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MANUFACTURE OF ACETYLENE AND ETHYLENE

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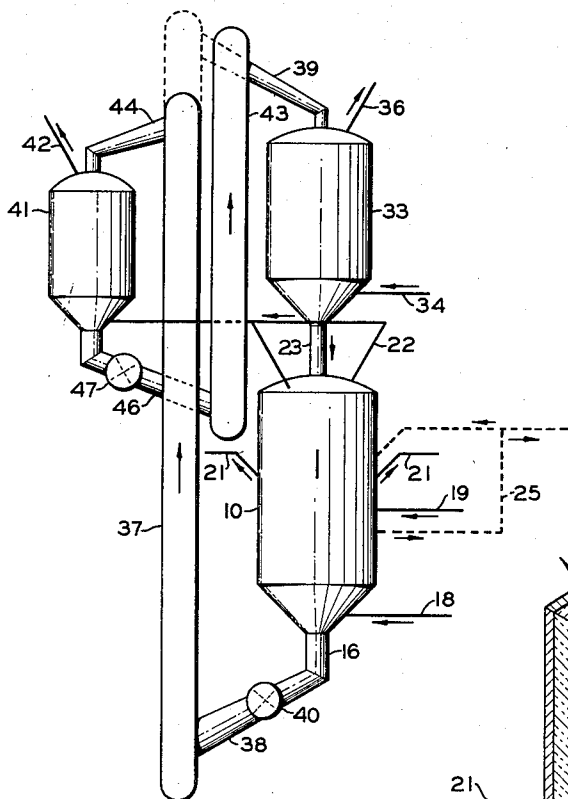


FIG. 3.

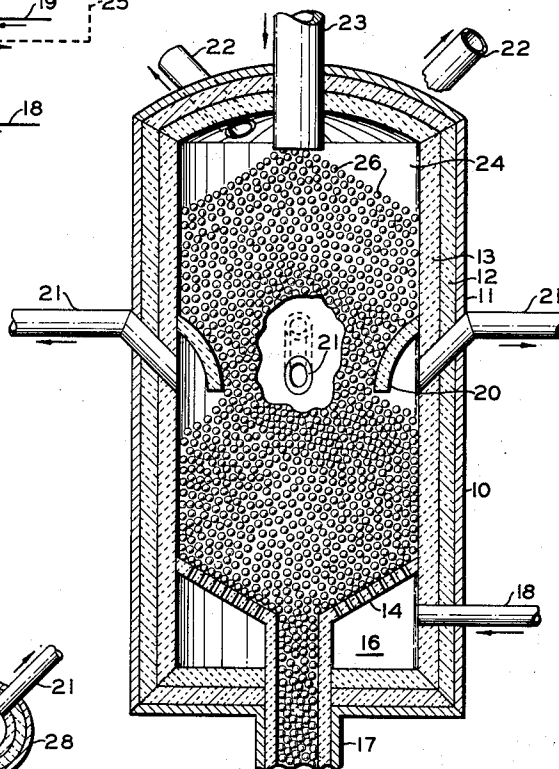


FIG. 1. INVENTOR.
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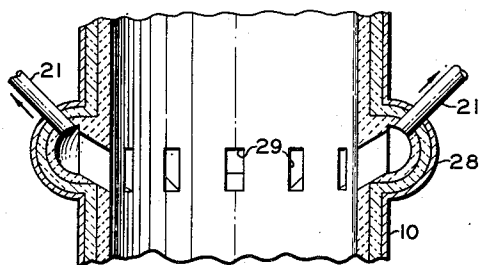


FIG. 2.

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MANUFACTURE OF ACETYLENE AND
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11 Claims. (Cl. 260—679)

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This invention pertains to the conversion of hydrocarbons to acetylene and ethylene in pebble heater type apparatus.

Pebble heater type apparatus is finding increasing favor in effecting the conversion of various types of hydrocarbon streams into more desirable hydrocarbons, particularly hydrocarbon conversions involving cracking and reforming. Typical pebble heater operation entails heating a gravitating mass of refractory pebbles in an upper heating chamber by contact with hot flue gas formed in the bottom of the chamber by combustion of a light hydrocarbon fuel with air, gravitating the resulting hot stream of pebbles through a restricted pebble throat or passageway into a lower chamber wherein the hot column of pebbles is contacted in countercurrent flow with a stream of hydrocarbon vapor under conversion conditions of temperatures, time, and pressure. The stream of pebbles emerges from the bottom of the reactor or furnace considerably cooled and flows downwardly to the lower end of a pebble elevator which elevates the pebbles to a chute leading into the upper part of the pebble heating chamber through which they are delivered to be reheated. In this manner heat is imparted to the refractory pebbles which are utilized to carry the heat for the process to the conversion chamber. In this type of operation, as contrasted with hydrocarbon conversion in a regenerative furnace, the flue gas for the process is not mixed with the hydrocarbon product and it is also possible to operate continuously on-stream in the conversion of the hydrocarbon.

The term "pebble" as referred to throughout the specification includes any particulate refractory contact material of suitable form, size, and density, to be readily flowable through the pebble heater chambers and capable of withstanding temperatures upwards of 3000° F. The pebbles are preferably spherical and range from $\frac{1}{8}$ to 1" in diameter. Uniform shapes and sizes are preferred but pebbles of irregular shapes and sizes are operable with less efficient results. Common materials utilized in forming pebbles include alumina, mullite, zirconia, thoria, periclase, synthetic and natural clays, either alone or in combination with each other.

A specific application of the pebble heater to hydrocarbon conversion is in the cracking of a vaporous hydrocarbon stream to acetylene. A column of refractory pebbles is heated in a pebble heating chamber by contact with hot combustion gas to a temperature at least 150° F. above the desired cracking temperature and the hot

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pebbles are gravitated through a reaction chamber in a contiguous compact column. The hydrocarbon to be cracked is introduced to the bottom of the reaction chamber and flows upwardly in contact with the descending pebbles so as to raise the temperature of the hydrocarbon to cracking temperature and crack the same to lighter hydrocarbons, particularly acetylene. Because of the fact that cracking to acetylene requires extremely high temperature, a relatively large amount of heat at the elevated temperatures, fast heating, and short reaction time for optimum yields, it is found that the effluent pebble temperature from the reaction chamber is so high that ordinary cast iron and steel transfer equipment cannot be used in elevating the pebbles to the pebble heating chamber. For example, it has been found that in cracking a hydrocarbon feed consisting principally of methane by this method, even though the feed is introduced at a temperature of 100° F. and the effluent product temperature is 2600° F., using pebbles from the pebble heating chamber at 2800° F. the effluent pebbles from the reactor are cooled down to only about 1500° F. These very high temperature pebbles necessitate a special design and high temperature alloys for the elevator equipment that carries the pebbles from the bottom of the reactor to the top of the pebble heating chamber. Another serious disadvantage is that the feeding of these high temperature pebbles into the pebble heating chamber results in an extremely high stack gas temperature and consequently in large heat losses in the stack gases.

The principal object of the invention is to provide a pebble heater process for manufacturing acetylene as a primary product and ethylene as a secondary product which effects optimum yields and more efficiently utilizes the available heat in the pebble stream. Another object of the invention is to provide a pebble heater acetylene and ethylene producing process which lowers the temperature of the effluent pebbles from the reactor sufficiently to permit the use of ordinary cast iron and steel elevator equipment. A further object of the invention is to reduce stack gas heat losses in a pebble heater process for making acetylene. Other objects of the invention will become apparent from the accompanying disclosure.

I have devised a process for the conversion of a gaseous hydrocarbon stream to acetylene which accomplishes the foregoing objectives. In accordance with this process a compact stream of

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pebbles is heated in the pebble heating chamber to a temperature in the range of 1800 to 3400° F. by contact with hot combustion gas produced by burning a light hydrocarbon fuel in the lower portion of the chamber. The hot compact stream of pebbles is continuously gravitated to a lower conversion or cracking chamber through which the pebbles pass in countercurrent contact with hydrocarbon in vapor phase so as to crack a considerable portion thereof to acetylene. The hydrocarbon feed in vapor form is introduced into the bottom of the conversion chamber which encloses the gravitating compact stream of pebbles so as to provide a feed preheating section in the lower portion, an ethylene forming intermediate section, and an acetylene forming upper section. As the hydrocarbon feed passes upwardly through the chamber it is brought to cracking temperature and a portion thereof is cracked to lighter hydrocarbons in the intermediate section. Ethylene makes up a substantial portion of the cracked gases in the intermediate section. A portion of this ethylene-rich gas is withdrawn directly from the intermediate section so as to reduce the proportion of hydrocarbon passing into the acetylene forming section, thereby providing faster heating of the ethylene and other hydrocarbon gases passing into the acetylene forming section. This feature results in higher yields of acetylene in terms of the hydrocarbon passed into this zone or section in comparison to the yield obtained without withdrawing an ethylene containing stream from the intermediate section. An acetylene-rich effluent is withdrawn from the top or upper section of the reactor at a temperature in the range of about 1700 to 3200° F.

By withdrawing a partially cracked hydrocarbon stream, preferably ethylene-rich, from the intermediate section of the reaction chamber it is feasible to control pebble outlet temperature so that effluent pebbles are cooled to a temperature below 800° F. By reducing the effluent pebble temperature from the reaction zone below this temperature, viz. 800° F., it is feasible to transfer the pebbles to the pebble heating chamber in ordinary cast iron and steel elevator equipment whereas without this effluent removal from the intermediate section the pebbles come out of the reactor so hot that it is necessary to use special alloy equipment to effect the transfer.

An attendant advantage of the process of the invention is in the lowering of the stack gas temperature from the pebble heating chamber. In normal operation the pebbles going into the pebble heating chamber are considerably above the temperature at which ordinary cast iron and steel elevator equipment can be used, for example, around 1500° F. Even when cracking the hydrocarbon stream to acetylene at the lower temperatures of the range it is difficult if not impossible to so operate that the effluent pebble temperature from the reactor is below 1000° F.

It can readily be seen that any withdrawal of partially cracked effluent from the intermediate section of the reactor aids in reducing pebble outlet temperatures and also in effecting faster heating and cracking of the partially cracked gases in the acetylene forming section so as to improve the yield of acetylene. However, it is preferred to withdraw a side stream from the intermediate section which is in the range of 30 to 90 weight per cent of the hydrocarbon feed. The acetylene may be recovered from this side

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stream as a product of the process and the remaining fraction may be recycled to the feed and cracked further. If desired, other constituents may be separated from the side stream before recycling the residue to the feed.

In another modification of the process and apparatus, the high temperature acetylene-rich effluent is contacted in countercurrent flow in a pebble quench chamber with pebbles transferred from the bottom of the reaction chamber to the top of the pebble quenching chamber so as to quickly reduce the temperature of the acetylene-rich product and preheat the pebbles which are then transferred to the pebble heating chamber by means of another elevator.

As discussed hereinafter in reference to the drawing the invention also provides for the introduction of a second, more refractory hydrocarbon feed to the reactor at an intermediate section thereof where the temperature is suitable for cracking the particular feed introduced at that point. When introducing a propane-rich feed to the bottom of the reactor, a preferable secondary feed is ethane. Any secondary feed should be preheated, of course.

In a further modification of the process of the invention, a portion of the ethylene-rich stream resulting from propane cracking in the lower portion of the reactor is taken off as a side stream just below the level of introduction of the ethane stream, and a portion or all of this ethylene-rich side stream is introduced to the acetylene-forming section of the reactor.

For a more complete comprehension of the invention, reference may be had to the drawing of which Figure 1 is a vertical cross-section of a pebble heater reactor for preforming the invention. Figure 2 is a partial vertical section of a pebble heater reactor similar to that shown in Figure 1 showing a different modification of the effluent withdrawal means, and Figure 3 is an elevational view showing diagrammatically the positional relation of the pebble heater reactor of Figure 1 in a conventional pebble heater arrangement.

Referring to Figure 1, numeral 10 designates a reaction chamber having metal shell 11, a pair of refractory linings 12 and 13 of which the inner lining 13 is made up of high temperature refractories capable of withstanding temperatures upwards of at least 3000° F. A perforate conical false bottom 14 in the lower section of the chamber is spaced apart from the bottom thereof to form a gas distributing space 15. Perforate conical bottom 14 joins an upright conduit leading into pebble outlet 17. Line 18 serves to introduce the hydrocarbon feed to the distributing space below conical bottom 14 for distribution upwardly through the reactor. A ring baffle 20 is disposed within the reactor intermediate the ends thereof to form an annular gas collecting space between the baffle and the lining of the reactor with which effluent conduits 21 communicate. This arrangement provides a means of withdrawing gaseous effluent from the intermediate section of the reactor. While the arrangement shown indicates the use of four effluent withdrawal lines, any number may be utilized for this purpose. Another group of effluent withdrawal lines 22 are positioned in the top of the reactor for withdrawing gaseous effluent therefrom. A pebble inlet conduit 23 is disposed axially of the reactor and extends therinto a short but substantial distance so as to provide a vapor space 24 between a bed of

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pebbles 26 (introduced through the conduit) and the dome of the reactor. Vapor collecting space 24 should be small enough to avoid unduly increasing residence time of the cracked hydrocarbon in this part of the reactor but should be sufficient in depth to avoid entrainment of the pebbles in the effluent gas passing out through lines 22.

The arrangement shown in Figure 2 utilizes a gas collecting or bustle ring 28 around reactor 10 at the approximate location of the effluent lines in Figure 1. A series of ports or openings 29 lead upwardly and outwardly from the interior of the reactor so as to avoid pebble flow into the bustle ring. This structure is preferred in most installations because it avoids converging pebbles toward the center of the bed in this area and permits vertical flow thereof.

The vertical location of the effluent takeoff structure in the intermediate section of the reactor depends upon the flow and reaction conditions desired as well as upon the character of the partially cracked gas which it is desired to remove from the intermediate section of the reactor. It can be readily determined by one skilled in the art, once the desired type of feed and reaction conditions are known, just where the proper vertical location of the effluent lines should be.

Figure 3 shows a reactor 10 similar to that of Figure 1 in vertical alignment with a pebble heating chamber 33 connected thereto by throat 23. Line 34 leads into the bottom of pebble heating chamber 33 and feeds a combustible mixture to burners positioned in the bottom of the heater or a hot combustion gas directly into the heating chamber. Combustion gas passes upwardly through the bed of pebbles to a stack 36 which carries the flue gas to any suitable use or disposal. Elevator 37 connects with pebble outlet 16 through chute 38 and with pebble quench chamber 41 through chute 44. Product effluent lines 22 connect with the lower section of quench chamber 41 and the cooled effluent is passed via line 42 to a steam or water quench not shown. A pebble feeder 40 is positioned in chute 38 and serves to control the flow of pebbles through the heater and reactor. A chute 45 connects the quench chamber pebble outlet conduit with the bottom of a second elevator 43 which elevates pebbles passing feeder 47 to chute 39 for delivery into heater 33.

In another modification of the apparatus, elevator 37 connects directly with chute 39 as shown by dotted lines, thereby eliminating quench chamber 41 from the primary pebble circulation system. In a further modification, quench chamber 41 may be positioned above and in line with the other two chambers so as to connect directly with pebble chute 39, thereby eliminating one of the elevators.

Reactor 10 of Figure 3 is modified so as to illustrate another feature of the invention whereby a second more refractory feed such as ethane is introduced to the reactor through line 19 at a level below that of effluent line 21. By introducing an ethane-rich feed at this point, the high temperature pebbles at this level are utilized to crack ethane and the temperature of the pebbles from the ethane cracking zone is still sufficiently high to crack less refractory propane. This arrangement and manner of operation permits greater flexibility of operation and makes for more efficient utilization of heat in the reactor.

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An effluent line (dotted) 25 shows a further modification of the invention which entails withdrawing an ethylene-rich stream from the upper end of the propane cracking section and returning the same to the reactor at a level above the effluent line 21 and in the lower section of the acetylene-forming section of the reactor.

The feed to the process is preferably a normally gaseous hydrocarbon stream comprising principally methane, ethane, propane, or butane, either as single component feed stocks or in admixture. Natural gas can be utilized as the feed stock and it is advantageous to use steam as a diluent with this feed. Steam may also be utilized as the diluent with the other feeds contemplated. Various types of diluents may be utilized, either truly inert or partially inert, in the process. Partially inert diluents are simply more refractory than the feed gas to be cracked. Steam and methane are examples of partially inert diluents for the less refractory hydrocarbon feeds. The ratio of diluents to hydrocarbon feed may vary considerably but will usually be in the order of 0.1 to 5 mols of diluent per mol of feed.

The proportion of feed withdrawn from the intermediate section of the reactor varies considerably but it is advantageous to maintain the proportion in the range of 30 to 90 weight percent based on the weight of the feed. It can readily be seen that the withdrawal of any portion of the hydrocarbon stream passing through the reactor as an effluent from the intermediate section of the reactor effects a proportionate increase in the rate of heating in the upper acetylene-forming section thereof and also lowers the effective pebble outlet temperature when compared to the temperature which would result if only the portion of the hydrocarbon feed passing through the upper section were passed through the lower section without any intermediate withdrawal.

The illustrative details set forth herein are not to be construed as imposing unnecessary limitations upon the invention, the scope of which is set forth in the claims.

I claim:

1. A process for manufacturing acetylene and ethylene which comprises maintaining a gravitating column of hot pebbles in an upright elongated enclosed reaction zone at an entering temperature in the range of 1800° to 2800° F.; passing a stream of normally gaseous hydrocarbon feed at a temperature below 500° F. into the lower end of said zone in contact with said column and in countercurrent flow with said pebbles so as to preheat said feed to cracking temperature in the lower section of said zone and cool said pebbles to a temperature below 800° F.; cracking said feed to ethylene in an intermediate section of said zone; withdrawing an effluent comprising ethylene directly from said intermediate section so as to reduce the volume of hydrocarbon passing upwardly from said intermediate section and thereby increase the rate of heating in the upper section of said reaction zone; passing the remaining hydrocarbon upwardly through said zone directly from said intermediate section through the next adjacent section of said zone and cracking same to acetylene in the upper section of said zone; and withdrawing an effluent comprising acetylene from the upper end of said zone.

2. The process of claim 1 in which the amount of effluent comprising ethylene is maintained

in the range of 30 to 90 weight per cent of the feed.

3. A process for manufacturing acetylene and ethylene which comprises heating a gravitating column of pebbles to a temperature in the range of 1800° to 3400° F. in an upper heating zone; gravitating said column through a separate lower reaction zone comprising an upper acetylene-forming section, an intermediate ethylene-forming section adjacent said upper section, and a lower feed preheating section adjacent said intermediate section; introducing a hydrocarbon feed in vapor form at a temperature below 500° F. into the bottom of said preheating section and passing same upwardly through said reaction zone in direct contact with said pebbles; preheating said feed to cracking temperature in said preheating section and cooling said pebbles therein to an outlet temperature below 800° F.; passing the preheated feed directly to said intermediate section and cracking said feed to ethylene therein and withdrawing an effluent comprising ethylene directly therefrom so as to reduce the volume of hydrocarbon passing upwardly from said intermediate section and thereby increase the rate of heating in the upper section of said reaction zone; passing the remaining portion of the hydrocarbon stream directly from said intermediate section through said upper section and cracking same to acetylene; withdrawing an effluent comprising acetylene from said upper section; and transferring the cooled pebbles to said upper heating zone.

4. The process of claim 3 in which the amount of effluent comprising ethylene is maintained in the range of 30 to 90 weight per cent of the feed.

5. The process of claim 3 in which said hydrocarbon feed is a propane-rich stream.

6. The process of claim 3 in which a second more refractory feed is introduced into said reaction zone intermediate the point of introduction of feed to the preheating section and the point of withdrawal of effluent from said intermediate section.

7. The process of claim 6 in which the feed to said preheating section is a propane-rich stream and said second feed is an ethane-rich stream.

8. The process of claim 3 in which the cooled pebbles egressing from said preheating section are contacted with the acetylene-rich effluent from the acetylene-forming section so as to quench said effluent and preheat said pebbles before the same are transferred to said upper heating zone.

9. The process of claim 3 in which an ethylene-rich side stream is withdrawn from the ethylene-forming section below the point of withdrawal of said effluent comprising ethylene and the same is introduced into the lower section of the acetylene-forming section.

10. In a process for cracking a vaporous hydrocarbon stream in a pebble heater by contacting said stream in countercurrent flow with an enclosed gravitating column of hot pebbles under conditions such that a portion of said stream is cracked to ethylene in an intermediate section of said column and to acetylene in the next adjacent upper section, the improvement comprising withdrawing an effluent comprising ethylene as a side stream from said intermediate section and passing the remaining stream upwardly through said next adjacent upper section so as to pass a larger amount of hydrocarbon through the lower and intermediate sections of said column, thereby reducing pebble outlet temperature to less than 800° F., and so as to pass a smaller amount of hydrocarbon through said upper section, thereby effecting more rapid heating and greater conversion to acetylene therein.

11. The process of claim 10 in which the amount of said side stream is in the range of 30 to 90 weight per cent of the feed.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,464,257	Pelzer et al.	Mar. 15, 1949
2,482,438	Robinson	Sept. 30, 1949
2,486,627	Arnold	Nov. 1, 1949
2,518,688	Hasche	Aug. 15, 1950
2,532,613	Dutcher	Dec. 5, 1950
2,582,016	Dutcher	Jan. 8, 1952