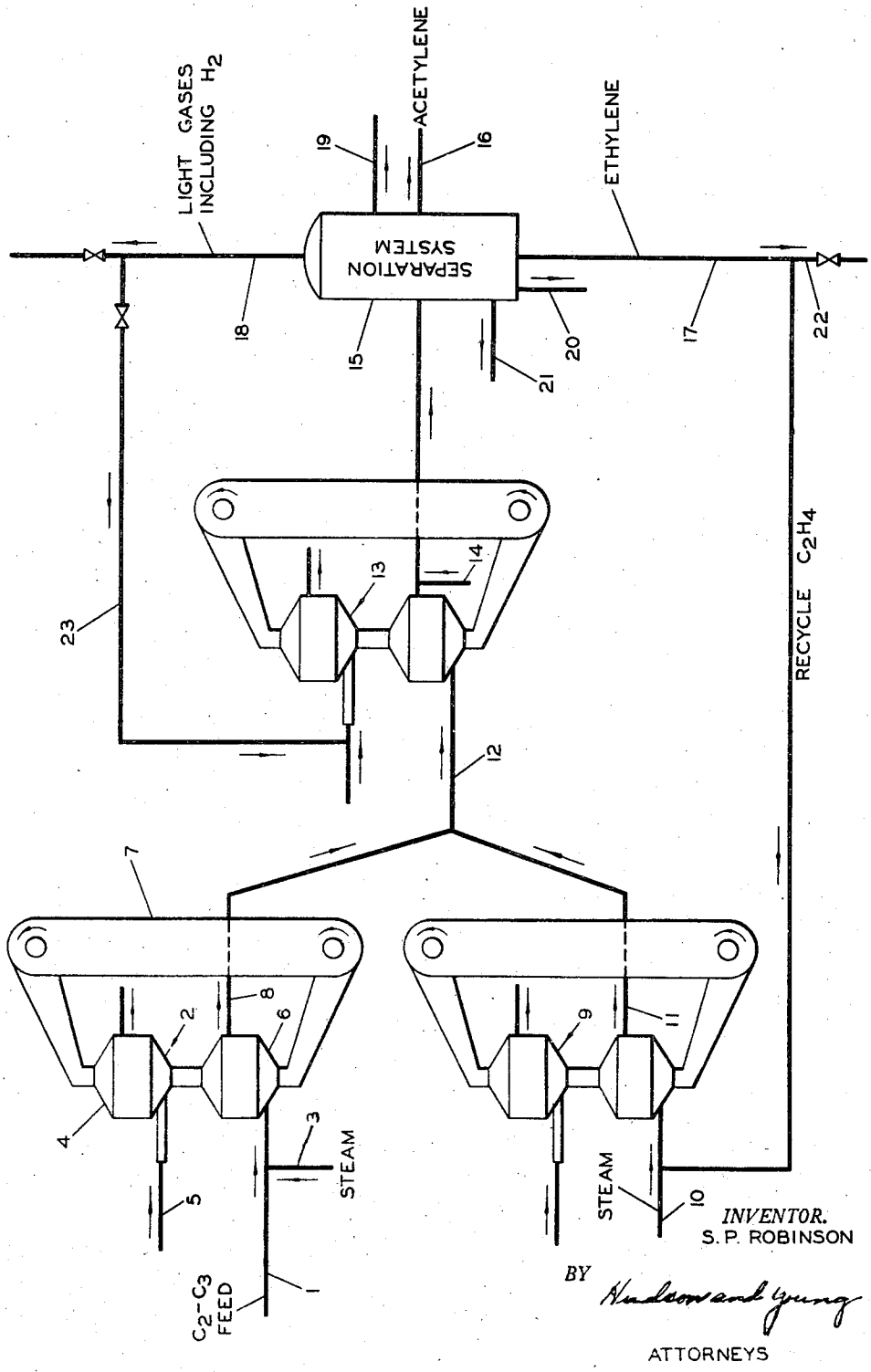
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ACETYLENE MANUFACTURE

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ACETYLENE MANUFACTURE

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This invention relates to acetylene manufacture. In one aspect it relates to an improved method of making acetylene from ethylene-rich gas. In another aspect it relates to manufacture of acetylene from a suitable hydrocarbon feed stock by a two-stage process involving cracking and/or dehydrogenation of the feed to form ethylene in good yield followed by catalytic conversion of hydrocarbon including ethylene in the effluent to acetylene. In another aspect it relates to an improved method of making acetylene from a feed stock consisting essentially of ethane or propane or, more commonly, a mixture of ethane and propane.

The principal object of the present invention is to provide an improved method of making acetylene. Another object is to provide an improved method of making acetylene from ethylene-rich gas. Another object is to provide an improved method of making acetylene from hydrocarbon feed stocks forming ethylene in good yield upon catalytic or non-catalytic pyrolysis. Many other objects of the present invention will more fully hereinafter appear.

The accompanying drawing portrays diagrammatically one arrangement of equipment which may very advantageously be used for carrying out the present invention.

In accordance with my invention an ethylene-rich gaseous stream is passed at a temperature of from 1600 to 2500° F. into contact with an extended mass of stainless steel as a catalyst at a temperature of from 1600 to 2500° F. for a time such that hydrocarbon including ethylene is converted to acetylene but that decomposition of acetylene is substantially prevented, the acetylene-containing effluent is continuously withdrawn and immediately quenched with water to a temperature of not over 500° F. While temperatures as low as 1600° F. may in some circumstances be employed for carrying out the acetylene-forming reaction, I prefer to use temperatures ranging from 2000 to 2500° F. Still more preferably I employ temperatures of from 2300 to 2500° F.

The contact or residence time in the reaction zone will depend largely upon the temperature employed. Generally speaking, the higher the temperature the shorter the contact or residence time in the reaction zone. The contact time may vary from 0.1 second at 2000° F. to 0.005 second at 2500° F. When the preferred temperature range of 2300 to 2500° F. is employed, the contact time may range from 0.02 second at 2300° F. to 0.005 second at 2500° F.

The pressure at which the acetylene-forming reaction is carried out should be low. Generally the total pressure will range from atmospheric to 15 pounds per square inch gauge.

I generally employ a large proportion of steam

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as a diluent in the acetylene-forming reaction. Usually this steam diluent is in admixture with the ethylene-rich hydrocarbon feed. The proportion of steam may vary from ½ to 15 mols of H_2O per mol of hydrocarbon feed. Generally it is preferred to use several mols of steam per mol of hydrocarbon, say from 2 to 4 mols of H_2O per mol of hydrocarbon. The steam functions to keep carbon formation at a minimum, to reduce partial pressure of hydrocarbon which favors acetylene formation, to keep down polymerization of olefins or acetylene, to reduce decomposition of acetylene and to passivate the stainless steel surfaces, thereby minimizing the normal tendency of the stainless steel to cause decomposition of acetylene to carbon and hydrogen.

As the feed to the acetylene-forming step I use any ethylene-rich hydrocarbon gaseous mixture. By "ethylene-rich" I mean containing a relatively large proportion of ethylene, usually at least 20 mol per cent on a dry basis and preferably at least 30 mol per cent. Since the predominent acetylene-forming reaction in the practice of my invention is dehydrogenation of ethylene to acetylene and since this reaction takes place more easily than other acetylene-forming reactions, it is important that the feed contain a high proportion of ethylene. The presence of other (higher boiling) hydrocarbons is not harmful since at the temperature prevailing in the acetylene-forming zone they will be cracked to ethylene, acetylene, and methane (and hydrogen), the only relatively stable hydrocarbon gases possible at this temperature.

All the ethylene is not cracked at the relatively short contact times employed, nor is deep cracking desired from an ultimate yield standpoint. Ethylene destruction (total ethylene converted) may vary over a wide range, say from 20 to 60 mol per cent of ethylene charged, but preferably does not exceed 35 to 40 mol per cent.

The catalyst for the acetylene-forming reaction is stainless steel with an extended surface. Any form of stainless steel having a highly extended surface may be used. An example is stainless steel turnings. Such turnings would almost invariably be employed in the form of a fixed bed. Other examples are shavings, granules, lumps, wire, etc.

I prefer, however, to use stainless steel balls in a pebble furnace arrangement. Stainless steel balls are employed in place of the ceramic pebbles used in the ordinary pebble furnace. These balls may have a size ranging from ⅛" to 1" in diameter. Ordinarily balls ⅜" in diameter are employed.

In the aspect of my invention wherein stainless steel balls are employed in a pebble-type furnace for the production of acetylene the present invention comprises a continuous process

which involves continuously flowing by gravity a contiguous fluent mass of stainless steel balls through a series of substantially vertically extending zones comprising a stainless steel ball heating zone, a reaction zone positioned at a lower level than the heating zone and a relatively narrow interconnecting zone, each of the zones being substantially filled with the contiguous mass of stainless steel balls and permitting a relatively unrestricted flow of balls therethrough from top to bottom. That section of the contiguous mass of balls flowing through the heating zone is contacted continuously with a countercurrent stream of hot combustion gas at a temperature and flow rate regulated to insure heating of the balls to at least 2000° F. and preferably 2300° F. but not over 2500° F. This heating may be accomplished in any manner but it is often preferred to use reducing gases for heating. An example is the use of hydrogen-rich gases which may be recovered at a later stage of the process from the reaction effluent. The section of the contiguous mass of stainless steel balls which is flowing through the reaction zone is continuously contacted, usually countercurrently, with a stream of the ethylene-rich hydrocarbon feed, usually in admixture with a large proportion of steam as a diluent. This feed may be introduced at a temperature substantially below the reaction temperature. However, since the reaction is highly endothermic, it may be preferred to have the feed gas at or above the reaction temperature. The feed is introduced at a rate regulated to insure heating of the hydrocarbon including ethylene to the reaction temperature of at least 2000° F. and preferably from 2300 to 2500° F., if it is not already at that temperature. A substantial portion of the hydrocarbon including ethylene in the feed is converted to acetylene during passage through the reaction section. The stainless steel balls are continuously removed from the lower portion of the reaction zone. Stainless steel balls are continuously introduced to the upper portion of the heating zone. Usually the rates of withdrawal and introduction of balls are equal and the withdrawn balls are elevated in any suitable manner for introduction into the heating zone. The reaction mixture is withdrawn immediately and is immediately quenched with water to a temperature of not over 500° F.

The stainless steel balls may be solid. Preferably, however, they are porous and may be made, for example, by processes similar to those used in powder metallurgy. For example, particles or granules of stainless steel of substantially uniform size may be compressed, with or without heating to a temperature below the sintering temperature at which fusion with elimination of some porosity would take place, to form porous balls of highly extended surface area. If desired, particles of stainless steel may be admixed with some material which will be burned out or melted out upon heating to elevated temperature. This mixture may then be shaped into balls and burned to form the desired porous structure. Use of highly porous balls is very advantageous since extra surface greatly increases the reaction obtainable from a given volume or weight of stainless steel.

If solid stainless steel balls are used, it is not necessary that the entire ball be of stainless steel. For example, for economy, the balls may be made with a core of ordinary iron or steel surrounded by an exterior layer of stainless steel.

In some cases the stainless steel balls may be hollow in order to reduce the heat capacity to the proper figure and lower the weight so that abrasion losses will be minimized. If hollow balls are used, the stainless steel shell may be either solid or porous.

The acetylene-forming reaction is highly endothermic. Use of stainless steel balls in a pebble-type furnace enables the endothermic heat of reaction to be supplied in a simple manner. The rate of circulation of the stainless steel balls through the pebble furnace and the space velocity or rate of feed entry may be readily adjusted to give the desired very short contact times. The heat capacity, heat transfer and other characteristics of the stainless steel balls may readily be adjusted so as to give the proper results. If desired, the feed may be superheated to a temperature above the reaction temperature to supply the endothermic heat of reaction.

Where fixed beds of extended stainless steel, such as stainless steel turnings, are used in the less preferred embodiment of my invention, some means must be provided to compensate for the endothermic acetylene reaction. For example, the feed gases may be superheated above the reaction temperature to offset the endothermic reaction. Or the fixed beds may be heated on a regenerative cycle in known manner. Desirably waste gases rich in hydrogen, such as the hydrogen-rich light gaseous stream recovered from the reaction effluent, are used for heating the bed or beds preparatory to their being placed on stream. In some cases both expedients may be used, that is, the feed may be heated to above the reaction temperature and the bed or beds may be heated on a regenerative cycle. As the bed stays on stream the effluent gas temperature drops. When it drops below a pre-determined figure, say 2000° F., the feed may be switched to an alternate bed in which the catalyst surface has been freshly cleaned (to burn off carbon deposits) and preheated say to 2300 to 2500° F.

The effluent gases leaving the acetylene-forming reaction are immediately quenched with water to a temperature of not over 500° F. In many cases the temperature to which the effluent gases are quenched will be 300° F. or below. For quenching, I highly prefer to use water fog sprays. Such water fog sprays provide extremely fine particles of water which give much faster evaporation and cooling. A water fog spray may have from one thousand to one million times as much surface as the spray produced by an ordinary sprinkler or atomizer. Water fog sprays of the type which have been found very effective for fighting fire are suitable. Quenching of reaction effluents with water fog sprays is disclosed in my copending application Serial No. 698,729, filed September 23, 1946.

As used herein, the term "stainless steel" refers to any steel containing at least 7 per cent of nickel and 17 per cent of chromium. The nickel content may vary from 7 to 30 per cent. The chromium content may vary from 17 to 35 per cent. The stainless steel alloy consists of nickel, chromium, iron and small amounts of carbon and usually small amounts of manganese. Typical stainless steels are 18–8, 26–20, 25–10 and 26–12. The first figure refers to the chromium content and the second figure to the nickel content. The nickel imparts the catalytic activity to the stainless steel. The chromium resists oxidation at high temperatures. Enough chromium is present so that the catalytic activity is not excessive which would result in decomposition of the acetylene all the way to carbon. At the same time

enough chromium is present so that the alloy will stand the high temperatures to which it is subjected. Iron has some catalytic activity for the reaction in question, but is not nearly as effective as nickel.

In a preferred embodiment of the present invention, the ethylene-rich feed to the acetylene-forming step is prepared in a suitable unit and fed substantially immediately (without cooling or separation) to the acetylene unit. I prefer to make the ethylene-rich feed by cracking although if fairly pure ethane is available it might be catalytically or non-catalytically dehydrogenated to ethylene. Suitable feed stocks for cracking include natural gases, C_2, C_2—C_3, C_3, and C_3 and higher cuts from natural gasoline and refinery streams, and liquid aromatic, paraffinic, naphthenic and olefinic streams from various sources. These are cracked in such a way as to produce maximum ethylene concentrations in the product gases. A preferred cracking feed is ethane or propane or, more commonly, a mixture of ethane and propane. Such gases are preferably cracked above 1600° F. and at a pressure of not over 5 pounds per square inch gauge in refractory ceramic cracking equipment, preferably a pebble furnace. Dilution of the feed stock to the cracking step with steam in an amount ranging from 0.5 to 15 mols of steam per mol of hydrocarbon feed is preferred. Generally I use several mols of steam, say from 2 to 4, per mol of hydrocarbon cracking feed. The steam diluent lowers the partial pressure, keeps down carbon formation, and minimizes polymerization of olefins formed and produces the above-noted effects in the acetylene-forming step. The resulting ethylene-rich gas, which preferably contains at least 30 mol per cent of ethylene on a dry basis, is immediately fed to the acetylene-forming unit. No separation is applied to the ethylene-rich gases issuing from the cracking furnace and they are not allowed to undergo any appreciable temperature drop. The exit temperature of the cracking gases may vary from 1600 to 2400° F. In general, the higher the exit temperature the more satisfactory the process because the equilibrium of the acetylene-forming reaction favors acetylene at high temperatures.

Preferably the ethylene-rich cracking effluent is admixed with undehydrogenated recycled ethylene recovered from the effluent of the acetylene-forming step, this recycled ethylene having been preheated to substantially the same temperature as the cracking effluent. The resulting mixture is then fed directly to the acetylene-forming step. I prefer to preheat the recycled ethylene in a pebble furnace; however, less preferably the ethylene recycle may be preheated in a third section of the pebble furnace in which the acetylene is formed. Thus the stainless steel balls withdrawn from the reaction zone may be dropped into a third section immediately below the reaction section and the ethylene recycle stream may be passed through this third section whereby it is preheated by contact with the hot stainless steel balls. This arrangement has the advantage that the stainless steel balls are cooled so that they can be handled without difficulty in the elevator.

In some cases the cracking or dehydrogenation of the original feed stock, such as an ethane-propane mixture, to ethylene may be conducted catalytically. For example, the pebbles used in the cracking furnace may be catalytic so that they catalyze the cracking or dehydrogenation of the original feed to ethylene.

In the accompanying drawing a suitable hydrocarbon feed capable of being cracked or dehydrogenated to good yields of ethylene enters the system via line 1. A preferred feed is ethane or propane or, more commonly, a mixture of ethane and propane. Corresponding olefins, mainly ethylene or propylene, may be present. This feed is cracked to ethylene in pebble furnace 2 in the presence of suitable quantities of steam diluent introduced via line 3. Pebble furnace 2 is of conventional design and comprises a pebble preheating section 4 wherein fuel gas injected via line 5 is burned and reaction section 6 wherein the hot pebbles bring about the desired reaction, namely cracking and/or dehydrogenation to ethylene. The pebbles flow down through the furnace 2 at a constant rate, being elevated by elevator 7 for return to preheating section 4. The reaction effluent leaves via line 8 and may be substantially immediately admixed with recycled ethylene which has been heated in a second pebble furnace 9 to about the temperature of the effluent from furnace 2. Steam is introduced to the feed to furnace 9 via line 10. The heated ethylene is discharged through line 11. The effluents from furnaces 2 and 9 are immediately mixed by merger of lines 8 and 11, as indicated in the drawing.

The resulting gaseous mixture is fed via line 12 into a pebble furnace 13 where it intimately contacts a mass of stainless steel balls and undergoes conversion to acetylene. Instead of a pebble furnace I may use a fixed bed of stainless steel in highly extended form such as balls or turnings. The stainless steel is preferably at a temperature of 2300 to 2500° F., this temperature being attained or maintained in any suitable manner. If unit 13 is a fixed bed, superheating of the feed may be employed.

The shortest possible transfer lines between furnaces 2 and 9 on the one hand and furnace 13 on the other are employed. In practice the three pebble furnaces would be disposed very near to one another, say on the points of an equilateral triangle, with the bodies of the furnaces as close together as possible and the elevators disposed radially outwardly of the bodies of the furnaces.

The acetylene-containing effluent leaving the reaction section of pebble furnace 13 is immediately quenched preferably with water fog sprays, generation and injection of which is indicated diagrammatically by line 14, to a temperature of 500° F. or preferably 300° F. or below to prevent re-reaction and side reactions. The quenched mixture is then passed to a separation system indicated diagrammatically by reference numeral 15, wherein the acetylene and ethylene are separately recovered in concentrated form in any known or suitable manner. The resulting acetylene and ethylene concentrates are withdrawn via lines 16 and 17, respectively. Light gases including hydrogen are taken off via line 18. These light gases may also include any methane that is present in the reaction mixture. Ethane may be withdrawn via line 19. High-boiling material may be withdrawn via line 20. This may include all material heavier than C_3. C_3 material may be withdrawn via line 21. If desired, the ethane and C_3 streams may be recycled to pebble furnace 2 for conversion to ethylene. Both propane and propylene give ethylene in good yields upon pyrolysis.

It will be understood that, depending upon the particular mode of separation employed, one or more of the materials other than acetylene and ethylene may be recovered in admixture with one or more other materials. For example, the ethane and propane may be recovered in admixture, or the ethylene may be recovered in admixture with ethane, or the C_3 and all heavier material may be recovered and withdrawn as a single stream.

One method of separating ethylene and acetylene in concentrated form from a mixture containing same is shown in Welling U. S. Patent 2,395,362. With appropriate additions and modifications such a method might be embodied in separation system **15**.

Separation system **15** may embody any desired arrangement or combination of steps including oil absorption selective solvent extraction, refrigeration or low temperature fractional distillation, gas scrubbing including scrubbing with selective solvents, azeotropic distillation, extractive distillation, fixed bed or continuous moving bed adsorption as with activated charcoal or silica gel, chemical separation or purification, etc.

In many cases the ethylene-containing stream withdrawn by line **17** may contain such quantities of material other than ethylene that it will be desirable to vent a portion from the system as by line **22**, in order to keep such other material from pyramiding to an objectionable extent as would occur if the entire stream were recycled through pebble furnace **9** to acetylene-forming unit **13**. If ethylene stream **17** is sufficiently pure, it is recycled in its entirety.

Light gases including hydrogen taken off via line **18** may often advantageously be used as fuel for the preheating section of pebble furnace **13**. This is indicated by line **23**. Such a hydrogen-rich gas acts as a reducing gas and prevents any tendency to oxidation of the stainless steel pebbles.

Separation system **15** will include suitable provision for removing the water present in the effluent from unit **13** as a result of the use of steam diluent in cracking or dehydrogenation unit **2** and in recycled ethylene heater **9**.

While the three pebble furnaces **2**, **9** and **13** are shown in the drawing as of the same size, this is purely diagrammatic and they may be of different sizes. Actually furnace **13** would in practice be small relative to furnace **2** because it is desired to have very fast heating and very short reaction time in furnace **13** to favor the formation of acetylene.

If desired, means may be provided for superheating the feed to unit **13** above the reaction temperature therein in order to compensate for the endothermic reaction. This is especially desirable where a fixed bed is used to effect formation of acetylene instead of the preferred pebble furnace.

Tar traps may be interposed in the lines between pebble heaters **2** and **9** and unit **13** and also in the line between unit **13** and separation system **15**.

It is preferred to use a large proportion of steam as the diluent in the ethylene recycle preheating step. I prefer to use a greater ratio of steam in this operation than is employed in the cracking step in pebble furnace **2**. This is because of the fact that the ethylene recycle stream is much higher in ethylene concentration and therefore much more subject to polymerization. For example I use 4 mols of steam per mol of ethylene fed to pebble furnace **9** and 2 mols of steam per mol of hydrocarbon fed to cracking furnace **2**.

I claim:

1. The process of preparing acetylene which comprises cracking a C_2 to C_3 paraffinic hydrocarbon stream in admixture with steam in an amount equal to two mols of steam per mol of hydrocarbon charged at a pressure of not over 5 pounds per square inch gauge and at a temperature of approximately 2000° F. to produce an effluent cracked gas having at least 30 mol per cent of ethylene on a dry basis, separately heating a recycle ethylene stream hereinafter identified in the presence of steam in an amount equal to four mols of steam per mol of ethylene to a temperature of approximately 2000° F., commingling said effluent cracked gas and said heated ethylene stream at the resulting temperature of about 2000° F., immediately and without separation or appreciable temperature drop passing the resulting gaseous mixture through a catalytic body of stainless steel, containing at least 7 per cent nickel, having a highly extended surface and previously heated to a temperature of from 2000 to 2500° F. to convert hydrocarbon including ethylene to acetylene, said body of stainless steel being maintained at temperatures within the range of 2000 to 2500° F. throughout said commingling step, immediately quenching the effluent gas with finely divided water to a temperature of not over 500° F., separating acetylene as the product and ethylene from the resulting quenched gas, and recycling said ethylene.

2. The process of preparing acetylene which comprises cracking a C_2 to C_3 paraffinic hydrocarbon stream in admixture with steam in an amount equal to two mols of steam per mol of hydrocarbon charged at a pressure of not over 5 pounds per square inch gauge and at a temperature of approximately 2000° F. to produce an effluent cracked gas having at least 30 mol per cent of ethylene on a dry basis, separately preheating a recycle ethylene stream hereinafter identified in the presence of steam in an amount equal to four mols of steam per mol of ethylene to a temperature of approximately 2000° F., commingling said effluent cracked gas and said heated ethylene stream at the resulting temperature of about 2000° F., immediately and without separation or appreciable temperature drop, passing the resulting gaseous mixture at said temperature into the reaction section of a pebble furnace and there contacting same with a contiguous fluent mass of stainless steel balls, containing at least 7 per cent nickel, maintained at temperatures within the range of 2300 to 2500° F. for a time not in excess of 0.02 second to convert hydrocarbon including ethylene to acetylene, continuously withdrawing the effluent and immediately quenching same with water to a temperature of not over 500° F., continuously withdrawing stainless steel balls from the bottom of said reaction section, elevating same and charging same to the upper portion of the preheating section of said pebble furnace located above said reaction section and there preheating said balls to a temperature of from 2300 to 2500° F. and continuously charging preheated balls from the bottom of said preheating section to the upper portion of said reaction section.

3. The method of claim 2 including the additional steps of separating light gases rich in hydrogen from the quenched effluent and employing said light gases as the combustion medium for heating said balls in said preheating section.

4. A continuous process for forming acetylene which comprises continuously flowing by gravity a contiguous fluent mass of stainless steel balls, containing at least 7 per cent nickel, through a series of substantially vertically extending zones comprising a stainless steel ball heating zone, a reaction zone positioned at a lower level than said heating zone, and a relatively narrow interconnecting zone, each of said zones being substantially filled with said contiguous mass of said stainless steel balls and permitting a relatively unrestricted flow of balls therethrough, continuously contacting that section of said contiguous mass of stainless steel balls flowing through said heating zone with a counter-current stream of hot combustion gas at a temperature and flow rate regulated to insure heating of said balls to a temperature of at least 2000° F., continuously contacting that section of said contiguous mass of balls flowing through said reaction zone with a stream of ethylene-rich gas containing essentially hydrocarbons as reactants introduced to said reaction zone at a temperature of at least 2000° F. and at a flow rate regulated to insure heating of said gas to the reaction temperature whereby a substantial portion of the hydrocarbon including ethylene is converted to acetylene, continuously removing stainless steel balls from the lower portion of said reaction zone, continuously introducing stainless steel balls to the upper portion of said heating zone, continuously withdrawing the effluent from said reaction zone and immediately quenching same with water, and recovering acetylene from the quenched mixture.

5. The method of making acetylene which comprises passing an ethylene-rich gaseous stream containing essentially hydrocarbons as reactants through a catalytic bed constituted by a highly extended mass of stainless steel containing at least 7 per cent nickel and maintained at temperatures within the range of 1600 to 2500° F. for a time such that hydrocarbon including ethylene is converted to acetylene but that decomposition of acetylene is substantially prevented, continuously withdrawing the effluent and immediately quenching same with water to a temperature not over 500° F.

6. A method according to claim 5 wherein the ethylene-rich gaseous stream is at a temperature within the range of 1600 to 2500° F.

7. A method according to claim 5 wherein the conversion to acetylene is effected in the presence of steam as a diluent in a proportion within the range of 0.5 to 15 mols of steam per mol of hydrocarbon feed.

8. A method according to claim 5 wherein the steel is in the form of porous balls having a highly extended surface area.

9. The method of making acetylene which comprises passing an ethylene-rich gaseous stream containing essentially hydrocarbons as reactants which is at a temperature of from 2000 to 2500° F. through a catalytic bed constituted by a highly extended mass of stainless steel containing at least 7 per cent nickel and maintained at temperatures of from 2000 to 2500° F. for a time such that hydrocarbon including ethylene is converted to acetylene but that decomposition of acetylene is substantially prevented, said time ranging from 0.1 second at 2000° F. to 0.005 second at 2500° F., continuously withdrawing the effluent and immediately quenching same with water to a temperature not over 500° F.

10. The method of making acetylene which comprises passing an ethylene-rich gaseous stream containing essentially hydrocarbons as reactants which is at a temperature of from 2000 to 2500° F. through a catalytic bed constituted by a highly extended mass of stainless steel containing from 7 per cent to 30 per cent nickel and maintained at temperatures of from 2300 to 2500° F. for a time such that hydrocarbon including ethylene is converted to acetylene but that decomposition of acetylene is substantially prevented, said time ranging from 0.02 second at 2300° F. to 0.005 second at 2500° F., continuously withdrawing the effluent and immediately quenching same with water to a temperature not over 500° F.

11. The method of making acetylene which comprises passing an ethylene-rich gaseous stream containing essentially hydrocarbons as reactants into the reaction section of a pebble furnace and there contacting said gaseous stream with a contiguous fluent mass of stainless steel balls containing at least 7 per cent nickel and maintained at temperatures within the range of 1600 to 2500° F. for a time such that hydrocarbon including ethylene is converted to acetylene but that decomposition of acetylene is substantially prevented, continuously withdrawing the effluent and immediately quenching same with water to a temperature not over 500° F., continuously withdrawing stainless steel balls from the bottom of said reaction section, elevating same and charging same to the portion of the preheating section of said pebble furnace located above said reaction section and there preheating said balls to a temperature of from 1600 to 2500° F., and continuously charging preheated balls from the bottom of said preheated section to the upper portion of said reaction section.

12. A method according to claim 11 wherein the temperature of the ethylene-rich gaseous stream is from 2000 to 2500° F. and wherein the stainless steel balls are maintained at temperatures of from 2000 to 2500° F. and wherein the contact time of said gaseous stream with said steel balls is not in excess of 0.1 second.

13. A method according to claim 12 wherein the stainless steel balls are maintained at temperatures within the range of 2300 to 2500° F. and wherein the contact time of the ethylene-rich gaseous stream with said stainless steel balls is not in excess of 0.02 second.

SAM P. ROBINSON.

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