

Feb. 11, 1958

S. P. ROBINSON

2,823,243

PROCESS AND APPARATUS FOR PYROLYSIS OF HYDROCARBONS

Filed March 19, 1956

2 Sheets-Sheet 1

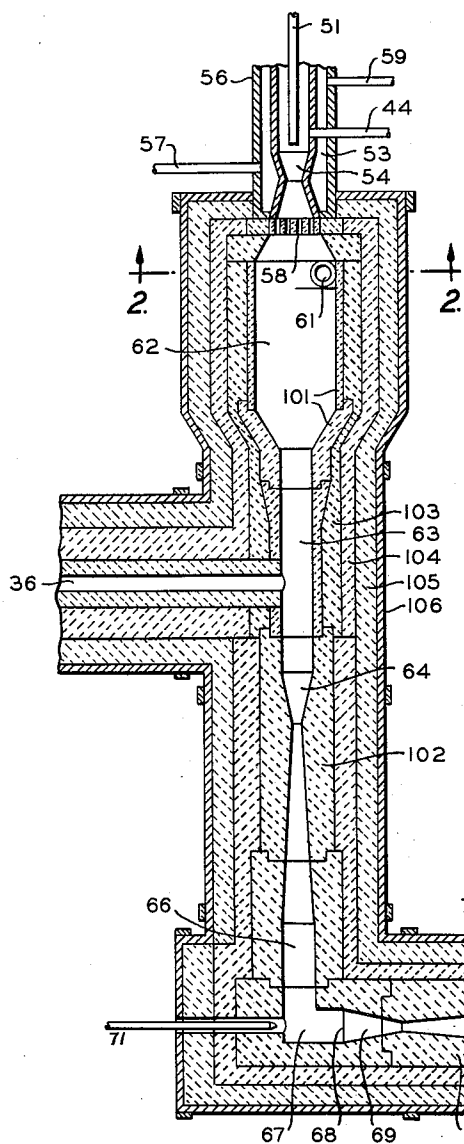


FIG. 1.

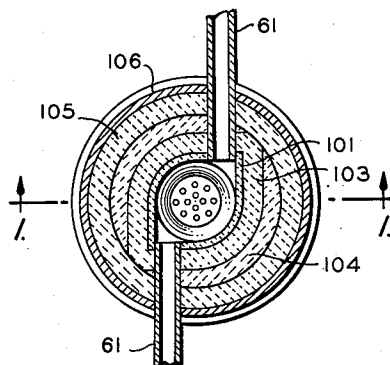


FIG. 2.

INVENTOR.
S. P. ROBINSON

BY

Hudson & Young
ATTORNEYS

Feb. 11, 1958

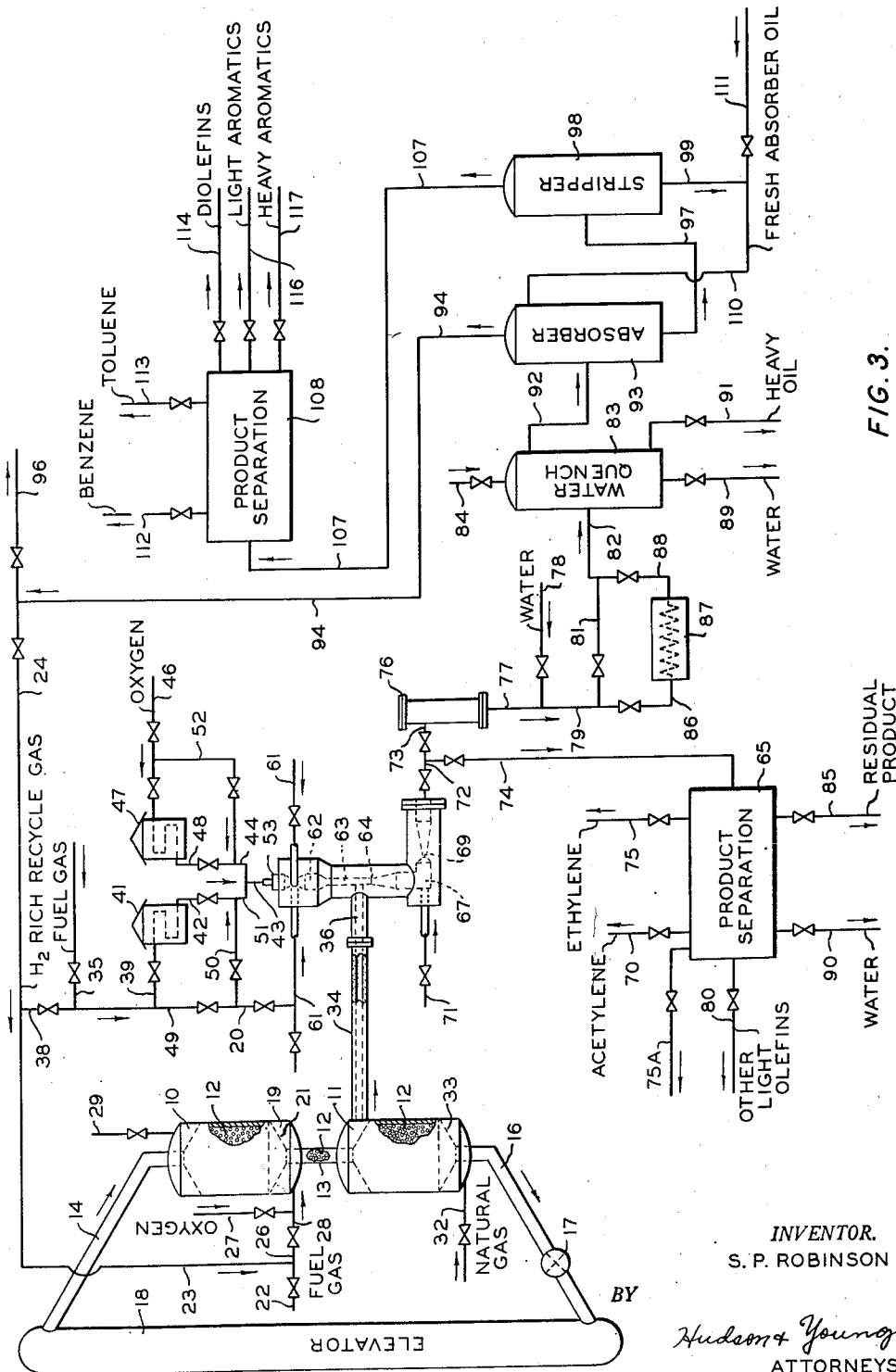
S. P. ROBINSON

2,823,243

PROCESS AND APPARATUS FOR PYROLYSIS OF HYDROCARBONS

Filed March 19, 1956

2 Sheets-Sheet 2



1

2,823,243

PROCESS AND APPARATUS FOR PYROLYSIS OF HYDROCARBONS**Sam P. Robinson, La Porte, Tex., assignor to Phillips Petroleum Company, a corporation of Delaware****Application March 19, 1956, Serial No. 572,309****11 Claims. (Cl. 260—679)**

This invention relates to the conversion of hydrocarbons at elevated temperatures. In one embodiment this invention relates to the production of acetylene. In one aspect this invention relates to the production of aromatic hydrocarbons. In another aspect this invention relates to a process, and apparatus, in which a gas may be quickly heated, maintained at a resulting elevated temperature for a predetermined time and then quickly quenched. In another aspect this invention relates to apparatus for use in the pyrolysis of a hydrocarbon gas to form acetylene-containing product and for the production of aromatic hydrocarbons and associated products from the acetylene product thus formed. This application is a continuation-in-part of my copending application Serial No. 85,344, filed April 4, 1949, now abandoned, which is a continuation-in-part of Serial No. 58,892, filed November 8, 1948, now U. S. Patent 2,608,594 (1952).

As is well known to workers in the art, hydrocarbons may be converted to acetylene by a high-temperature heat treatment, such as passage through an electric arc, partial combustion at high temperatures, or the like. Temperatures in excess of 2000° F. are necessary to obtain good yields of acetylene, although some acetylene may be formed at much lower temperatures. It is also well known that at an appropriate temperature, say in the range of about 1000 to 1200° F., acetylene polymerizes rapidly to benzene and other normally liquid aromatic hydrocarbons. Therefore, it is possible to convert a gaseous hydrocarbon to normally liquid aromatic hydrocarbons by subjecting a gaseous hydrocarbon to a primary heat treatment, at high temperature, in which acetylene is formed, and then subjecting the acetylene-containing gas product to a secondary heat treatment at a relatively low temperature, such as from 1000 to 1200° F., as already mentioned.

However, in the temperature range of 1000 to 1200° F., the contact time required for formation of economically feasible yields of light aromatic hydrocarbon product is so long as to promote various side reactions, such as polymerization of acetylene product to form high molecular weight cyclic hydrocarbons, and rehydrogenation of acetylene product to ethane. Under such conditions, high and selective yields of light aromatic hydrocarbons are not obtained. In the past, this has been the case even to a larger extent when operating at temperatures higher than 1000 to 1200° F. due to concomitantly increased carbon and polymer formation, resulting in even lower yields of desired product.

This invention is concerned with a process and apparatus for the pyrolysis of hydrocarbons to form pyrolysis product rich in acetylene, and for the production, when desired, of light aromatic hydrocarbons together with relatively minor amounts of diolefin hydrocarbons and heavier aromatics from the acetylene-containing pyrolysis product.

An object of this invention is to provide process and apparatus for conversion of hydrocarbons.

Another object of this invention is to provide apparatus for the pyrolysis of hydrocarbons to acetylene.

2

Another object is to provide apparatus for the pyrolysis of hydrocarbons to form pyrolysis product rich in acetylene and for the production of light aromatic hydrocarbons together with relatively minor amounts of diolefin hydrocarbons and heavier aromatics from the acetylene-containing pyrolysis product.

Another object is to provide a hydrocarbon pyrolysis process for the manufacture of acetylene.

Another object is to provide apparatus for quickly heating a hydrocarbon gas to a predetermined elevated temperature for a predetermined time and then quickly reducing said temperature to a predetermined lower temperature level.

Another object is to provide apparatus for quickly heating a hydrocarbon gas to a requisite elevated temperature for forming acetylene-containing product by pyrolysis, maintaining the pyrolysis temperature level for the requisite contact time and then quickly reducing the temperature of the resulting pyrolysis product mixture to a lower temperature level at which acetylene and olefins contained in the pyrolysis product are not undesirably further reacted.

It is still another object to provide a two-stage process for the manufacture of aromatic hydrocarbons wherein an acetylene-containing gas product is formed in a first stage, and is then converted in a second stage to light aromatic hydrocarbons.

Another object is to provide apparatus and process for utilization of temperatures higher than those employed heretofore in the manufacture of aromatic hydrocarbons from an acetylene-containing gas.

Other objects will be apparent, to one skilled in the art, from the accompanying discussion and disclosure.

In accordance with a broad embodiment of this invention, process and apparatus are provided for pyrolyzing a hydrocarbon gas to form acetylene-rich pyrolysis product, and for forming aromatic hydrocarbons together with relatively minor amounts of diolefins and other hydrocarbon materials from the initial pyrolysis product. In various applications of my invention it is sometimes desired to dispense with any further reaction of acetylene-containing product to form aromatic hydrocarbons, and instead, to recover valuable pyrolysis products, particularly acetylene and ethylene. Obviously, a part of the pyrolysis product can be utilized in a subsequent aromatic hydrocarbon forming step, and a part recovered prior to any further reaction, and utilized elsewhere.

In the practice of one embodiment of my invention, hydrocarbon pyrolysis of the type discussed above, and reaction of product of the pyrolysis to aromatic hydrocarbon-containing materials, is effected in a novel apparatus comprising an open-end elongated cylindrical combustion chamber connected at one end with an oxygen-hydrogen burner to axially receive hot combustion gas from oxygen-hydrogen burning therein, and connected at the other end with a co-axially disposed elongated cylindrical chamber of smaller diameter; a first Venturi tube connected co-axially at its upstream end with the smaller cylinder chamber; a second Venturi tube connected at its upstream end with the downstream portion of the first Venturi tube, preferably angularly, generally having its longitudinal axis at substantially a right angle to that of the first Venturi tube; an auxiliary reaction chamber connected to the downstream end of the second Venturi tube; inlet means in the combustion chamber positioned in close proximity to the burner end for admitting a tempering fluid into the combustion chamber in a direction tangent to its interior cylindrical side wall, hydrocarbon inlet means intermediate the combustion chamber and the first said Venturi tube for admitting hydrocarbon gas into the smaller diameter chamber; and quench fluid inlet means intermediate the exit throat of the first Venturi tube and the mixing throat of the second Venturi tube for admitting quench fluid into admixture with hot pyrolysis product,

When the Venturi tubes are disposed at substantially a right angle, the quench inlet is co-axially disposed with respect to the second Venturi tube. Hydrocarbon gases introduced into the apparatus are preferably preheated, and this is advantageously done in a pebble heater apparatus of the type generally known in the art.

Pebble heater apparatus referred to hereinabove usually comprises a series of substantially vertically-extending zones, often in vertical alignment with each other. Usually two such zones are employed and are connected by a relatively narrow connecting zone, or throat. The top or upper zone is commonly referred to as the pebble heating chamber and the lower zone as the gas reaction or gas heating chamber. A combustion zone, or chamber, is positioned adjacent or in close proximity to the sides of the lower portion of the heating chamber. Combustion gas from a combustion chamber is passed through the mass of pebbles in the pebble heating chamber. A contiguous mass of particulate contact material, often referred to as pebbles, fills the pebble heating zone, the interconnecting zone or throat, and the gas reaction or heating zone, and flows downwardly through these zones by gravity. Pebbles are discharged from the bottom of the gas reaction zone at a controlled rate, and returned, usually by elevating means, to the inlet in the upper portion of the pebble heating zone. A contiguous moving pebble mass thereby fills the pebble heating zone, gas heating zone, and the interconnecting zone, or throat, at all times.

The term "pebble" as used in this specification denotes any refractory material in fluent form, size, and strength, which will flow readily by gravity through the various chambers of a pebble heater apparatus. Pebbles are, preferably, substantially spherical and are about $\frac{1}{4}$ inch to 1 inch in diameter, the preferred range being about $\frac{1}{4}$ inch to $\frac{1}{2}$ inch.

Hydrocarbon gas to be converted to acetylene-rich pyrolysis product is preferably preheated in a gas reaction chamber of a pebble heater apparatus of the type above discussed, to a temperature usually below that at which substantial hydrocarbon cracking takes place, which is usually below from 2000 to 2200° F. at a level dependent upon the specific hydrocarbon being heated. In any case, it is usually desired that the amount of hydrocarbon cracking be not greater than 20 percent. Hydrogen or hydrogen-rich fuel gas is burned with oxygen, and hot gases formed from the combustion, pass axially through the central longitudinal portion of the combustion chamber. It is preferred generally to burn approximately stoichiometric proportions of hydrogen and oxygen, and under such conditions the flame temperature is from about 4500 to about 5300° F. and is preferably from about 5000 to about 5300° F. Such temperatures are higher than those at which known present day refractory fabricating materials are economically utilized. Accordingly, a tempering gas, preferably steam or hydrogen, is introduced into the combustion chamber through at least one tangential inlet in close proximity to its burner and, in an amount to absorb heat from the combustion gas and thereby to temper same to a temperature of about 4200° F. or below. Tempering gas, thus tangentially added follows an initial inward spiral path in the combustion chamber and then moves helically downstream, from the burner end, adjacent the chamber wall. The helically moving tempering gas forms a protective blanket adjacent the combustion chamber walls, by virtue of which, the walls are protected from the peak oxygen-hydrogen combustion temperatures, and absorbs heat from the axially flowing combustion gas so that the overall combustion gas temperature is reduced from about 5000° F. to 4200° F. or less, as discussed above. Furthermore, the helically moving gas imparts a swirling motion to the hot axially moving combustion gas. Heated hydrocarbon gas is withdrawn from the gas heating cham-

ber of the pebble heater apparatus, and injected, preferably in a radial direction, into admixture with the axially moving, swirling, hot combustion gas. Operating in this manner a highly efficient mixing of hydrocarbon gas and axially moving combustion gas takes place. The hot combustion gas thus contacted with the preheated but relatively cool hydrocarbon gas, transfers the necessary amount of heat to the hydrocarbon gas to elevate its temperature to a predetermined value suitable for its pyrolysis to form acetylene-rich hydrocarbon product. Mixing of hydrocarbon-combustion gas is nearly complete upon initial contact of these gases and the pyrolysis reaction is thus initiated. However, in order to effect further and complete mixture of these gases in a very short time the admixture is passed into a first Venturi tube of selected dimensions in which mixing of the hydrocarbon and combustion gas is completed. This final mixing takes place as the gaseous mixture passes through the constricted-most portion of the Venturi tube at which point the linear velocity is accelerated and a great amount of additional turbulence is set up, whereby mixing is complete at the predetermined temperature level. Pyrolysis of the hydrocarbon components to the desired extent in the completely uniformly mixed combustion gas-hydrocarbon mixture is obtained by the time the gases pass from the Venturi tube exit throat. The length and angle of the Venturi tube mixing throat, the diameter of the constricted-most portion and the length and angle of the exit throat of the Venturi tube are selected in order to provide not only complete mixing, but also to retain the pyrolysis reactants for the necessary contact time so that the exit flowing gas mixture from the Venturi tube is pyrolyzed to form acetylene in a maximum yield. In order to prevent over-reacting of the pyrolysis mixture at the desired temperature level it is necessary to quickly terminate the pyrolysis at the end of the requisite contact time. This is done by quickly quenching the pyrolysis reaction mixture as it flows from the exit throat of the Venturi tube. It is necessary that mixing of quenching fluid and hot gases be effected efficiently, quickly and completely. The exit flow of gases from the Venturi tube is advantageously turned sharply, e. g. at about a right angle into a second Venturi tube and at the same time admixed with quenching fluid introduced at a point in the turn of the gas flow in a direction coaxial with respect to the second Venturi tube, through the quench fluid inlet. Mixing of the quench fluid and pyrolysis product gas is effected almost completely as a result of a great amount of turbulence which is set up at the point of turn in the gas flow and by virtue of the injection into that zone of turbulence, of the quench fluid, usually steam or water. Quick and complete mixing of the quench fluid and pyrolysis product is effected by passing the resulting admixture through the second Venturi tube wherein the linear velocity of these gases is accelerated and an additional gas turbulence is set up and a uniformly quenched mixture is provided at the required lower temperature. Effluent quenched pyrolysis product, rich in acetylene, can then be recovered without further reacting same, or can be passed into an auxiliary reactor or "soaking-chamber" where it may be converted to aromatic hydrocarbons and other product. It is to be understood that diverting the direction of flow of hot pyrolysis product may be dispensed with, if desired. In such instances, however, mixing of quench fluid and hot product gas is effected less efficiently, and less close control over desired reacting conditions is obtained.

The accompanying diagrammatic drawing illustrates a preferred form of apparatus and a preferred process of my invention. It is to be understood that various modifications of the illustrated process and apparatus may be made and still remain within the scope of my invention. Figure 1 is a transverse sectional view of an apparatus embodying my invention and taken on line 1—1 of Figure 2. Figure 2 is a sectional view of the same apparatus

taken on the line 2—2 of Figure 1. Figure 3 is a diagrammatic flow sheet embodying the apparatus illustrated in Figures 1 and 2, together with other apparatus used in practicing a preferred embodiment of the process of this invention.

Referring now to Figure 1, burner assembly 53 comprises conduit inlets 44 and 51 arranged to respectively admit oxygen and hydrogen separately and axially for mixing in mixing throat 54, and burning at the tip downstream from flame arrestor 58. Water inlet 57 and water outlet 59 provide circulation of water through water jacket 56. Elongated cylindrical combustion chamber 62, open at both ends, is connected at one end with burner assembly 53 to axially receive hot combustion gas from hydrogen-oxygen burning adjacent flame arrestor 58, and is co-axially connected at its other end with elongated cylindrical chamber 63, open at both ends, and having a smaller diameter than that of chamber 62. Chamber 63 is co-axially connected at its other end, i. e., its downstream end, with the upstream portion, or mixing throat, of Venturi tube 64. L-shaped cylindrical connecting conduit 67 connects Venturi tube 64 with a second Venturi tube 69 and is connected co-axially at its upstream end 66 with the exit throat of Venturi tube 64, and is connected co-axially at its downstream end 68 with the mixing throat of Venturi tube 69. Upstream portion 66 of connecting conduit 67 may be of any desired length in order to provide for any desired extension of contact time of the pyrolysis reaction ordinarily substantially completed in Venturi tube 64. Upstream member 66 may be of minimum length to provide the necessary connecting length between Venturi tube 64 and the point of contact of pyrolysis product with quenching fluid. Similarly, the lower portion 68 of quenching chamber 67 may be of any desired length to insure the proper amount of time for mixing of quench fluid with pyrolysis product gas. I have found that by diverting the flow of gases about 90° the additional amount of turbulence set up is so great as to require a lower portion 68 of minimum length. Except for the fact that lower portion 68 of connecting conduit 67 provides a suitable means for connecting the two Venturi tubes as above described, the amount of quenching necessary would be effected in the mixing throat of Venturi tube 69 and completed in Venturi 69 to provide a uniformly quenched pyrolysis product mixture having a temperature at a predetermined level. Auxiliary reaction chamber 76 may be any suitable chamber for maintaining the exit flowing quenched pyrolysis product mixture from Venturi tube 69 in a desired temperature range for a predetermined contact time to convert unsaturated compounds therein, particularly ethylene and acetylene to aromatic hydrocarbon product. Chamber 76 is optionally utilized, and when so employed, is connected with the exit throat of Venturi tube 69 at its conduit inlet 73, preferably axially disposed with respect to Venturi tube 69. Gas outlet conduit 70 and liquid outlet conduit 75 are located at the lower portion of chamber 76. Hydrocarbon inlet 36 is disposed to admit hydrocarbon gas, to chamber 63, preferably radially. However, hydrocarbon gas may be introduced to chamber 63, from line 36, in any direction, if desired. Quench fluid inlet 71 is disposed to admit quenching fluid, usually water or steam, into connecting conduit 67 in a direction coaxial with respect to lower portion 68 of conduit 67 and Venturi tube 69. Inlets 61 are disposed to admit tempering gas, preferably hydrogen or steam, into combustion chamber 62 at points in close proximity to its burner end, in a direction tangent to its inner cylindrical wall and preferably with the predominating component of motion perpendicular to a plane containing the longitudinal axis of chamber 62. Inlets 61 are positioned in close proximity to the burner end of chamber 62 so as to introduce a protective and tempering gas layer into chamber 62 to cover

its entire interior wall surface. Inlets 61 are further illustrated in Figure 2.

The entire apparatus above described is necessarily fabricated of selected refractory materials. Obviously a wide selection can be made, by one skilled in the art, from the various types of refractory materials available on the open market. However, at the high temperatures already mentioned herein I generally prefer insulating refractories of the type illustrated in Figure 1 wherein liner 101 is a very highly abrasion-resistant, stabilized zirconia, liner 102 of Venturi tubes 64 and 69 is a 99 percent alumina having strong abrasive-resistant properties, above about 3100° F. Layer 103 is a 3000° F. insulating fire brick. Layer 104 is a 2600° F. insulating fire brick, layer 105 is a 2000° F. insulating fire brick and layer 106 is a magnesia insulating material. The insulating materials represented herein are typical of those from which suitable insulating materials may be selected. Obviously, other specific insulating materials may be selected by one skilled in the art in order to more closely meet the specific requirements of an individual set of conditions employed.

With respect to Figure 2, tangential inlets 61 of Figure 1 are shown in sectional view taken along line 2—2 of Figure 1. Gas introduced through conduits 61 enters chamber 62 tangentially, as already described. In some instances of operation, one tangential inlet is sufficient. However, it is within the scope of this invention to employ a plurality of such inlets, preferably disposed equidistant about the periphery of chamber 62. However, inlets 61 may be disposed at various selected points, as desired.

I have found that although mixing of hydrocarbon and combustion gases may be effected in the apparatus of this invention to a high degree without the use of Venturi tubes, the mixing is not complete in the short allotted time for forming acetylene product, but is quickly and completely effected within such a short time, with the aid of the Venturi tubes above discussed. The importance of quick and complete mixing of gases in any process for acetylene production by pyrolysis of hydrocarbons is well known. In order to prevent under-reacting and/or over-reacting during the pyrolysis, temperatures well above 2000° F. are required together with extremely short contact times as discussed hereafter. It is for such applications that the apparatus of this invention is especially suitable. The minimum linear velocity of gases in Venturi tubes 64 and 69 is about 200 feet per second and is greatly accelerated at the constricted-most portion. Such gas velocities cause the turbulence to provide perfect and final mixing in the allotted time, in each Venturi tube. The exit throat of Venturi tube 64 is designed for maximum pressure head recovery, and for this purpose may generally form an angle of about one-third that of the Venturi tube inlet throat, with the longitudinal axis of the exit throat about three times the length of the longitudinal axis of the inlet throat. The selected dimensions of Venturi tube 69 are of course dependent on the amount of quenching fluid introduced from quenching fluid inlet 71. However, in order to effect a quick and final mixing of quench fluid with pyrolysis product, the angle of the exit throat about twice the length of the longitudinal axis of the inlet throat and the longitudinal axis of the outlet throat about twice the length of the longitudinal axis of the inlet throat. It is to be understood that the specific dimensions to be utilized can be selected over a broad range by one skilled in the art in consideration of the maximum pressure head recovery sought, and required linear velocity of gases through the Venturi tubes.

With respect to Figure 3, I have illustrated by means of a diagrammatic flow sheet a preferred process of my invention embodying the apparatus illustrated in Figures 1 and 2, together with a pebble heater apparatus, and auxiliary apparatus for product separation, recovery, and the like. Referring then to Figure 3, pebble heating zone

10 and gas heating zone 11 are insulated chambers, each containing a contiguous mass of pebbles 12 and connected by a heat insulated conduit, forming pebble throat 13. Conduits 14 and 16 serve as pebble inlet and outlet for chambers 10 and 11 respectively. Star valve (or other type of pebble feeder) 17 regulates the rate of flow of pebble mass 12, through chamber 10, throat 13 and chamber 11, and feeds pebbles flowing from the bottom of chamber 11 into bucket elevator 18 for delivery into pebble inlet 14 and on into chamber 10. Combustion chamber 19 is positioned subjacent pebble heating chamber 10. Chambers 10 and 19 are separated by perforate support 21 through which combustion gas formed in chamber 19 ascends to pass in direct heat exchange relation with pebble mass 12 in chamber 10. Fuel gas, usually natural gas, from line 22, and/or hydrogen recycle gas from lines 23 and 24, described herebelow, is introduced through line 26 and mixed with oxygen or air from line 27 to form a combustion mixture in line 28 which is burned in combustion zone 19. Hot combustion gas formed in zone 19 ascends through perforate support 21 at a temperature in the range of 2200 to 3500° F. The temperature of the pebbles leaving zone 10, i. e., entering zone 11, is from 1800 to 2800° F. and may be controlled to higher or lower levels by regulating the proportion of oxygen introduced through line 27, the proportion of hydrogen-rich gas introduced from lines 23 and 24, and by regulation of the rate of pebble flow through chamber 10. Pebble temperatures may be lowered by introducing an inert gas diluent to the combustion chamber to effect reduction in flame temperature. Combustion gas in zone 10 is passed as effluent from zone 10 through line 29 to further utilization not shown. Methane feed stock, often natural gas is introduced through line 32 into the lower portion of gas heating chamber 11, entering at a point below perforate gas distribution plate 33, and is passed therethrough in direct heat exchange relation with pebbles previously heated in zone 10, and is heated to a temperature within the range of 1800 to 2400° F., a more preferable temperature range being from 1900 to 2200° F. The extent of any hydrocarbon cracking in zone 11 is limited by employing a sufficiently short contact time, generally less than one second. I find, usually, that I can tolerate as much as 20 percent cracking when preheating methane in this manner, and I prefer in any case to limit the extent of cracking by minimizing the heating time. Pressure conditions in the pebble heater apparatus are preferably atmospheric or nearly so. Pressures from 2 to 6 p. s. i. g. are preferred, although pressures as high as 25 p. s. i. g. may be employed when desired. Hydrogen recycle gas from lines 38 and 39 is preheated in preheater 41 to a temperature usually within the range of 500 to 1200° F., and passed through lines 42 to 51 into line 43 wherein it is mixed with commercial grade oxygen, i. e., from 90 to 95 percent or higher purity, or any suitable oxygen-rich combustion supporting gas from line 44, initially passed from line 46, preheated in preheater 47 and passed into line 44 through line 48. In some cases preheating of hydrogen recycle gas and/or oxygen is unnecessary, and in any such case hydrogen-recycle gas can be passed directly from line 38 to line 43 through lines 49, 50 and 51, and oxygen can be passed directly from line 46 to line 43 through lines 52 and 44. Hydrogen and oxygen in line 43 are present preferably in stoichiometric proportions for complete burning, although an excess of hydrogen may be advantageously employed. Hydrogen-oxygen gas from line 43 is passed into water jacketed burner assembly 53 and burned. Hydrogen-oxygen combustion gas formed by burning in burner 53 is passed axially into the central longitudinal portion of combustion chamber 62 at a temperature usually within the range of 5000 to 5300° F. If desired, a stoichiometric excess of hydrogen can be introduced into burner assembly 53. In view of the fact that insulating refractory materials in present day commercial use are uneconomically applied at such

elevated temperatures, the refractory walls of combustion chamber 62 must be protected from such extreme temperatures and the combustion gas temperature must be reduced, i. e., tempering to below about 4200° F. Both these steps are accomplished in cylindrical combustion zone 62. This is done by injecting steam, although hydrogen from lines 20 and 49 may be advantageously employed, through lines 61 tangentially into cylindrical chamber 62 through a single inlet or through a plurality of such inlets in the burner end of chamber 62. Steam tempering gas thus introduced forms a helically moving protective gas blanket as already described. In this manner steam thus tangentially introduced absorbs heat from the hot combustion gas moving through the central longitudinal portion of chamber 62 while simultaneously forming a relatively cool protective gas blanket adjacent the cylindrical inner wall of chamber 62 during the tempering. Furthermore, the helically moving steam in chamber 62 imparts a rapid swirling motion to the axially moving hot combustion gas.

Effluent heated hydrocarbon gas, at an elevated temperature but not as hot as combustion gas in zone 62, is withdrawn from heating chamber 11 through line 34 and passed through line 36, radially into cylindrical chamber 63 where it initially contacts, and is rapidly intermixed with, the swirling hotter combustion gases, and is very rapidly further heated. The rapid swirling motion of hot combustion gas, together with the radial introduction of hydrocarbon gas into admixture therewith, provide for a maximum amount of turbulence and concomitantly a high degree of hydrocarbon and combustion gas mixing. The resulting turbulent admixture in chamber 63 is then passed into Venturi tube 64 at an initial linear velocity not less than 200 feet per second, and preferably higher. The upper limit of linear gas velocity in Venturi tube 64 is determined by the abrasion resistant properties of refractory fabricating materials which limit is usually from 300 to 500 feet per second. Venturi tube 64 is of sufficient length to provide for a completion therein of hydrocarbon-combustion gas mixing and pyrolysis of hydrocarbons to acetylene-rich pyrolysis product. I have found that the time-temperature relationship necessary for the acetylene-forming reaction to be completed in Venturi tube 64 can be obtained when the length of the exit throat is about three times that of the inlet throat. Pyrolysis gas product passed from Venturi tube 64 is quenched in quenching zone 67 in direct heat exchange relation with steam introduced into zone 67 through inlet 71.

The temperature of the gas mixture passing into venturi 64 is regulated by the temperature of the preheated gas from line 36 and the temperature of the tempered combustion gas from chamber 62 and is in the limits of 2400 to 3500° F., although a more preferable temperature is from 2600 to 3000° F. The acetylene-forming pyrolysis reaction is initiated at the point of hydrocarbon-combustion gas contact. However, it is only after complete and efficient mixing of hydrocarbon with hot combustion gas that the acetylene-forming reaction is completed. The overall acetylene-forming reaction takes place at a temperature in the range above discussed, at a reaction time within the limits of 0.001 to 0.05 second, the larger proportion of which takes place in Venturi tube 64.

Gaseous pyrolysis product is passed from Venturi tube 64 into connecting conduit 67 wherein its direction of flow is turned by about 90° while at the same time steam is introduced as a quench. A high degree of turbulence is set up in zone 67 as the result of diverting the direction of flow of gases, and it is into this highly turbulent mixture that quench steam or other fluid is introduced. The steam is added in an axial direction with respect to Venturi tube 69, further discussed herebelow. The amount of quenching fluid introduced through line 71 is obviously dependent upon the amount of quenching needed, i. e., as to whether or not acetylene-containing

pyrolysis product is to be reacted further to form an aromatic-containing hydrocarbon product discussed more fully hereafter, or free acetylene is to be recovered for utilization elsewhere. In the latter case water may be advantageously used to produce faster cooling to a lower temperature. In any event, the resulting pyrolysis product admixture in zone 67 is passed into and through Venturi tube 69 wherein final and complete mixing of quenching fluid and pyrolysis product is effected. Effluent quenched gas from Venturi 69 is passed through lines 72 and 73 to auxiliary reaction chamber 76, or withdrawn through lines 72 and 74 and passed to separation means 65 for separation and recovery of selected product fractions. Separation zone 65 comprises various types of well-known product recovery equipment, not individually illustrated, especially suitable for recovering selected fractions from the material admitted from line 74, such as distillation, solvent extraction, absorption, settling storage, and the like. Selected product fractions separated in zone 65 include light gases (e. g. H_2), acetylene, ethylene, and other light olefins, or diolefins, together with residual carbonaceous by-product and water which are withdrawn respectively from zone 65 through lines 75A, 70, 75, 80, 85, and 90. In the latter case effluent gas from Venturi tube 69 is quenched to a temperature below that at which acetylene and/or ethylene in the pyrolysis product further reacts appreciably to form polymer or to form carbon and hydrogen, which temperature is preferably below about 500° F.

However, I often prefer to pass the quenched pyrolysis product from Venturi tube 69 to aromatics-forming chamber 76 for the conversion of unsaturated pyrolysis product, particularly the acetylene and ethylene components, to an aromatic hydrocarbon-containing product. When operating in this manner, the amount of quenching steam introduced through line 71 is regulated to cool the pyrolysis product to an aromatics-forming temperature within the range of 1800 to 2300° F.

In aromatics-forming chamber 76, pyrolysis product from Venturi tube 69 is maintained at its existing temperature (1800 to 2300° F.) for a duration of from 0.05 to 5.0 seconds to form predominantly light aromatic hydrocarbons, particularly benzene and toluene together with relatively small amounts of diolefin hydrocarbons and heavier aromatic hydrocarbons formed as by-product. I prefer usually to quench acetylene-containing pyrolysis product in zone 67 so that gases enter chamber 76 at a temperature in a preferred range of 1900 to 2200° F., and under such conditions a contact time within the limits of 0.2 to 3.0 seconds may be selected.

Affluent from zone 76 is passed through line 77 and quenched to a temperature in the range of about 400 to 800° F. by admixture in line 79 with water spray introduced through line 78. The resulting admixture is passed through lines 81 and 82 to water quench tower 83 wherein it is contacted countercurrently with water introduced through line 84 and cooled to a temperature usually within the range of 100 to 200° F. If desired, material in line 79 may first be passed through line 86, cooler 87, and line 88 to line 82, with or without water introduced through line 78. Water may be drained from zone 83 through line 89, and any heavy by-product oils removed through line 91. Product-containing gas is passed from zone 83 through line 92 to an absorber-stripper system, preferably of the conventional type employing a mineral seal oil absorbent. Material in line 92 is introduced to absorber 93 and passed therein countercurrently in relation to down-flowing fresh and/or stripped mineral seal oil introduced through line 110. Hydrogen-rich gas is passed from an upper portion of absorber 93 through line 94 for combustion in zone 19 and/or burner 53. Any excess recycle gas in line 94 may be withdrawn through line 96. Enriched absorber oil is passed through the lower portion of zone 93 through line 97 and introduced into stripper 98 maintained under distillation conditions

whereby the rich oil is heated and absorbed materials are liberated as vapors. Vaporized material is passed through line 107 from stripper 98 to product separation means 108 comprising coolers, separators, distillation equipment, storage tanks and the like not individually illustrated, which can be used to effect a separation of various selected product fractions. Lean absorber oil is passed from the lower portion of stripper 98 through lines 99 and 110 to absorber 93. Fresh absorber oil can be introduced to the absorber system through line 111. Selected product fractions separated in zone 108 include benzene withdrawn through line 112, toluene withdrawn through line 113, cyclopentadiene and other diolefins withdrawn through line 114, and a fraction containing light aromatic hydrocarbons such as styrene, methylstyrene, and xylenes, withdrawn through line 116. A relatively heavy fraction of aromatics comprising naphthalene, anthracene and other, heavier aromatics and/or tars is withdrawn through line 117.

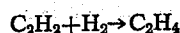
During the non-process periods or when starting up, natural gas is introduced into the water cooled burner through lines 35, 49 and 50 and burned with oxygen, and after pyrolysis is under way, the natural gas feed to the burner is replaced with the recycle hydrogen stream. Fresh hydrogen may be introduced into the burner system through line 30, when desired.

For convenience and clarity certain apparatus such as pumps, surge tanks, accumulators, valves, etc. have not been shown in the drawing. Obviously such modifications of the present invention may be practiced without departing from the scope of the invention.

As already described, a feature of my invention resides in the formation of aromatic hydrocarbons from acetylene at temperatures from 600 to 1000° F. above those ordinarily employed, and the advantages of this higher temperature operation have already been pointed out. I am able to utilize such high aromatic-forming temperatures by operating in the presence of hydrogen. Under such conditions, dehydrogenation of acetylene with consequent carbon formation, and hydrogenation of acetylene to ethane with consequent low yields of desired product is substantially prevented, and higher and more efficient conversions of acetylene are obtained. Some hydrogenation of acetylene to ethylene may occur, but if so, it is in no way disadvantageous. The temperature conditions are chosen such that partial hydrogenation to ethylene is possible and favorable, but at which total hydrogenation of acetylene to ethane or of any ethylene to ethane, is not promoted. The contact time is so chosen that dehydrogenation of acetylene, and polymerization of acetylene is kept at a minimum, and so chosen that unsaturates such as butadiene, cyclopentadiene, and C_6 dienes are formed together with high yields of light aromatic hydrocarbons particularly, benzene and toluene. Only minor amounts of heavier aromatic components, tars and the like are formed at these selected temperatures and contact times. Typical of preferred time-temperature relationships employed in the practice of the aromatics-forming step of my invention are indicated as follows:

Time, sec.:	Temp., ° F.
1.5 to 5.0	1800
1.0 to 3.0	1900
0.6 to 2.0	2000
0.4 to 1.2	2100
0.2 to 0.6	2200
0.05 to 0.2	2300

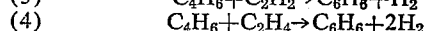
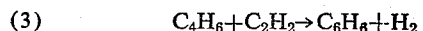
I am not certain as to the exact mechanism of the reaction taking place in the aromatics-forming step. However, it is possible that (1) acetylene is first partially hydrogenated to ethylene as indicated by the equation



(2) ethylene and acetylene then copolymerize to form butadiene as indicated by the equation



and (3), butadiene thus formed copolymerizes with ethylene or acetylene followed by dehydrogenation and cyclization to benzene, as indicated by the following equation



In any case, some hydrogenation of acetylene to ethylene undoubtedly takes place under the conditions of my process and possibly contributes to the high yields of benzene by virtue of its reaction with butadiene. Furthermore, the presence of any ethylene formed has a stabilizing effect upon the reactant gases and may contribute to maintaining the low carbon yields obtained.

The amount of hydrogen present in the aromatics-forming step is important in that it is advantageous that at least 40 percent of the gas in the aromatics-forming step consists of hydrogen. Usually the amount of hydrogen produced in the acetylene-forming step is more than that needed to supply the necessary hydrogen to the aromatics-forming step, and no hydrogen from any other source is required.

Any gaseous hydrocarbon stock may be employed in the practice of my invention for conversion to acetylene. The process has a distinct advantage, in that methane, or a methane-rich gas such as conventional dry natural gas, can be economically converted. The resulting acetylene-rich product is satisfactory in any case for use in the aromatic-forming step. Lower temperatures may be required for conversion of the heavier hydrocarbons to acetylene, but usually the conditions of the aromatic-forming step are substantially unchanged.

My invention is illustrated by the following example. The reactants, their proportions, and other specific ingredients are presented as being typical and should not be construed to limit the invention unduly.

Example

Natural gas of the following composition:

Component:	Volume percent
CH_4 -----	92
C_2H_6 -----	4
C_3H_8 -----	1
N_2 -----	3

is passed into the gas heating chamber of a pebble heater apparatus at a rate of 2040 standard cubic feet per hour and heated therein to 2000° F. for a contact time of 0.3 second at a pressure of 4 p. s. i. g. Under such conditions of preheating, about 20 percent cracking takes place. The composition of heated natural gas passed from the pebble heater chamber is approximately as follows:

Component:	Volume percent ¹
H_2 -----	7.1
CH_4 -----	84.8
C_2H_2 -----	1.9
$\text{C}_2\text{H}_4 + \text{C}_3\text{H}_4$ -----	3.3
N_2 -----	2.9
$\text{C} + \text{tar}$ ----- (by weight) --	2.9

¹ Carbon and tar-free bases.

Simultaneously, a hydrogen-rich recycle gas of about 85 percent hydrogen purity, is passed from a purification step discussed hereafter at a rate of 3420 standard cubic feet per hour, based on hydrogen, into a water jacketed burner in admixture with commercial grade oxygen introduced at the rate of 1710 standard cubic feet per hour, and the resulting admixture burned. The flame resulting from this burning is formed at a temperature of about 5000° F., and is directed axially into a cylindrical elongated combustion chamber, attached to the burner to axial-

ly receive combustion gas therefrom. Steam is tangentially introduced into the cylindrical elongated combustion chamber, in a direction perpendicular to the longitudinal axis of the combustion chamber, at a rate of 210 pounds per hour through two conduit inlets near the burner end of the combustion chamber, disposed about 180° apart. Steam thus added, absorbs heat from the hot combustion gas and tempers it to about 4000° F. The tangentially added steam follows an initial inward spiral path and then flows helically downstream through the combustion chamber adjacent the chamber inner wall, imparting a swirling motion to the axially flowing combustion gas as it travels through the combustion chamber. Effluent heated hydrocarbon gas from the gas heating chamber of the pebble heater apparatus is passed radially into the swirling tempered combustion gas mixture. A resulting natural gas-combustion gas admixture is formed at about 3000° F. and is passed into the mixing throat of a Venturi tube having a longitudinal axis eleven inches in length and a total angle of 21 degrees. The constricted-most portion of the Venturi tube has a diameter of two inches; the exit throat has a total angle of 7 degrees and has a longitudinal axis 33 inches in length. Hydrocarbon-combustion gas admixture is passed from the Venturi tube mixing throat through the constricted-most portion of the Venturi tube at an accelerated linear velocity, and thereby quickly and completely mixed. The 33 inch Venturi tube exit throat is of sufficient length to provide for the contact time required for pyrolysis of the hydrocarbon gas at 3000° F. to acetylene-rich product, which in this case, is 0.01 second. The approximate composition of the pyrolysis product, on a steam, carbon and tar-free basis, is as follows:

Component:	Volume percent
H_2 -----	66.8
CH_4 -----	8.7
C_2H_2 -----	17.6
$\text{C}_2\text{H}_4 + \text{C}_3\text{H}_4$ -----	3.0
N_2 -----	1.6
CO -----	2.2
O_2 -----	0.1

Acetylene-containing product is passed from the Venturi tube exit throat, and quickly quenched with steam to terminate the reaction and prevent further reaction to undesirable products, particularly tar, carbon, hydrogen, and polymer. This is done by diverting the direction of flow of the effluent product gas 90°, simultaneously injecting quench steam at the rate of 613 pounds per hour into the product gas at the 90° turn in a longitudinal direction downstream and passing the quenched product mixture into the mixing throat of a second Venturi tube, having a longitudinal axis of 9 inches and a total angle of 24 degrees. The diameter of the constricted-most portion of this Venturi tube is 4 inches; the exit throat has a longitudinal axis of 16 inches in length, and a total angle of 8 degrees. The quenched mixture in the Venturi tube mixing throat is passed on through the constricted-most portion of the Venturi tube at an accelerated linear velocity, and on through the exit throat. Quenched product gas is passed from the second Venturi tube at a temperature of 2100° F. into an auxiliary reaction chamber wherein the quench gas mixture is maintained at its existing temperature for a contact time for 0.8 second. Under such conditions, the acetylene-containing gas is converted to a crude aromatic hydrocarbon-containing product obtained in a yield of 1.0 gallon per MSCF of natural gas charged to the pebble heater, containing about 70 percent benzene, and 10 percent toluene, with the remaining product comprising cyclopentadiene and other diolefins in the C_4 to C_6 range together with other light aromatics such as xylenes, styrene and methyl styrene, and relatively minor amounts of heavier aromatics, predominantly naphthalene and anthracene.

The hydrogen-rich recycle stream referred to herein-

above is recovered from the product mixture in the auxiliary recovery equipment and is recycled to the burning step above described. This hydrogen-rich recycle gas has the following approximate composition.

Component:	Volume percent
H ₂ -----	84.2
CH ₄ -----	11.0
N ₂ -----	2.0
CO -----	2.7
O ₂ -----	0.1

Natural gas is burned in place of hydrogen at the rate of 855 C. F. H. during non-process periods, or when starting up.

As will be evident, to those skilled in the art, various modifications of this invention can be made, or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the claims.

I claim:

1. A process for the pyrolysis of a hydrocarbon to produce pyrolysis products including acetylene which process comprises burning hydrogen with oxygen to form a combustion gas having a temperature in the range 4500 to 5300° F., passing said combustion gas in a longitudinal direction of flow, maintaining a helically moving blanket of tempering gas annularly disposed about the said longitudinally flowing combustion gas in sufficient amount to cool said combustion gas to a temperature not higher than 4200° F., preheating a gaseous hydrocarbon to a temperature in the range 1800 to 2400° F., introducing thus preheated gaseous hydrocarbon into admixture with said combustion gas in a generally transverse direction thereto, whereby mixing of combustion gas and gaseous hydrocarbon is effected and said hydrocarbon is heated to a pyrolysis temperature in the range 2400 to 3500° F., increasing the linear velocity of the resulting mixture to a value in the range 200 to 500 feet per second, substantially decreasing said velocity and maintaining said mixture in a high state of turbulence for a time in the range 0.001 to 0.05 second, introducing a quenching fluid into said mixture to quench said mixture below pyrolysis temperature and simultaneously abruptly and sharply changing the direction of flow of said mixture, increasing the linear velocity of the quenched mixture while maintaining the quenched mixture in a high state of turbulence, and recovering pyrolysis products from the quenched mixture.

2. A process according to claim 1 wherein said combustion gas produced by said burning of hydrogen has a temperature in the range 5000 to 5300° F.

3. A process for the pyrolysis of hydrocarbons to produce ethylene and acetylene, comprising burning hydrogen with oxygen to form combustion gas at a temperature of from about 5000° F. to about 5300° F., maintaining combustion gas thus formed in a longitudinal direction of flow, maintaining a helically moving blanket of tempering gas annularly disposed about said longitudinally flowing combustion gas in an amount to absorb heat from said combustion gas and cool same to a temperature not higher than 4200° F., said helically moving tempering gas imparting a swirling motion to said combustion gas, preheating gaseous hydrocarbon to a temperature in the range of from 1800 to 2400° F., introducing the gaseous hydrocarbon thus preheated into admixture with swirling longitudinally moving combustion gas in a radial direction with respect to the longitudinal flow of said combustion gas whereby mixing of combustion gas and gaseous hydrocarbon is initiated and heat is transferred from said combustion gas to said hydrocarbon to heat same to a temperature in the range of 2400 to 3500° F., increasing the linear velocity of the resulting tempering gas-hydrocarbon-combustion gas admixture to a value in the range 200 to 500 feet per second, then decreasing said velocity and maintaining

said admixture in a high state of turbulence for a contact time within the range of from 0.001 to 0.05 second, whereby acetylene and ethylene-containing hydrocarbon pyrolysis product is formed, introducing quenching fluid in a predetermined amount into said pyrolysis product to quench same to a temperature below about 500° F. and abruptly changing the direction of flow of same through about a right angle, increasing the linear velocity of the resulting pyrolysis product-quenching fluid admixture and then maintaining same in a high state of turbulence whereby quenching of pyrolysis product is completed and a predetermined uniform temperature level is provided, passing quenched pyrolysis product to a product separation means and therein separating ethylene and acetylene, and recovering said ethylene and acetylene as products of the process.

4. A process for the pyrolysis of hydrocarbons to produce ethylene and acetylene, comprising burning hydrogen with oxygen of at least 90 percent oxygen purity to form combustion gas at a temperature of about 5000° F., maintaining combustion gas thus formed in a longitudinal direction of flow, maintaining a helically moving blanket of tempering gas annularly disposed about said longitudinally flowing combustion gas in an amount to absorb heat from said combustion gas and cool same to a temperature not higher than 4200° F., said helically moving tempering gas imparting a swirling motion to said combustion gas, preheating gaseous hydrocarbon to a temperature in the range of from 1800 to 2400° F., introducing the gaseous hydrocarbon thus preheated into admixture with swirling longitudinally moving combustion gas in a radial direction with respect to the longitudinal flow of said combustion gas whereby mixing of combustion gas and gaseous hydrocarbon is initiated and heat is transferred from said combustion gas to said hydrocarbon to heat same to a temperature in the range of 2400 to 3500° F., increasing the linear velocity of the resulting tempering gas-hydrocarbon-combustion gas admixture to a value in the range 200 to 500 feet per second, then decreasing said velocity and maintaining said admixture in a high state of turbulence for a contact time within the range of from 0.001 to 0.05 second, whereby acetylene and ethylene-containing hydrocarbon pyrolysis product is formed, introducing quenching fluid in a predetermined amount into said pyrolysis product to quench same to a temperature below about 500° F. and abruptly changing the direction of flow of same through an angle of 90 degrees, increasing the linear velocity of the resulting pyrolysis product-quenching fluid admixture and then maintaining same in a high state of turbulence whereby quenching of pyrolysis product is completed and a predetermined uniform temperature level is provided, passing quenched pyrolysis product to a product separation means and therein separating ethylene and acetylene, and recovering said ethylene and acetylene as products of the process.

5. A process for the pyrolysis of hydrocarbons, comprising burning hydrogen with oxygen of at least 90 percent oxygen purity to form combustion gas at a temperature of about 5000° F., maintaining combustion gas thus formed in a longitudinal direction of flow, maintaining a helically moving blanket of tempering gas annularly disposed about said longitudinally flowing combustion gas in an amount to absorb heat from said combustion gas and cool same to a temperature not higher than 4200° F., said helically moving tempering gas imparting a swirling motion to said combustion gas, preheating gaseous hydrocarbon to a temperature in the range of from 1800 to 2400° F., introducing gaseous hydrocarbon thus heated into admixture with swirling longitudinally moving combustion gas in a radial direction with respect to the longitudinal flow of said combustion gas whereby intimate and rapid mixing of combustion gas and gaseous hydrocarbon is initiated and heat is transferred from said combustion gas to said hydro-

carbon to heat same to a temperature in the range of 2400 to 3500° F., increasing the linear velocity of the resulting tempering gas-hydrocarbon-combustion gas admixture to a value in the range to 200 to 500 feet per second, then decreasing said velocity and maintaining said admixture in a high state of turbulence for a contact time within the range of from 0.001 to 0.05 second, whereby acetylene-containing hydrocarbon pyrolysis product is formed, diverting the direction of flow of said pyrolysis product at an angle of about 90°, introducing quenching fluid in a predetermined amount longitudinally into said acetylene-containing product when in diverted flow, again increasing the linear velocity of the resulting admixture of pyrolysis product and quench fluid to a value in the range of 200 to 500 feet per second, then decreasing said velocity and maintaining the admixture in a high state of turbulence whereby quenching of pyrolysis product is completed and a predetermined uniform temperature level is provided, maintaining the quenched product mixture at a temperature within the range of 1800 to 2300° F. for a contact time of 0.05 to 5.0 seconds, whereby aromatic hydrocarbons and unsaturated aliphatic hydrocarbons are formed as product, separating said product into selected hydrocarbon fractions, and recovering said fractions.

6. The process of claim 5 wherein said tempering gas is steam.

7. The process of claim 5 wherein said tempering gas is hydrogen.

8. Hydrocarbon conversion apparatus comprising, in combination: a generally cylindrical combustion chamber; burner means positioned in one end of said combustion chamber and in open communication therewith; inlet means in open communication with said combustion chamber and positioned substantially tangentially with respect to the inner surface of said combustion chamber and adjacent said burner means; conduit means in open communication with said combustion chamber at the end thereof opposite said burner means; inlet means in open communication with said conduit means at an intermediate part thereof; a Venturi tube in open communication with said conduit means at the end thereof opposite said chamber, said Venturi tube being substantially coaxial with said conduit; another Venturi tube in open communication with the first-mentioned Venturi tube, the axes of the two Venturi tubes being noncoaxially and angularly disposed with respect to each other; inlet means intermedi-

ate the two Venturi tubes and generally coaxially positioned with respect to the second-mentioned Venturi tube; and outlet means in open communication with the second-mentioned Venturi tube.

9. Apparatus for pyrolysis of hydrocarbons, comprising, in combination, burner means for burning hydrogen with oxygen, a first substantially unobstructed cylindrical elongated refractory section connected at one end with said burner means to axially receive hot combustion gas from burning therein, a second cylindrical elongated section open at both ends and having a smaller diameter than said first cylindrical section and co-axially connected to said first section opposite the burner end, fluid inlet means opening into said first section through its side wall near the burner end and disposed to admit fluid in a direction tangent to the inner side wall of said first section and perpendicular to its longitudinal axis, hydrocarbon inlet means opening radially into said second cylindrical section, a first refractory Venturi tube co-axially connected at its upstream end to said second section, a second refractory Venturi tube in open communication at its upstream end with the downstream end of said first Venturi tube and having its longitudinal axis disposed at a right angle to the longitudinal axis of said first Venturi tube, quench fluid inlet means opening through the side wall intermediate said first and second Venturi tubes and axially disposed with respect to said second Venturi tube, an auxiliary reaction section connected to the downstream end of said second Venturi tube and positioned at right angles thereto, outlet means positioned intermediate said second Venturi tube and said auxiliary reaction section, and outlet means in said auxiliary reaction section.

10. The apparatus of claim 9 in which the angle of the exit throat of said second Venturi tube is about one-half the angle of the inlet throat thereof and the length of the outlet throat of said second Venturi tube is about twice the length of the inlet throat thereof.

11. The apparatus of claim 9 in which the length of the exit throat of said first Venturi tube is about three times the length of the inlet throat thereof.

References Cited in the file of this patent

UNITED STATES PATENTS

2,374,518	Wolk et al. _____	Apr. 24, 1945
2,608,594	Robinson _____	Aug. 26, 1952
2,750,420	Hepp _____	June 12, 1956
2,750,434	Krejci _____	June 12, 1956

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,823,243

February 11, 1958

Sam P. Robinson

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 10, after "tem=" insert ==perature, maintaining the heated gas at that temperature==; column 6, line 50, after "turbulence" insert ==necessary==; line 62, strike out "about twice the length of the longitudinal axis" and insert instead ==of Venturi tube 69 may be about one-half that==.

Signed and sealed this 6th day of May 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents