained under flame cracking conditions such as have just been described for the prior art. Only a negligible amount of propylene is formed in this portion of the feed undergoing cracking. Another part of the feed, however, is incompletely mixed with the hot gases and as a consequence does not reach a temperature high enough to react at the venturi throat, only part of the feed penetrates well into the stream of hot combustion gases and is thoroughly mixed therein. This undergoes conversion to produce high yields of propylene and ethylene with lesser yields of acetylene. When rapidly quenched after no more than 0.4 second at the reaction conditions, conversion is instantaneously stopped so that the final reaction mixture contains propylene in the amount of about 10 to 15%, ethylene in the amount of about 20 to 25%, and acetylene in the amount of about 20 to 25%, based upon the weight of the hydrocarbon charged, with less than 0.05 pound of carbon per pound of reactant hydrocarbon being formed.

Stated in another way, it appears that a portion of the charge stock which is not thoroughly mixed with the combustion gases tends to flow along the walls of the venturi and of the reaction chamber. The temperature of this portion is lower than that of the more thoroughly mixed portion which passes through the central part of the venturi and the reaction chamber. As a consequence of the longer time period and lower temperature, conversion to propylene is favored in that part of the feed. The portion of the reactant hydrocarbon which mixes rapidly and thoroughly with the hot combustion gases, forms ethylene and acetylene, but is swept out of the reaction chamber sufficiently rapidly as to prevent the formation of excessive carbon due to decomposition of acetylene into its elements.

When the acetylene is formed large amounts of heat are absorbed from the combustion gases since the endothermic heat of reaction is high. For example this heat of reaction for conversion of propane to acetylene, methane and hydrogen is about 110,000 B.t.u./lb. at 1400° K. As a result, the combustion gases are cooled to a temperature at which, when they are finally mixed with the previously unmixed portion of the hydrocarbon feed, the temperature is raised to temperatures at which only mild cracking occurs. The mild cracking reactions occurring at the lower temperatures also appear to occur at slower rates than the high-temperature severe cracking which leads to acetylene formation. Therefore, longer contact times are required for producing propylene than for producing gases rich in acetylene. In my process the production of propylene is favored by passing a portion of the hydrocarbon feed through the reaction zone at relatively lower temperature and lower velocity than the rest of the feed.

The mild cracking reactions also absorb considerable amounts of heat. Thus, propane forms propylene and hydrogen with absorption of about 55,000 B.t.u./lb. mol at 1200° K. This absorption of heat lowers the average temperature still more. This tends further to reduce the conversion of propylene to acetylene. Also the decomposition of acetylene is reduced. However, the quench step is necessary since the rate of acetylene decomposition is still quite rapid even at temperatures as low as 700° C. As stated, the total residence time should not be over 0.4 second.

Since incomplete or non-uniform mixing is important to the process of this invention the diameter of the mixing zone is generally six inches or greater. In zones of smaller diameter mixing seems to be rapid and substantially complete with the result that only very small or "nonsence" proportions of propylene are formed.

It has heretofore been thought that complete and substantially desirable products and all of which are present in quantities such that they can be commercially recovered. In the prior art processes the reaction products were deficient either in propylene or acetylene, since conditions were unfavorable to the production of both simultaneously in economically recoverable yields. The small proportion of propylene merely represented a waste by-product, and hence, a waste of charge stock.

I have indicated that the linear velocity of the hot combustion gases is in the range of 500 to 1500 feet per second or higher and the velocity of the hydrocarbon cracking feed is in the range of 50 to 250 feet per second. These are suitable ranges of velocities for the gas streams when using a reaction zone having a minimum diameter (venturi throat) of 7 to 11 inches and illustrate the relationship of the velocities of the relatively low-velocity hydro-
carbon feed stream and high-velocity combustion gas stream. Thus the combustion gas flows at a linear velocity of about six times as rapid as that of the hydrocarbon feed. In other words, the hydrocarbon feed is introduced into the high-velocity stream of hot combustion gases at a velocity of about one-sixth the velocity of the combustion gases and this substantial difference in velocities gives rise to the result I have described, namely, the non-uniform mixing of the hydrocarbon-feed and the establishment of somewhat different cracking conditions in sub-zones within the reaction zone.

The following examples are presented to illustrate the invention, but should not be construed as limiting it to the exact conditions given:

**Example I**

In a flame cracking furnace similar to that shown in FIGURE 1, in which the diameter of the throat of the venturi was 8.5 inches and the velocity of the cracking stock in channel 12 adjacent to the interior of the furnace was 93.5 feet per second, 183 standard cubic feet per minute (hereinafter abbreviated as "s.c.f.m.") of natural gas was burned with 1650 s.c.f.m. of air diluted with 176 s.c.f.m. of steam to produce the hot combustion gases to crack 250 s.c.f.m. of a propane-butane mixture containing about 10 mol percent propane, about 88 mol percent butane and about 2 mol percent other hydrocarbons. All streams were preheated to about 550° C. The contact time was 0.025 second, based on the final temperature of the gases prior to quenching. The temperature of the combustion gases was about 1975° C. The average temperature of the gases leaving the reaction zone was about 875° C. The pressure was about 2 p.s.i.g. The gases were quenched to about 120° C. The gaseous mixture from the reaction zone of the furnace was rapidly quenched to a temperature below the reaction temperature by water sprays. In this example 10 percent by weight of the cracking stock was cracked to propylene, 22 percent by weight to acetylene, and 23.5 percent by weight to ethylene.

**Example II**

In a flame cracking furnace in which the diameter of the throat of the venturi was 9.5 inches and the velocity of the cracking stock in its channels adjacent to the interior of the furnace was 130 feet per second, 230 s.c.f.m. of natural gas was burned with 2600 s.c.f.m. of air diluted with 220 s.c.f.m. of steam to produce the hot combustion gases to crack 435 s.c.f.m. of a propane-butane mixture containing about 10 mol percent propane, about 88 mol percent butane and about 2 mol percent other hydrocarbons. All streams fed to the furnace were preheated to about 575° C. The contact time was 0.047 second, based on the final temperature of the gases prior to quenching. In this case the combustion gas temperature was about 2000° C., final reaction temperature about 860° C. and the temperature of the gases leaving the quenching zone was about 130° C. The gaseous mixture from the reaction zone of the furnace was rapidly quenched to a temperature below the reaction temperature by water sprays. In this example 11.2 percent by weight of the reactant hydrocarbon was cracked to propylene, 21.6 percent by weight to acetylene, and 22.7 percent by weight to ethylene.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that certain modifications can be effected without departing from the scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A flame cracking process for the simultaneous production of substantial yields of acetylene, ethylene and propylene by the non-uniform mixing, in an elongated cracking zone, of a gaseous hydrocarbon feed stream containing a paraffin of at least 3 carbon atoms per molecule with hot combustion gases formed by burning a hydrocarbon fuel which comprises: (A) directing said hot combustion gases into said elongated cracking zone at a linear velocity of about 500 to about 1500 feet per second; (B) introducing said gaseous hydrocarbon feed stream, at a linear velocity of about 50 to about 250 feet per second, into said elongated cracking zone; (C) quenching the effluent from said elongated cracking zone, said effluent having a temperature of about 800° C. to about 1150° C., within 0.01 to 0.4 second after the initial contact of said hydrocarbon feed stream and said hot combustion gases; and (E) recovering a cracking product containing at least 0.1 pound of propylene and at least 0.2 pound each of acetylene and ethylene per pound of said gaseous hydrocarbon feed.

2. The process of claim 1 in which the gaseous hydrocarbon feed is introduced into the stream of hot combustion gases at a linear velocity of about one-sixth the linear velocity of said hot combustion gases at the point of introduction.

3. The process of claim 1 in which said gaseous hydrocarbon feed stream consists predominantly of propane and butane and is introduced into said hot combustion gases at a venturi at the inlet of said elongated cracking zone, said venturi having a constriction diameter of at least about 6 inches.

4. The process of claim 1 in which said gaseous hydrocarbon feed stream is natural gas and is introduced into said hot combustion gases at a plurality of points spaced radially about a venturi at the inlet of said elongated cracking zone, said venturi having a constriction diameter of about 7 to about 11 inches.

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ALPHONSO D. SULLIVAN, Primary Examiner.

JOSEPH R. LIBERMAN, Examiner.