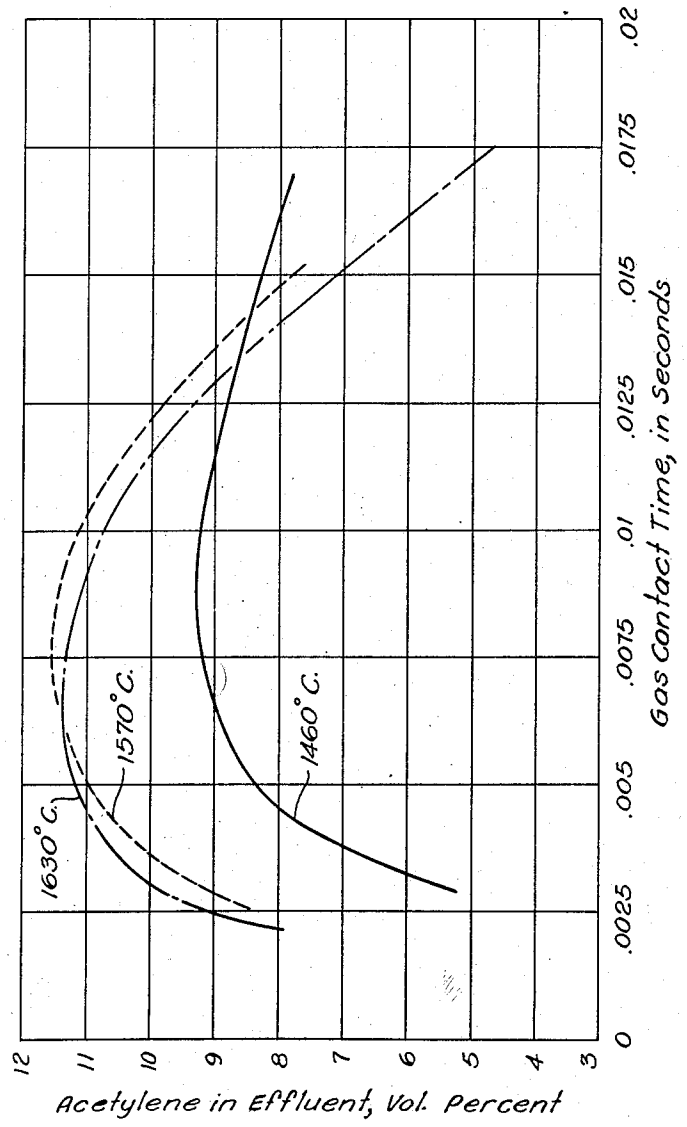
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PRODUCTION OF ACETYLENE BY PYROLYSIS

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PRODUCTION OF ACETYLENE BY PYROLYSIS

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This invention relates to production of acetylene, and more particularly, to an improved process for preparation of acetylene by pyrolysis of feed materials comprising essentially methane.

In the preparation of acetylene by pyrolysis of hydrocarbons, cyclically operated regenerative type furnaces are generally used. The feed materials are passed through a reaction zone in the furnace which contains refractory or other surfaces heated to a high temperature and are heated to the cracking temperature by contacting the heated surfaces. After the heated surfaces have been subjected to the feed stream for a period of time, the introduction of the feed stream is discontinued, the surfaces reheated to substantially their initial temperature, and the feed again admitted.

The various processes for pyrolysis of hydrocarbons which have been disclosed in the literature and United States patents are principally applicable to hydrocarbons other than methane which presents problems not common to the other hydrocarbons. Attempts have been made to use methane at substantially atmospheric pressure, but the amount of acetylene obtained was not significant. With feed gases comprising essentially methane, decomposition products containing less than one volume percent acetylene are obtained, while with other hydrocarbons, an acetylene content of around 10 percent may be realized. Wulff's United States Patents Numbers 1,880,308 and 1,880,309 point out the inapplicability of methane in the pyrolysis of hydrocarbons to acetylene. These patents teach that the pyrolysis of hydrocarbons under reduced pressure will increase the yields of acetylene. They also disclose that the reduction in pressure may be accomplished by the use of inert diluents, such as steam and mercury and state that methane may be considered as an inert diluent in hydrocarbon streams.

In the United States Department of Commerce Publication Board Report Number 80,331, a process for pyrolysis of methane is disclosed wherein methane is cracked to acetylene in a regenerative type furnace at an absolute pressure of 70 to 80 mm. of mercury. In the report it is shown that the low pressure shifts the equilibrium to favor acetylene formation and that these low pressures are required to obtain around 10 volume percent of acetylene in the effluent from the furnace. Since these extremely low pressures must be used, the process is economically unattractive. Very large equipment is required and large power expenditure is incurred in operating the vacuum and compression systems necessary for the process.

Methane is the cheapest and the most available of the hydrocarbon gases. The inability to utilize this gas in many reactions has resulted in the necessity of disposing of the gas as a fuel. Thus, a process where methane could be economically converted to acetylene and be more profitably utilized is very desirable.

It is, therefore, among the principal objects of this invention to provide an improved process for the preparation of acetylene by direct pyrolysis of methane in which

high conversion of methane to acetylene is obtained without the use of extremely low pressures.

In the pyrolysis of hydrocarbon gases comprising essentially methane where the hydrocarbon stream is passed through a reaction zone, the above and other objects can be accomplished by the steps of the invention, which comprise passing the hydrocarbon stream through a reaction zone heated to pyrolysis temperature and removing the soft carbon from the reaction zone after not more than 5 seconds of pyrolysis.

In these processes when the heated surface is subjected to hydrocarbon feed materials, two types of carbon are deposited upon the surface. One type, herein referred to as "soft" carbon, forms rapidly. It has been discovered in the development that led to this invention that this soft carbon is detrimental to the production of acetylene. The soft carbon burns very readily with a visible flame when the hot surface containing small deposits of the soft carbon is contacted with air. If the deposits of this carbon are allowed to accumulate, it maintains its detrimental effects and burns at a much decreased rate requiring considerably longer time to remove it. The other form of carbon, herein referred to as "hard" carbon, burns very slowly when subjected to air at high temperatures. The short periods of burning which are required to remove the soft carbon, do not remove appreciable amounts of the hard carbon. Since this hard carbon does not materially affect the yields of acetylene, its removal is not essential.

The detrimental effect of the soft carbon is greater at higher surface temperatures. At temperatures around 1570° C., the acetylene content in the decomposition product drops very rapidly from around 11 volume percent to about 6 volume percent if the carbon is not removed. At lower temperatures the rate of acetylene formation decreases, but not as rapidly. The detrimental effect of the soft carbon thus is more pronounced when using feeds comprising essentially methane than other lower hydrocarbons since higher temperatures are required for such feeds.

The formation of the soft carbon is also much more pronounced for feed streams comprising essentially methane because of the higher temperatures required for the cracking. When the heated surface is contacted with the feed stream for periods longer than 5 seconds, sufficient amounts of the soft carbon are deposited to appreciably affect the yields of acetylene. Heretofore in pyrolysis of hydrocarbons, the heated surface was subjected to the feed streams for periods of around one minute and the conversion of methane to acetylene was not significant at other than extremely low pressure. As a result of the discoveries made during the work leading to the present invention, it is possible through hindsight knowledge to attribute the low yields obtained these previous investigators to the soft carbon formation. By subjecting the heated surface to hydrocarbon feeds for short periods of time, it is possible to obtain high conversion of methane to acetylene without the need of the extremely low pressure to shift the equilibrium. It is preferred to subject the heated surfaces to the feed stream at substantially atmospheric pressure for a period no greater than 2.3 seconds and in some instances for as short a period as 0.1 second before removing the soft carbon. By cracking methane at substantially atmospheric pressure, the costs of vacuum operation and high compression are eliminated. Even though the operation of the process of the invention at the extremely low pressures used in the prior art will give higher yields than those previously obtained, it is economically infeasible to operate at pressures below 0.5 atmosphere. At pressures above atmospheric, lower yields are realized and the

compression costs become excessive above 1.5 atmospheres.

The removal of the soft carbon may be accomplished by mechanical or other means, but since the carbon is readily combustible when small amounts are present, it is preferably removed by contacting the deposited hot surfaces with air. Also in many regenerative furnaces which are filled with refractory material and do not have smooth passages, such as tubes, the removal of the carbon by mechanical means would be difficult. The time required to burn the soft carbon is relatively short. Essentially all of the soft carbon can be removed by contacting the surface with air for the same length of time that the surface was subjected to the feed stream. Thus if the heated surface is subjected to the hydrocarbons for 2.3 seconds, the required burning time to remove the soft carbon would likewise be of the order of 2.3 seconds. The rate of flow of the air employed may be greater than the hydrocarbon feed rate used. Generally the air is fed at a rate from 3 to 8 times that of the hydrocarbon feed stream.

In converting hydrocarbons to acetylene by pyrolysis, it is necessary to heat the hydrocarbons to temperatures above 1100° C. Sufficient heat must be supplied not only to increase the sensible heat of the hydrocarbons, but also to supply the aditional heat required for the heat of reaction resulting in the formation of acetylene. For the conversion of methane to acetylene, this heat requirement is considerably greater than for the formation of acetylene from other lower hydrocarbons. When a feed stream comprising a high proportion of methane contacts the heated surface with sufficient turbulence to heat the stream to the required temperature and acetylene is formed in the decomposition, considerably more heat is utilized. Thus, the heated surface is more rapidly cooled. Under ordinary conditions, a heat transfer rate of about 40,000 B.t.u. per square foot per hour may be obtained. At this rate if the heated surface is initially at 1600° C., it would cool to around 1550° C. in about 2.5 seconds. Thus, by subjecting the heated surface to hydrocarbon feed for a short time not only is the effect of soft carbon miminzed, but the pyrolysis is carried at a more uniform high temperature which improves the yields.

In the pyrolysis of hydrocarbons, the rate of decomposition of the hydrocarbon increases with the cracking temperature to which the hydrocarbon is heated. Thus, the extent of the decomposition obtained can be regulated by controlling the cracking time and the decomposition temperature. In conversion of hydrocarbons to acetylene, the acetylene formed will likewise decompose if subjected to the cracking temperature for short periods of time. Thus, the hydrocarbons must be heated to a temperature above 1100° C. and maintained at this high temperature for only a fraction of a second.

The actual cracking time is difficult to determine accurately. When the feed streams are introduced into the heated zones of the furnaces, they are generally at room temperature so that part of the contacting time is utilized in preheating the gases to the cracking temperature. Since the amount of time involved in the preheating and cracking is only a fraction of a second, it is relatively impossible to accurately determine the actual cracking time apart from perheating time. To express the cracking time on a uniform basis, a contact time or the length of time the hydrocarbons are subjected to the heated zone of the furnace is often used. The determination of the contact time must also be based upon fixed conditions. In the heated zones of the furnace there is an increase in volume of the gases due to the thermal expansion and decomposition. The contact time, as used herein, is based upon the volume of the feed streams assumed to be at 1200° C. and 1 atmosphere pressure. The increase in volume due to the decomposition is not taken into account. Thus, the contact time is expressed as the volume of the heated zone divided by the flow rate of the feed, assuming the feed is at 1200° C. and 1 atmosphere pressure.

Based upon the definition of "contact time" described above, the contact time for feed streams comprising essentially methane may be in the range of 0.002 to 0.03 second and the temperature of the heated surfaces should be initially in the range of 1350° to 1700° C. It is preferred to use a contact time in the range of 0.004 to 0.015 second and to have the initial temperature of the heated zones from 1550° to 1600° C. As the temperature of the heated zone is lowered below the preferred range, a longer contact time may be used, but the percent of acetylene obtained in the effluent will decrease. The effect of temperature and contact time for a feed stream containing essentially 95 volume percent methane, 2.94 volume percent nitrogen, and 1.29 volume percent ethane are shown in the attached figure, wherein the abscissa represents the contact time, the ordinate the acetylene content of the effluent in volume percent, and the curves represent the volume percent of acetylene obtained in the effluent at different initial temperatures of the heated zone. The details and data upon which the attached figure is based are given in Example 1 below. It will be noted that the amount of acetylene obtained increased with an increase in contact time to a maximum point and then decreased as the contact time was extended. The decrease in acetylene at the longer contact time is probably due to the decomposition of the acetylene. At the higher temperatures, higher yields of acetylene were obtained and the range of the contact times in which high acetylene yields at the particular temperature would be realized was narrower than for the lower temperatures. An effluent containing at least 11 volume percent acetylene was obtained for a contact time in the range of 0.004 to 0.009 second at 1630° C., while for 1570° C. the range was from 0.005 to 0.011 second. A maximum acetylene concentration of about only 9.3 percent was obtained at 1460° C. at a contact time of 0.01 second. For this temperature, the contact time could be extended over a much longer period without greatly decreasing the amount of acetylene obtained.

While the formation of the soft carbon is not critical for feed gases other than those which comprise essentially methane, this invention may be practiced with other feed hydrocarbons, such as ethane, propane, or mixture thereof with and without methane. Since the soft carbon may be readily removed only when small amounts of the carbon are present and not when it is allowed to accumulate, the frequent removal of the soft carbon will also increase the efficiency of the pyrolysis of these feeds.

Although the discussion herein has been mainly limited to regenerative type furnaces, it is apparent to those skilled in the art that the principles of the invention may be embodied in other types of equipment. Tubes or other passages wherein the surfaces are externally heated and the soft carbon continuously removed from the heated surface mechanically, thus eliminating the cyclic operation, may be used. It is advantageous to use a regenerative type furnace and to remove the soft carbon by burning, since the soft carbon removal step and the reheating may be combined. In the operation of the regenerative furnace, the optimum cycle time will depend upon the time required to reheat the heated surface so that the optimum cycle time will vary with the particular situation.

The following examples further illustrate the invention.

Example 1

A reactor comprising a refractory tube 20 inches long with a 7/64 inch inside diameter and composed essentially of pure aluminum oxide, was heated by a resistance ribbon wrapped around the outside of the tube to provide a reaction zone in the reactor. Runs were made at substantially atmospheric pressure with the tube at three temperatures, 1460° C., 1570° C., and 1630° C. The

temperature of the tube was determined by an optical pyrometer. The tube was heated by the resistance ribbon to the required temperature and a feed gas containing 95.0 percent methane, 2.94 percent nitrogen, 1.29 percent ethane, and the balance water vapor and other inerts, all in volume percent, was passed through the tube. The feed was passed through for a length of time approximately 1.56 seconds. After the flow of feed was stopped, air was introduced into the tube at a rate of about 5 times the flow of the feed of gases for about 2 seconds. A flame appeared at the end of the tube as the soft carbon was burned. Following the removal of the soft carbon, the tube was reheated to substantially the initial temperature by use of the resistance ribbon and the feed again passed through. The time required to reheat the tube was usually from 5 to 10 seconds.

Different runs were made at the three temperatures in which the rate of the feed material was changed so that a different contact time was provided.

The contact time was determined by assuming the feed gases were at 1200° C. and may be represented by the following equation:

$$\text{Contact time} = \frac{\text{Volume of the heated zone in the tube}}{\text{Rate of the feed materials}}$$

The effluent from the tube was analyzed for acetylene, ethylene, methane, and hydrogen. The expansion of the gas due to the decomposition was determined by metering the effluent after it was cooled. The volume percent of acetylene obtained in the effluent is plotted in the attached figure. The results with other pertinent details are shown in the table below:

Length of Hot Zone, Inches	Temperature of Hot Zone, ° C.	Contact Time, Seconds	Effluent, Volume Percent				Percent Volumetric Expansion Due to Pyrolysis	Percent CH_4 Converted to C_2H_2
			C_2H_2	C_2H_4	CH_4	H_2		
15.8	1,460	.0171	7.68	.57	3.66	86.0	85.8	30.6
15.8	1,460	.0115	8.8	.53	4.8	83.1	89.5	36.7
15.8	1,460	.0101	9.12	.54	5.2	82.3	88.0	38.0
15.8	1,460	.00459	8.1	.82	15.46	72.4	42.4	29.6
15.8	1,460	.00375	6.26	.90	30.1	60.5	47.0	33.0
16.4	1,570	.014	4.52	.60	5.57	87.6	85.0	18.7
16.4	1,570	.0101	9.15	.49	1.99	84.2	84.1	35.1
16.4	1,570	.0053	9.31	.53	8.09	78.4	77.6	38.6
16.4	1,570	.00407	8.97	.67	14.7	72.7	65.2	39.2
16.4	1,570	.0152	6.25	.44	1.24	89.5	87.3	24.0
16.4	1,570	.0157	9.4	.48	1.07	85.0	89.5	36.4
16.4	1,570	.0096	11.2	.44	1.59	83.1	86.3	43.1
16.4	1,570	.0074	11.51	.44	2.74	82.0	85.5	45.1
16.4	1,570	.00518	10.8	.48	4.46	78.5	85.1	44.5
16.4	1,570	.00377	10.6	.78	12.0	74.0	70.5	45.4
16.4	1,570	.00287	9.18	1.15	18.35	68.6	63.2	42.8
18	1,630	.018	3.98	.49	4.68	86.7	93.5	17.0
18	1,630	.0115	10.1	.43	.83	85.0	90.7	39.2
18	1,630	.00927	10.7	.38	.96	84.5	85.5	40.3
18	1,630	.00691	11.3	.39	1.50	83.5	94.0	45.4
18	1,630	.0045	10.95	.68	5.41	80.5	88.7	45.9
18	1,630	.00334	10.25	.86	9.77	76.4	73.9	42.8
18	1,630	.00266	9.34	1.07	14.8	72.3	63.7	40.3
18	1,630	.00230	8.25	1.36	21.4	66.2	54.9	38.2

Example 2

To determine the effect of soft carbon on acetylene formation, a 20 inch aluminum oxide tube with a 3/32 inch internal diameter was heated to 1460° C. over 17.2 inches of its length by means of a resistance ribbon wrapped around the outside of the tube. A feed gas substantially of the same composition as used in Example 1 was passed through the tube at substantially atmospheric pressure at a rate such that the contact time determined as in Example 1 was about 0.02 second. The gas was passed through the tube for a period of around 0.9 second, the tube reheated to substantially its initial temperature, and fresh feed gas again passed through for about 0.9 second at the same rate. This procedure was repeated and fresh feed gas was passed through the tube seven times. No air was allowed to enter the tube during the reheating. A sample of the effluent was taken during each time the feed was passed through the tube and analyzed. The acetylene content in the effluent decreased as the carbon was allowed to accumulate. The results obtained are as follows:

Sample No.	Volume percent acetylene in effluent
1	6.06
2	6.35
3	5.82
4	5.10
5	4.76
6	4.37
7	3.78

A similar experiment was run with the tube at 1395° C. The same feed gas and contact time as above were used. The length of time that the gas was passed through the tube was about 1.1 seconds instead of 0.9 second. The effect of the soft carbon was not as pronounced as for 1460° C. After the feed gases had been passed through for 5 times, the soft carbon was burned out by use of air and the feed passed through the sixth time. The removal of the carbon restored the yield of acetylene. The results obtained are as follows:

Sample No.	Volume percent acetylene in effluent
1	5.03
2	5.21
3	5.11
4	4.76
5	4.45
After carbon removal	5.30

What is claimed is:

1. In the pyrolysis to acetylene of feed materials comprising essentially methane wherein pyrolysis is effected by passing said feed materials into contact with a surface heated to pyrolysis temperature and a soft carbon is formed thereon during the contact of said feed materials, the improvement which comprises passing said feed materials into contact with the heated surface such that the heated surface is subjected to the feed materials for a period of time not greater than 5 seconds and subsequently removing the soft carbon from the surface.

2. In the pyrolysis to acetylene of feed materials comprising essentially emthane wherein the pyrolysis is effected by passing said feed materials into contact with a surface heated to pyrolysis temperature and a soft carbon is deposited upon the heated surface during passage of said feed materials and wherein said feed materials are intermittently passed into contact with the heated surface for a given period of time and the heated surface

is reheated to pyrolysis temperature in intervals between the passage of said feed materials, the improvement which comprises passing the feed materials at a pressure in the range of 0.5 to 1.5 atmospheres into contact with the heated surface such that the heated surface is subjected to said feed materials for a period of time not greater than 5 seconds and removing the soft carbon from the heated surface in the intervals between passage of the feed materials.

3. A process according to claim 2 wherein the soft carbon is removed from the heated surface by passing air into contact with the heated surface.

4. A process according to claim 2 wherein the feed materials are passed into contact with the heated surface at substantially atmospheric pressure.

5. A process according to claim 4, wherein the heated surface is subjected to the feed materials for a length of time not greater than 2.3 seconds.

6. In the pyrolysis of feed materials comprising essentially methane to produce acetylene wherein the pyrolysis is effected by passing the feed materials into contact with a surface heated to pyrolysis temperature and a soft carbon is deposited upon the heated surface during the passage of said feed materials and wherein said feed materials are intermittently passed into contact with the heated surface for a given period of time and the heated surface is reheated to the pyrolysis temperature in the intervals between the passage of said feed materials, the improvement which comprises heating the heated surface to a temperature in the range of 1350° to 1700° C., passing the feed materials into contact with the heated surface at a pressure in the range of 0.5 to 1.5 atmospheres for a length of time not greater than 5 seconds in a manner such that individual particles of the feed will have an average contact time in the range of 0.002 to 0.03 second and will be heated to a temperature of at least 1100° C., and removing the soft carbon from the reaction zone in the intervals between the passage of the feed materials.

7. A process according to claim 6, wherein the soft carbon is removed from the reaction zone by passing air therethrough.

8. A process according to claim 6, wherein the feed materials are passed through the reaction zone substantially at atmospheric pressure.

9. A process according to claim 8, wherein the feed materials are passed through the reaction zone for a length of time of not greater than 2.3 seconds.

10. A process according to claim 9, wherein the reaction zone is heated to a temperature in the range of 1550° to 1600° C. and the average contact time for said feed materials is in the range of 0.004 to 0.015 seconds.

References Cited in the file of this patent

UNITED STATES PATENTS

1,843,965	Wulff	Feb. 9, 1932
2,751,424	Hasche	June 19, 1956
2,765,358	Pichler et al.	Oct. 2, 1956

FOREIGN PATENTS

382,690	Great Britain	Nov. 3, 1932