April 17, 1951 S. P. ROBINSON 2,549,240

ACETYLENE MANUFACTURE

Filed Nov. 8, 1948 2 Sheets-Sheet 1

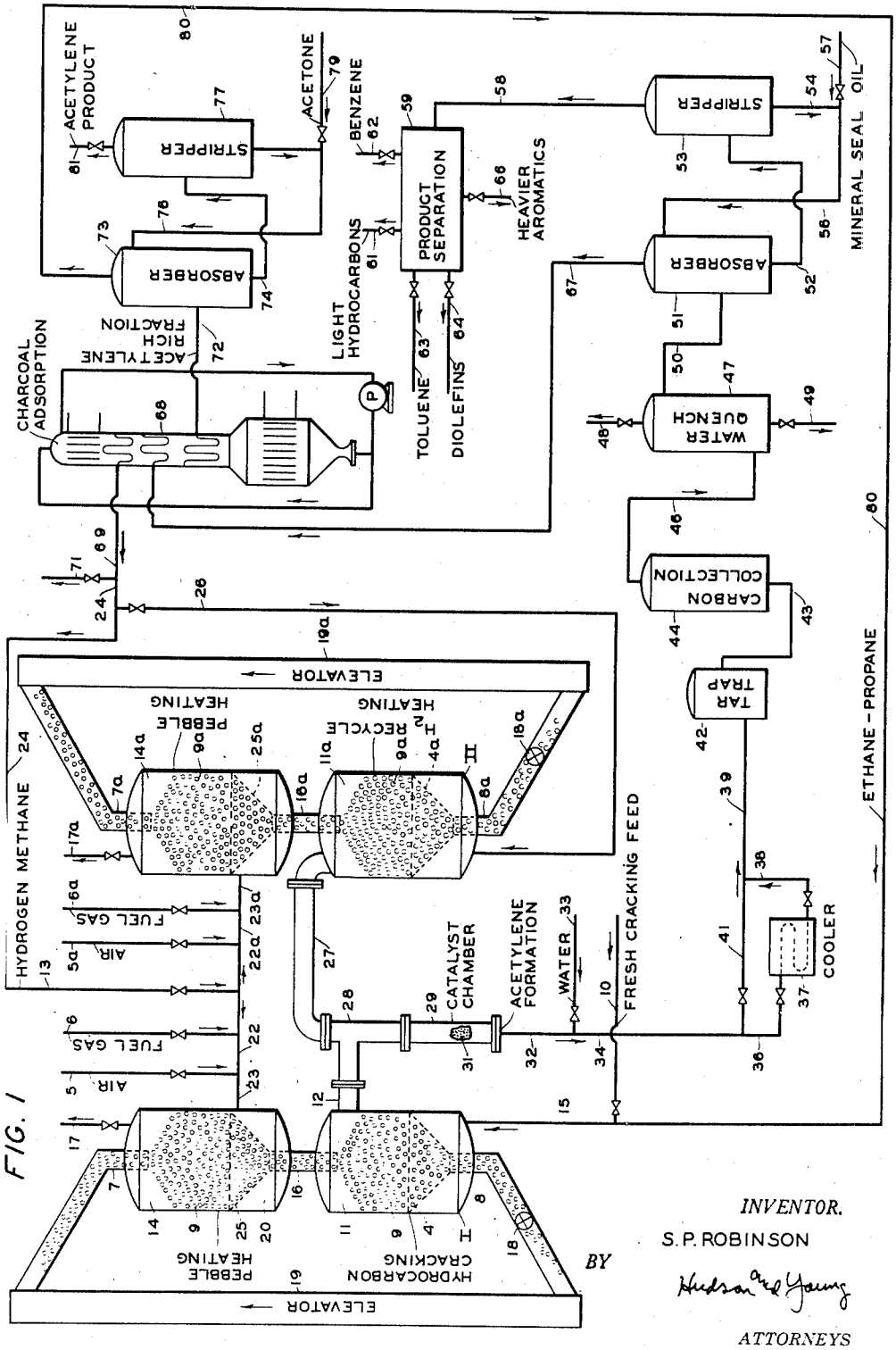


FIG. 1

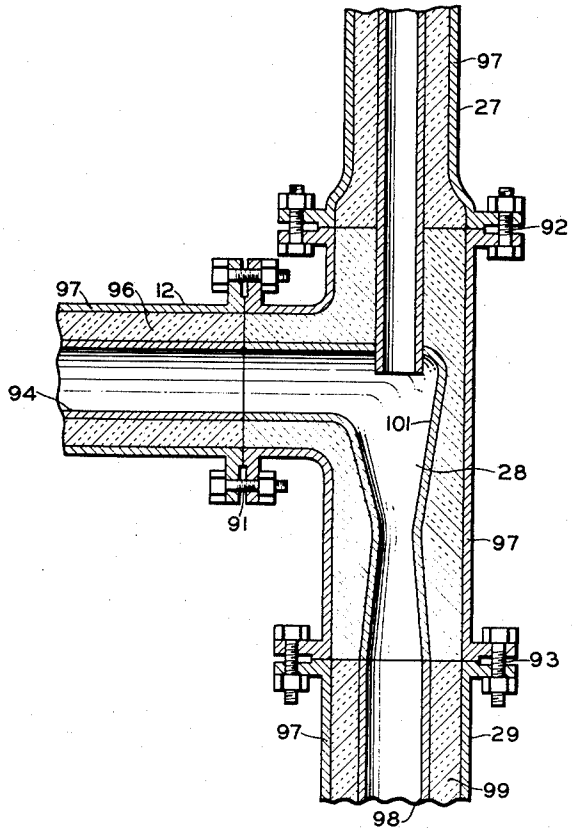
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FIG. 2



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2,549,240

ACETYLENE MANUFACTURE

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10 Claims. (Cl. 260—679)

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This invention relates to the manufacture of acetylene. In another aspect this invention relates to the manufacture of acetylene from a hydrocarbon gas. In another aspect this invention relates to the efficient conversion of a hydrocarbon gas to acetylene, in high yield.

Acetylene has many industrial uses. Acetylene is used directly or indirectly in the manufacture of aldehydes, acids, polymerization products, and various other compounds. Various methods have been proposed for the manufacture of acetylene. Perhaps one of the oldest methods for making acetylene is its manufacture from calcium carbide. Other well-known processes for acetylene manufacture include such as electric processes employing the heat of an electric arc, the partial combustion of hydrocarbons, the pyrolysis of hydrocarbons, and the recovery of by-product acetylene from other commercial processes such as thermal or catalytic cracking of hydrocarbons. Among the processes proposed heretofore, acetylene has, in many instances, been produced only in uneconomical and limited yields.

Since acetylene is very active chemically and is the basic material for the manufacture of many organic compounds, the cost of the manufacture of acetylene is of major importance, and this invention is concerned with a process wherein acetylene is economically manufactured from a gaseous hydrocarbon material in high yield and at a high conversion efficiency.

An object of this invention is to provide a process for the manufacture of acetylene.

Another object is to utilize hydrocarbons in the manufacture of acetylene.

Another object is to provide a process for the conversion of a hydrocarbon to acetylene in high and selective yields.

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

In accordance with this invention, acetylene is produced by first cracking a hydrocarbon gas to form ethylene in selective and high yield, and then admixing the total hot cracking-product with added hydrogen heated to a temperature above the hydrocarbon cracking temperature, and the resulting hot cracking-product-hydrogen mixture passed through a bed of titanium dioxide catalyst, whereby acetylene is formed in high yield and recovered in a subsequent series of purification steps.

In a preferred embodiment of my invention the hydrocarbon cracking step and the hydrogen heating step are each conducted in a separate pebble heater apparatus, each of which, in the practice of my invention, may comprise 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

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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 contacting material, often referred to as pebbles, fills the pebble heating zone, the connecting zone or throat, and the gas reaction zone, and flows downwardly through these zones by force of 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 and on into the pebble heating chamber. A contiguous moving pebble mass thereby fills the pebble heating zone, gas reacting or 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 the pebble heater apparatus. Pebbles are preferably substantially spherical, and are about $\frac{1}{32}$ of an inch to 1 inch in diameter, the preferred range being ¼ inch to ½ inch.

In the following description, one method of operating my process will be specifically disclosed. The figures are diagrammatic illustrations of apparatus in which my process may be practiced. It is to be understood that the flow diagram is diagrammatic only and may be altered in many respects by those skilled in the art and yet remain within the intended scope of my invention.

Figure 1 is a schematic flow diagram of a preferred process of my invention. Figure 2 is a detailed diagrammatic illustration of a portion of apparatus only briefly illustrated in Figure 1. Referring to Figure 1, in pebble heater apparatus I, pebble heating zone 14 and gas reaction zone 11 are insulated chambers, each containing a contiguous fluent mass of pebbles 9 and connected by a heat insulated conduit, forming pebble throat 16. Conduits 7 and 8 serve as pebble inlet and outlet for chambers 14 and 11, respectively. Star valve (or other type of pebble feeder) 18 regulates the rate of flow of pebble mass 9 through chamber 14, throat 16 and chamber 11, and feeds pebbles flowing from the bottom of chamber 11 into bucket elevator 19 for delivery into pebble inlet 7 and on into chamber 14. Combustion chamber 20 is positioned subjacent pebble heating chamber 14. Chambers 14 and 20 are separated by perforate support 25 through which combustion gas formed in chamber 20 ascends to pass in direct heat exchange relation with pebble mass 9 in chamber 14. Fuel gas, usually natural gas from line 6 and/or hydrogen recycle gas from lines 13 and 24, described hereafter, is introduced through line 22 and admixed with oxygen, or an oxygen

containing gas, preferably air, from line 5 to form a combustion mixture in line 23 which is burned in combustion zone 20. Hot combustion gas formed in zone 20 ascends through perforate support 25 at a temperature selected to heat pebbles in chamber 14 to a temperature sufficiently above a predetermined temperature of a subsequent cracking step described hereafter, so that the cracking reactants are brought to the requisite temperature in a very short time and maintained at such a level for the requisite time. Such a required pebble temperature is usually within the range of from 1400 to 2800° F., and is regulated by the combustion gas temperature which in turn is dependent on the specific components of the combustion mixture and the proportions of oxygen therein, and by the rate of pebble flow through chamber 14. Combustion gas having imparted heat to pebbles in zone 14 is passed as effluent from zone 14 through line 17 to further utilization, not shown. Ethane-propane cracking stock, containing a relatively high proportion of ethane to propane, is introduced into the lower portion of gas reaction chamber 11 through lines 10 and 15, entering at a point below gas distribution plate 4, and is passed through chamber 11 in direct heat exchange relation with pebbles previously heated in zone 14 to a temperature sufficiently high to heat the cracking stock to a temperature within the range of 1400 to 2000° F. and to maintain that temperature level for a contact time within the range of 0.05 to 1.5 seconds whereby cracking takes place to produce an ethylene-rich cracking product. Pressure conditions within the pebble heater apparatus I are preferably above atmospheric. Pressures from 0 to 5 p. s. i. g. are often utilized, although a pressure as high as 15 p. s. i. g. may be employed, in some cases. Effluent gas from reaction chamber 11 comprises ethylene-rich cracking product which is passed through line 12 to a mixing T or venturi 28 wherein it is quickly mixed with and further heated by a hydrogen-rich recycle stream from a subsequent purification step, previously heated to a temperature above the cracking effluent temperature, in the gas heating chamber of pebble heater apparatus II. Pebble heater apparatus II may be mechanically similar to pebble heater apparatus I, and is so illustrated. Portions of pebble heater II corresponding to numbered portions of pebble heater I are numbered identically except that the character "*a*" is added to identify that portion as a part of pebble heater II. Pebbles in chamber 14—*a* are heated in the same manner as already described for heating pebbles in chamber 14, to a temperature above the predetermined temperature of a subsequent heating step in heating chamber 11—*a*.

Hydrogen-rich recycle gas from a subsequent purification step described hereafter, in lines 26 and 24 is introduced into the lower portion of gas heating chamber 11—*a* entering at a point below perforate gas distribution plate 4—*a*, and is passed therethrough in direct heat exchange relation with pebbles previously heated in zone 14—*a* at a sufficiently high temperature to heat the hydrogen-rich recycle gas in contact therewith to a temperature within the range of 2200 to 3500° F. for a contact time within the range of from 0.05 to 1.5 seconds. Pressure conditions in pebble heater II may be identical with those of pebble heater I. Effluent hydrogen-rich recycle gas heated in chamber 11—*a* is passed as effluent through line 27, is admixed in venturi 28 with effluent cracking gas product from chamber 11 entering from line 12, in a volume ratio to cracking gas product within the limits of from 1:1 to 10:1, to form a hydrogen-cracking product admixture at a temperature within the limits of 2000 to 2600° F. A hydrogen-cracking product admixture from venturi 28 is passed at its existing temperature to catalyst chamber 29 and through a fixed bed of highly calcined titanium dioxide catalyst 31 contained therein, for a reaction time within the limits of 0.01 to 1.0 second. Effluent from catalyst zone 29 is passed through line 32 and quickly quenched by contact with water injected directly into line 32 from line 33, to a temperature below 1000° F., above which some undue polymerization and/or dehydrogenation of acetylene may take place. Preferably, material in line 32 is quenched to about 350° F. This may be effected by means of the water quench already described. However, if desired, material from line 32, quenched as already described, may be passed through lines 34 and 36, to heat exchange means 37, usually a waste heat boiler, and therein cooled to the desired temperature, usually about 350° F., in indirect heat exchange with water. Effluent from cooler 37 is then passed through lines 38 and 39 to tar trap 42. If desired, material from line 34 may be passed directly to line 39 through line 41. Gas in line 39 is passed tangentially into trap 42 wherein viscous and solid tarry materials are removed. Off gas from tar trap 42 may contain small carbon particles not arrested in trap 42 and is passed through line 43 to carbon collection system 44 comprising any one of a number of known carbon arresting means such as various filter means, Cottrell apparatus, or the like. I prefer a system employing fiber glass bag filters subject to shaking and/or oil washing, such an arrangement being well known to those skilled in the art. Carbon is removed from the gas in zone 44, and carbon-free off gas therefrom is passed through line 46 to water quench tower 47 and passed in countercurrent flow therein to downwardly flowing water or water spray introduced through line 48 and discharged through line 49. Effluent gas from quench zone 47 is discharged at a temperature of from about 100–140° F. more often about 120° F. Gas from quench zone 47 is then passed through line 50 to an absorber-stripper system of conventional design, employing absorbent of the mineral seal oil type. Gas from line 50 is introduced to absorber 51 and passed in countercurrent flow therein to downwardly flowing stripped and/or fresh mineral seal oil which absorbs all materials from the gas, heavier than propane, which materials are formed in small quantities in catalyst zone 29 as by-product. Enriched absorber oil is passed from the lower portion of absorber 51 through line 52 to stripper 53 and maintained therein under distillation or "stripping" conditions whereby the rich oil is separated from its absorbed materials. Lean absorber oil is passed from stripper 53 through lines 54 and 56 into the upper portion of absorber 51. Fresh absorber oil is added, when desired, to line 56 and line 57. Materials heavier than propane, desorbed from absorber oil in stripper 53 are passed therefrom through line 58 to product separation means 59 comprising coolers, separators, distillation equipment, storage tanks and the like not individually illustrated, which can be used to effect a separation of various selected fractions from the propane and heavier materials intro-

duced through line 58. From separation means 59 are withdrawn normally gaseous hydrocarbons through line 61, benzene through line 62, toluene from line 63, diolefin hydrocarbons from line 64, and selected heavier aromatic materials from line 66. Unabsorbed gas from absorber 51 is passed through line 67 to charcoal adsorption unit 68 wherein a hydrogen fraction containing hydrogen in an amount of from 40 to 100 per cent, more often from 40 to 80 per cent and an acetylene-rich residual fraction are separated. A hydrogen-rich gas containing methane as the heaviest component is passed from charcoal adsorption unit 68 through lines 69 and 24 for recycle through line 26 to pebble heater chamber 11—*a* and, when desired, to combustion chamber 20 and/or combustion chamber 20—*a* through line 13, as already described. Any excess hydrogen-rich recycle gas in lines 69 and 24 may be withdrawn through line 71 for other utilization, not shown. Charcoal adsorption means 68 as employed herein, is well known to those skilled in the art, and employs the principle of selective adsorption of hydrocarbons by a moving bed of activated carbon particles, with the subsequent removal of the adsorbed hydrocarbon by heat and steam, and is especially well applied to the separation of the materials from line 67 as already described. An acetylene-rich fraction containing some ethane and ethylene and still smaller amounts of propane and propylene is desorbed from the activated carbon in adsorber 68 and passed through line 72 to an absorber-stripper system employing acetone as an absorbent. Material in line 72 is introduced to absorber 73 and passed countercurrently therein to downwardly flowing stripped and/or fresh acetone introduced through line 76 whereby acetylene is substantially completely selectively absorbed in acetone. Enriched acetone is passed from absorber 73 through line 74 to stripper 77 wherein under distillation conditions of pressure and temperature, acetylene is desorbed from the rich acetone absorbent. Lean acetone absorbent is returned to absorber 73 through line 76. Fresh acetone may be introduced to the system through line 79. Residual gas comprising ethane in a major proportion together with relatively small amounts of ethylene, propylene and propane is recycled through lines 80 and 15 to gas cracking chamber 11 in admixture with fresh feed from line 10. Overhead from absorber 73 may be recycled and reacted to extinction. Acetylene product of high purity separated in stripper 77 is passed therefrom through line 81 and recovered in high yield, as product of the process.

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.

Figure 2 is a diagrammatic cross sectional view of a preferred arrangement and construction of venturi 28, catalyst zone 29 together with lines 12 and 27 by means of which I may conduct the mixing step and reaction step of the process of my invention, at the required high temperature conditions and gas velocities. Referring to Figure 2, effluent line 12 is rigidly attached to venturi 28 by flange 91. Line 27 and reactor 29 are rigidly attached to venturi 28 by flanges 92 and 93 respectively. Lines 12 and 27, venturi 28 and reactor 29 are all highly insulated and maintained in close proximity to each other to minimize heat losses, prevalent at the temperatures employed in those vessels. Line 12 may be lined with a dense, hard-burned, small grained, high purity, supported alumina lining 94 to resist abrasion, and this lining is backed by a light-weight mullite or alumina insulating material 96. Outer jacket 97 may be any suitable alloy steel. Reactor 29 may be fabricated of the same materials as line 27 already described. The lining of venturi 28 is fabricated preferably of alumina 101, but of a very small grain, dense, hard-burned structure to resist abrasive effects resulting from high gas velocities. Outer shell 97 of venturi 28 may comprise any suitable alloy steel.

The TiO_2 catalyst employed in the practice of this invention is preferably a precipitated gel type catalyst. Various procedures are well known for preparing such a catalyst. I may prepare the catalyst employed in this invention by coprecipitating $Ti(OH)_4$ and $Al(OH)_3$ gels in which the ratio of TiO_2 to Al_2O_3 may usually be in the range of from 0.01 to 0.30:1. The precipitated mixture is dried, then extruded, generally into pellets, and calcined at a temperature within the range of 2600–3000° F. for a duration of from 2 to 12 hours, preferably 2 to 6 hours. Generally, I prefer to calcine the TiO_2 catalyst at about 2600° F. for from 2 to 6 hours. An alternate means of preparing a TiO_2 catalyst suitable for use in the practice of my invention is to form spheres from commercial rutile (TiO_2) and plasticizing ball clay, and calcining the resulting spheres at a temperature of about 2600° F. for a duration of from 2 to 12 hours, preferably 2 to 6 hours. The preferred TiO_2 content of the gel type catalyst may usually be varied from 5 to 25 per cent, and the TiO_2 content of the spheres formed from rutile and ball clay may generally be from 70 to 95 per cent.

I am not certain of the mechanism of the reactions taking place during the formation of acetylene in the practice of my invention. However, there are apparently at least 3 reactions taking place simultaneously at this stage, as indicated by the following equations.

1. Partial dehydrogenation of ethylene to acetylene

$$C_2H_4 \rightarrow C_2H_2 + H_2$$

2. Dehydrogenation of acetylene to carbon and hydrogen

$$C_2H_2 \rightarrow 2C + H_2$$

3. Polymerization of unsaturates

$$C_2H_4 + C_2H_2 \rightarrow C_4H_6$$

The rate of reaction 1 is highest, followed in order by reactions 3 and 2. To obtain high acetylene yield it is necessary to employ the necessary high temperature and a contact time sufficiently long to favor formation of large quantities of acetylene, but at the same time to employ the least drastic conditions of temperature and time, in order that appreciable decomposition and polymerization reactions of the types suggested by Equations 3 and 2 do not occur, or for that matter, to minimize any side reactions resulting from any degree of dehydrogenation and/or polymerization. I have found that I may minimize such dehydrogenation and/or polymerization side reactions by conducting my acetylene-forming reaction in the presence of a highly calcined TiO_2 catalyst described more fully hereafter. I have found that by employing an active TiO_2 catalyst

calcined at a temperature of about 2600 to 3000° F. for 2 to 12 hours, whereby I presumably reduce catalyst activity and surface area, I may form acetylene from the ethylene-containing cracking-product at temperatures significantly lower than those normally required when forming acetylene from ethylene in the absence of a catalyst. By this practice, I apparently have decreased the rate of the reactions of the types illustrated by Equations 2 and 3 to a disproportionately greater extent than I have decreased the rate of the preferred reaction indicated by Equation 1. Employing such a TiO_2 catalyst at the temperatures already described, I have provided for a high conversion of preformed ethylene to actylene in a minimum of reaction time.

By conducting the acetylene-forming reaction in the presence of excess diluent hydrogen I have "buffered" undesirable side reactions and, at the same time, have reduced hydrocarbon partial pressures in the reaction zone. By the utilization of diluent hydrogen I have definitely minimized the extent and occurrence of undesirable side reactions taking place in the acetylene-forming step. I further utilize the hydrogen-rich recycle stream as a heat carrier, as already described, by means of which I am able to quickly raise the temperature of the ethylene-rich cracking product to the requisite reaction temperature. Furthermore, by utilization of such hot hydrogen-rich recycle gas I maintain the temperature drop across the catalyst bed, and carbon deposition on the catalyst, at a minimum. Furthermore, by using hot hydrogen as a diluent and heat carrier instead of, for example, steam, I utilize a by-product stream of low fuel value, instead of a more costly material that would necessitate additional capital investment. Accordingly, by eliminating the use of steam diluent I prevent the formation of undesirable carbon oxides occurring from any water-gas reaction, i. e., the formation of CO and CO_2 by reaction of steam with hydrocarbon, which formation decreases the acetylene yield, abets corrosion and hinders purification of the initial acetylene product.

By employing the charcoal absorption unit, as already described, separation of hydrogen and methane from the product gas is precise regardless of the quantity of hydrogen by-product, and substantially no acetylene is present in the recycled gas. Consequently, large scale hydrogen dilution as practiced in my invention is in no way harmful to ultimate recovery of acetylene product.

In the practice of the process of my invention, I utilize temperatures significantly below those employed in the manufacture of acetylene non-catalytically from an ethylene-rich gas, and consequently I may employ commercial scale equipment which can be fabricated of less expensive materials.

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

Example

A mixed ethane-propane depropanizer overhead from natural gasoline plant operation having the following composition:

Component:	Volume per cent
CH_4	6.25
C_2H_6	27.77
C_3H_8	65.10
C_4H_{10}	0.87

is cracked in the gas reaction chamber of a pebble heater apparatus at a temperature of 1700° F. for a contact time of 0.25 second to produce cracking product having the following composition:

Component:	Volume per cent
H_2	23.3
CH_4	31.7
C_2H_2	1.3
C_2H_4	32.9
C_2H_6	4.5
C_3H_6	1.6
C_3H_8	0.2
C_4H_6	1.2
C_4H_8	1.0
C_4H_{10}	
Heavier	2.3

At the same time, a hydrogen-rich recycle gas stream, described hereafter, containing 73 per cent hydrogen and 27 per cent methane by volume is heated to 2700° F., for 0.15 second in the gas heating chamber of an auxiliary pebble heater. Under these heating conditions the methane is partially cracked producing a gas of the following composition:

Component:		
Hydrogen	volume per cent [1]	76.0
CH_4	do	21.2
C_2H_2	do	2.8
Carbon and tar	weight per cent	7

[1] Carbon and tar-free basis.

The effluent cracking-product and heated hydrogen-rich recycle streams are mixed in a high velocity Venturi throat and the resulting admixture passed vertically downward therefrom into a catalyst chamber packed with ⅛" calcined TiO_2 catalyst pellets of the precipitated gel type, containing 7 per cent by weight TiO_2. Approximately 2.55 standard gas volumes of the heated hydrogen recycle gas is required per volume of cracking effluent, for heating. With higher ethane concentrations in the admixture passed from the Venturi mixing throat, less heated hydrogen recycle gas would be necessary. The approximate composition of the admixture being passed from the Venturi mixing throat to the catalyst chamber, but before passage through the catalyst chamber is as follows:

Component:	Volume per cent
H_2	59.8
CH_4	23.4
C_2H_2	2.4
C_2H_4	9.3
C_2H_6	1.3
C_3H_6	.5
C_3H_8	--
C_4+	3.3

Gas is passed from the Venturi mixing throat at a temperature of 2200° F., through the catalyst bed for a contact time of 0.10 second. Total gas product leaving the catalyst bed has the following approximate composition:

Component:		
H_2	volume per cent [1]	64.5
CH_4	do	24.3
C_2H_2	do	6.3
C_2H_4	do	1.9
C_2H_6	do	0.2
C_3H_6	do	2.8
Tar and carbon	weight per cent	7.0

[1] Carbon and tar-free basis.

Effluent product gas from the catalyst chamber is quickly quenched by direct water injection

whereby it is cooled in a very short time to a temperature below about 1000° F., under which conditions polymerization and dehydrogenation of acetylene in the reaction product is substantially prevented. The partially quenched gas is further cooled to a temperature of about 350° F. in a waste heat boiler. Quenched gas is then passed tangentially into a tar trap wherein tarry materials are separated and then to a carbon collection system comprising fiber glass bag filters. The partially cooled gas upon being passed from the bag filters is passed into a water quench tower and cooled to 120° F. Product gas, thus cooled, is compressed to 100 p. s. i. g. and passed to an absorption-stripper system of conventional type, employing mineral seal absorber oil, wherein all gaseous components having a molecular weight higher than that of propane are first absorbed by lean absorber oil and then stripped from the rich absorber oil. Absorbed product includes by-product materials such as diolefin type hydrocarbons, light aromatic hydrocarbons such as benzene, toluene, xylene, and various heavier aromatics. The propane and lighter gas components, unabsorbed, are passed from the absorber column to a moving bed type carbon absorption tower, wherein a hydrogen-rich gas containing methane and a residual acetylene-rich gas C_2—C_3 product fraction are separated. Hydrogen-methane gas containing 73 per cent hydrogen and 27 per cent methane is passed from the carbon absorption tower and is recycled to a gas heating chamber of a pebble heater, and ultimately to the reaction, already described. The residual C_2—C_3 fraction contains about 76 per cent C_2H_2, 22 per cent C_2H_4 and 2 per cent other C_2—C_3 hydrocarbons, and is passed to an absorber system employing acetone absorbent wherein acetylene product is selectively adsorbed. Non-acetylene hydrocarbons are recycled to the cracking step, already described. The acetylene-rich acetone absorbent is stripped, and acetylene is recovered as a product of the process.

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 manufacture of acetylene, comprising contacting a mixture of hydrogen and ethylene with a catalyst consisting essentially of titanium dioxide at a temperature within the limits of 2000 to 2600° F., and for a contact time of from 0.01 to 1.0 second, whereby acetylene is formed; said catalyst having been previously calcined at a temperature of from 2600 to 3000° F. for a duration of from 2 to 12 hours so as to effect suitable activation for dehydrogenation of ethylene to acetylene, and recovering said acetylene as a product of the process.

2. A process for the manufacture of acetylene, comprising contacting a mixture of ethylene and hydrogen with a catalyst consisting essentially of titanium dioxide at a temperature within the limits of 2000 and 2600° F. for a contact time within the limits of 0.01 and 1.0 second, whereby acetylene is formed, and recovering said acetylene as a product of the process.

3. A process for the manufacture of acetylene, comprising introducing hydrogen in admixture with ethylene into contact with a catalyst consisting essentially of titanium dioxide, for a contact time of from 0.01 to 1.0 second, and at a temperature within the limits of 2000 and 3600° F., whereby acetylene is formed; said catalyst having been previously calcined at a temperature of about 2600° F. for a period of from 2 to 6 hours, and recovering said acetylene as a product of the process.

4. The process of claim 1 wherein said catalyst is a precipitated gel type catalyst containing from 5 to 25 per cent by weight TiO_2.

5. The process of claim 1 wherein said catalyst is prepared from rutile and a plasticizing clay, and contains from 70 to 95 per cent by weight of TiO_2.

6. The process of claim 1 wherein said catalyst is disposed as a fixed bed and wherein said mixture of hydrogen and ethylene is passed through said fixed bed at an initial temperature in said range of 2000 to 2600° F., and wherein effluents from said fixed bed are quickly quenched to a temperature below 1000° F.

7. The process of claim 1 wherein said mixture of hydrogen and ethylene is formed by admixing a stream of ethylene-rich product of hydrocarbon cracking with a hydrogen-methane stream containing from 40 to 80 volume per cent hydrogen, and wherein the volume ratio of said hydrogen-methane stream to said ethylene-rich stream is within the limits of 1:1 and 10:1.

8. The process of claim 7 wherein said volume ratio is within the limits of 2:1 and 6:1.

9. A process for the manufacture of acetylene, comprising passing a mixture of hydrogen and ethylene at an initial temperature within the limits of 2000 and 2600° F. through a fixed bed of catalyst consisting essentially of granular titanium dioxide previously calcined at a temperature of from 2600–3000° F. for a period of from 2–12 hours, at a contact time of from 0.01 to 1.0 second, and at a pressure within the limits of 0 to 15 p. s. i. g., whereby acetylene is formed together with by-product hydrogen, separating acetylene-containing product thus formed into a hydrogen-rich fraction and a residual acetylene-rich fraction, recycling at least a portion of said hydrogen-rich fraction as part of the above said mixture of hydrogen and ethylene, and recovering acetylene from said acetylene-rich fraction.

10. The process of claim 9 wherein said hydrogen-rich fraction contains from 40 to 80 volume per cent hydrogen.

SAM P. ROBINSON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,995,136	Winkler et al.	Mar. 19, 1935
2,030,070	Morrell	Feb. 11, 1936
2,167,471	Auerbach	July 25, 1939
2,389,636	Ramseyer	Nov. 27, 1945

FOREIGN PATENTS

Number	Country	Date
470,258	Great Britain	Aug. 9, 1937
750,496	France	May 29, 1933
823,303	France	Oct. 11, 1937