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PROCESS FOR PREPARATION OF ACETYLENE

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Fig.1.

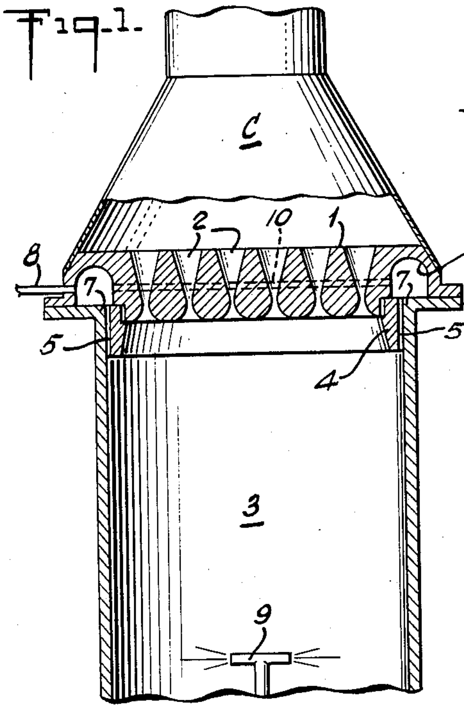


Fig.4.

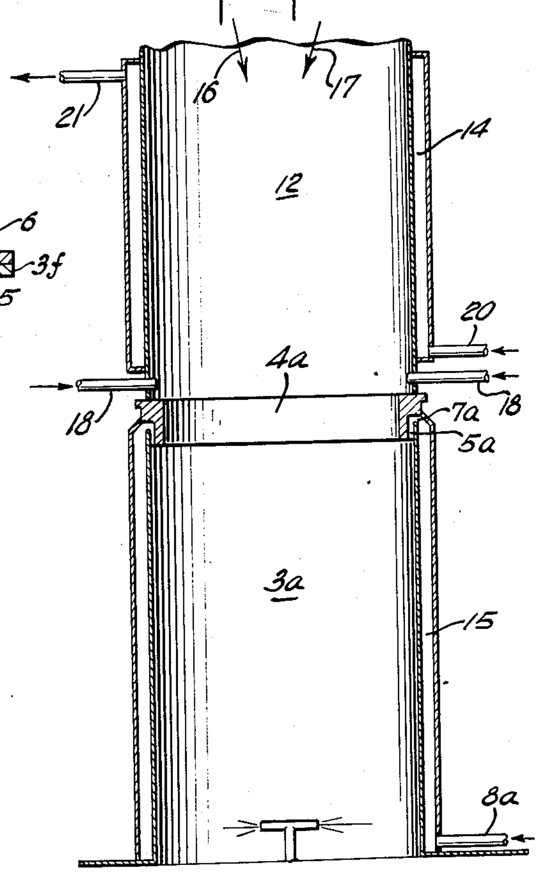


Fig.2.

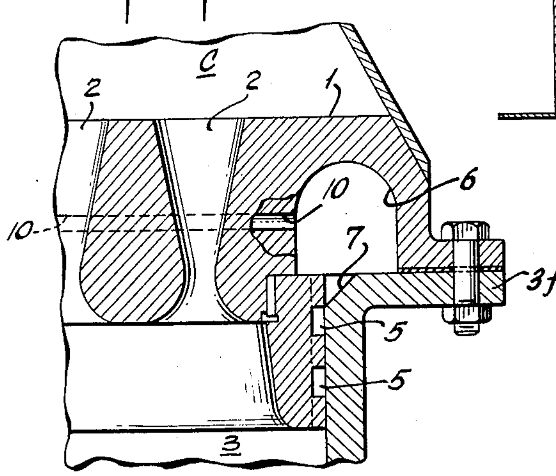


Fig.5.

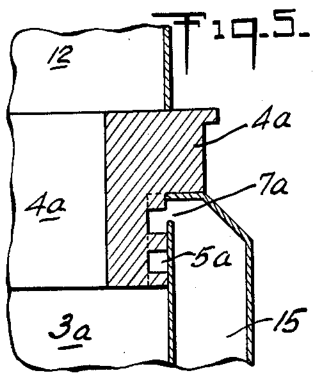
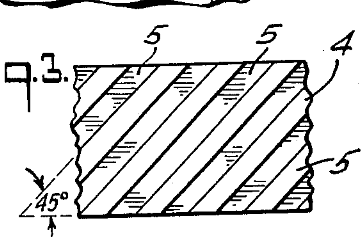


Fig.3.



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PROCESS FOR PREPARATION OF ACETYLENE

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This invention relates to thermal treatment of hydrocarbons and to apparatus for carrying out such treatment, and is particularly concerned with furnaces and methods for the preparation of unsaturated hydrocarbons, especially acetylene and olefines such as ethylene.

These unsaturated hydrocarbons may be prepared by heating more saturated hydrocarbons for a short time to high temperatures, either in the gaseous state or in the form of finely divided liquids. For this purpose, a hydrocarbon raw material may be subjected to a partial combustion or introduced into hot combustion gases. The various apparatuses which have already been proposed for this purpose suffer from certain disadvantages, especially due to deposit of carbon on the walls of the chambers in which pyrolysis occurs. These deposits have to be periodically removed, in order to continue regular operation of the process, with a satisfactory yield of the unsaturated hydrocarbon products. Furthermore, furnaces which are entirely of, or partially manufactured of, refractory materials have been found to suffer from leakages after a certain period of operation and, although metal chambers are more resistant to such leakage, they are subject to disadvantage due to thermal expansion and possible undesirable catalytic action of the metal.

It is an object of this invention to produce continuously, unsaturated hydrocarbons with high yields, and to provide equipment for such production which is free from the disadvantages mentioned above.

According to the invention of a prior copending application, Serial No. 432,216, filed May 25, 1954, of which this application is a continuation-in-part there is provided a pyrolysis chamber, and a burner or other means for intermingling and feeding gases into a reaction zone within the chamber, and a ringlike distributing device near the top of the reaction zone for supplying an annular screen (sometimes referred to herein as a curtain) of fluid inside of the walls of the pyrolysis chamber so that the reaction zone is surrounded and confined by the fluid screen. This invention is also utilized here.

According to the present invention, the distributing ring is designed to establish spirally directed flow of the liquid on the inner wall of the chamber, advantageously by numerous jets directed along said wall and merging together so as to produce a descending screen of liquid helically flowing on the inner surface of the chamber.

Thus, according to the present invention, the effective walls of the pyrolysis zone are liquid and dynamic instead of solid and static, and the flowing liquid covers the entire area of the chamber wall, and flows together immediately if any discontinuity should occur. The liquid thus serves to entrain particles of solids or other deposits from the pyrolysis zone, and to protect the walls from undesirable effects of the thermal reaction, and likewise to protect the reaction mixture from any catalytic effect of the metallic walls of the chamber.

The liquid screen which forms on the wall is substantially homogeneous even if said liquid should encounter an irregularity; and the liquid can conveniently be supplied at relatively low pressure and flows at a relatively low rate of speed. Thus, the solid walls of the pyrolysis chamber are not exposed to the reaction and a high

efficiency of the protective curtain is obtained. It is an important advantage of this invention that the device for establishing and maintaining the surrounding screen of fluid can be added to, and used with, existing apparatus designed for pyrolysis of hydrocarbon, without otherwise substantially modifying the structure.

In the accompanying drawings, we have shown diagrammatically, and will describe below, several preferred embodiments of the invention. These are selected and presented here to illustrate the principles of the invention and the best manner of embodying it in practical operation, and are not intended to be exhaustive of the invention but, on the contrary, to so explain, and instruct others with regard to the invention that they may be enabled to utilize the invention and to modify and substitute within the scope of the invention as may be best adapted to the conditions of each particular use.

In these drawings,

FIGURE 1 is a fragmentary view, partly in elevation and partly in vertical section, with the grooved ring 4 sectioned parallel to the grooves 5, of a reaction chamber embodying the present invention and adapted for carrying out the process of the present invention.

FIGURE 2 is a fragmentary enlarged section of a detail of FIGURE 1.

FIGURE 3 is a schematic diagrammatic development of the outside face of the ring 4, showing the angular relation of the liquid-supplying channels through which the screen-forming liquid flows.

FIGURE 4 is a view, in vertical axial section, of another embodiment of the invention designed particularly for pyrolysis of hydrocarbons by injecting them into hot combustion gases, and

FIGURE 5 is a fragmentary sectional view on an enlarged scale of one section of the distributing ring of FIGURE 4.

Referring first to FIGURES 1 to 3, a disc-like distributor 1 is provided at the top of a vertical cylindrical pyrolysis chamber 3 and at the lower end of a conduit C which supplies a continuous flow of the feed hydrocarbon mixture, with a small amount of oxygen sufficient to give the desired partial combustion. Channels 2 extend through this disc distributor 1, to form burner jets for the supply of hydrocarbon and oxygen into the reaction chamber 3. The Venturi-like spaces which form these jets provide a zone of increased velocity in which the linear flow rate of the gas mixture is more rapid than the rate of flame propagation in the gas. This, plus the cooling effect of the distributor disc, prevents flame from striking or exploding back through the distributor disc.

Fitted into the top of the chamber 3, and peripherally around the bottom of the distributor 1, is a ring 4 which distributes and directs a flow of liquid so that it forms a continuous annular screen around the combustion space on the inside of the chamber 3. This ring 4 is helically grooved on its outer periphery, which is fitted against the inner surface of the chamber 3. Such grooves are shown at 5 in FIGURES 1 to 3, and advantageously are helically arranged at a 45° slope, as indicated diagrammatically in FIGURE 3.

An annular channel 6 is formed near the periphery and on the underside of the disc 1 to serve as a header conduit for supplying the curtain fluid to the distributor ring 4, such fluid being conveniently supplied through a pipe 8, as shown on the lefthand side of FIGURE 1. Adjacent the channel 6, the bottom of the ring 1 is fitted on the one side to a flange 3F on the top of the chamber 3 and, at the other side, to the top of the ring 4. The outer face of the ring 4 is fitted to the inner surface of the chamber 3. The grooves 5 provide channels between ring 4 and the chamber walls, for flow of the screen liquid. The grooves 5 advantageously extend at a substantial angle to the normal and to the axial planes of the chamber **3**, so that a helical flow is induced and the jets of curtain liquid which flow out from the grooves **5** soon spread, under the influence of gravity, to completely cover the area around the reaction space in the chamber **3**. Even if the liquid should encounter an irregularity, gravity will flow the liquid down around it on the far side and thus maintain full coverage of the wall.

To facilitate the flow of liquid from the annular channel **6** into the grooves **5**, the upper corner of the chamber **3** is chamfered, as indicated at **7**.

A jet spray is shown diagrammatically at **9**. This supplies quenching water at the bottom of the reaction zone **3**, whereby to cool the gases and terminate the reaction, and also serves, to some extent, to wash out undesired reaction products from the gases.

Heat-exchange pipes or other channels for circulating cooling fluid may be provided in the disc **1**, as indicated at **10** on FIGURES 1 and 2.

In the practice of the invention in this apparatus, the reaction gases are supplied through the inlet conduit C to the distributor disc **1**, and flow through the Venturi-like openings **2** into the interior of the reaction chamber **3**. In the example here described it was found advantageous to maintain a gas flow rate of about 80 meters per second. At the same time, the curtain fluid, e.g., water, flows in through the inlet pipe **8** and the annular channel **6** and over the chamfered edges **7** into the helical grooves **5** in the distributor ring **4**, and emerges in streams from the bottoms of the grooves **5**, respectively, which, when released from the confining grooves, spread out under the influence of gravity and centrifugal force and surface attraction, so as completely to cover the interior of the chamber **3** with a flowing screen of water. The flow of water in the curtain is at a rate about 40–50 cm./sec. in the apparatus shown. The fluid thus forms a substantially continuous stream which is helically displaced over the inside walls of the pyrolysis chamber and remains in contact with the inside walls. By reason of its flow rate, its residence time in the reaction chamber is too short for serious loss of the liquid curtain by evaporation.

By the use of the distributing device, the solid and static walls of the pyrolysis zone are, in practice, replaced by continuous and dynamic liquid walls which entrain the carbon particles deposited from the pyrolysis reaction mixture. At the same time, the screen of fluid makes it possible to maintain a substantially unchanging pyrolysis zone, to protect the walls from the thermal effects of the reaction and to avoid any catalytic influence which the solid material of the chamber walls might otherwise have on the reaction itself. To any extent that the screen liquid vaporizes, it introduces a barrier space between the actual reaction and the liquid screen. To a corresponding extent, this reduces deposit and solution of the reactants and reaction products on the liquid screen. It also reduces further vaporization. The liquid should be kept as much as possible in the screen, and not projected into the hot gases.

In comparison with previously proposed devices, and under the same conditions in the pyrolysis chamber, the liquid screen is more homogeneous, and lower pressures and lower flow rates may be used. No substantial parts of the walls of the pyrolysis chamber remain unprotected.

The gaseous reaction products formed by the combustion reactions in the pyrolysis chamber **3** are quenched by transverse ejection of water at **9**.

If the reaction is such as to give a serious tendency to overheating of the distributor **1**, cooling fluid is passed through the pipes or other channels **10**.

Referring now to FIGURES 4 and 5 of the drawing, a distributor ring *4a* receives the screen fluid and distributes it around the interior of the chamber *3a* in the same manner as described above. This distributor ring *4a* is externally grooved like the distributor ring **4** and is fitted to the inside wall of chamber *3a*, as shown in FIGURES 4 and 5.

Above the ring *4a* is a combustion chamber **12**, the exterior wall of which is provided with an annular cooling jacket **14**.

The wall of the chamber *3a* is likewise jacketed, the interior of the jacket **15** communicating with the grooves *5a* through openings, or an annular opening, *7a*, so that the curtain fluid which enters the jacket at *8a* passes up through the jacket and into the grooves *5a* and thence is discharged through the grooves *5a* onto the interior of the chamber wall to form a continuous helically-downwardly flowing fluid curtain which covers and protects the wall.

In the operation of the furnace just described, fuel gas and oxygen enter the combustion chamber **12** at the top, as indicated by the arrows **16** and **17**, and are burned within the chamber **12**. The hydrocarbon which is to be treated by pyrolysis is injected under pressure through the inlet pipes **18** into the hot gases from this combustion in the chamber **12**, and the resulting mixture then passes into the pyrolysis chamber *3a*. If the hydrocarbon is liquid, it will be injected as a spray or a fine jet which will break up into a spray.

In a specific example, with a reaction chamber *3a* of 14 cm. diameter the throughput of the gaseous mixture through the chamber *3a* is about 1200–1500 standard cubic meters per hour equivalent to a flow rate of approximately 30 centimeters per second. The temperature to be maintained in the reaction chamber depends upon the nature of the starting hydrocarbon and of the unsaturated hydrocarbons to be obtained. Generally, in the furnace of FIG. 1, the temperatures are in a range of 600 to 700° C. and in general will not exceed 1400° C. In the furnace of FIG. 4, the temperature is very high in chamber **12**, but in chamber *3a* it does not exceed 1100° C., due to the cooling produced firstly by the hydrocarbon to be pyrolyzed, injected from **18**, and then by the endothermic pyrolysis reaction starting immediately at the level of pipes **18**.

Cooling fluid meanwhile flows through the jacket **14** from the inlet at **20** to the outlet **21** and along the wall of chamber *3a*, advantageously at a rate about 40–50 cm./sec.

Water is the fluid generally used. Other liquids, which are non-inflammable or ignite with difficulty, and are not too volatile to remain liquid on the wall, may be employed instead; for instance, heavy oils. Such oils are more adherent than water to the inside walls of the furnace, and make it possible to achieve higher temperature conditions in the furnace. A wetting agent may be added to the screen fluid to reduce the surface tension thereof, or to improve its tendency to spread over and remain on the surface while flowing readily thereover.

The throughput of the fluid, and as a consequence the rate of flow in the screen, should be sufficient that the contact time and the thermal exchange between the screen and reacting gases is very brief. As a consequence there is substantially no evaporation, in any case less than 5%. On the other hand the throughput should be kept lower than 300 liters per hour per decimeter of the chamber periphery, and advantageously below 250 liters of water. With higher throughput, there is danger of eddies in the curtain supply causing the curtain liquid to project into the gases. Water may be supplied at ordinary pressures such as 1.5–2 kg./cm.

Whatever the throughput of the fluid forming the screen may be, the fluid should not project itself into the reacting gases.

The fluid screen, since it is formed directly at the inlet of the pyrolysis chamber, completely covers and protects the wall of the chamber. Consequently, the pyrolysis reaction is carried out under the best thermal conditions and in a zone the dimensions of which are fixed to give high acetylene yield.

The following are examples of particular operations taking advantage of the invention described above:

Example I

A mixture of 1900 cubic meters per hour of a coke oven gas fraction having approximately 85% of C_1 and C_2 hydrocarbons and 1000 cubic meters per hour of oxygen is introduced into the furnace represented in FIGURE 1 through the inlet pipe C and through the openings **2** of distributor **1**, these gases being at a temperature of approximately 450° C. as they pass through the distributor.

2.5 cubic meters per hour of water are introduced through pipe **8** and annular channel **6** of the groove **7** and into the helical grooves **5**. This water, discharging onto the wall of the chamber **3** from the ends of the grooves **5**, forms a liquid water screen with helical flow along the internal face of the metallic wall of the combustion and pyrolysis chamber **3**.

The rection of partial combustion in the chamber yielded 3400 cubic meters per hour of the pyrolysis gas containing 10 kilograms per hour of carbon black. These pyrolysis gases are quenched near the bottom of the chamber by a transverse water spray **9**.

The resulting acetylene content amounted to 7.2% of the effluent gases. Approximately half of the carbon black quantity was entrained with the pyrolysis gas and was removed from the latter during the purification steps. The remaining portion was recovered with the effluent water from the reactor, which included both the water from the liquid screen and the quenching water from the spray **9**.

Even after weeks of operation in this manner, inspection of the reactors reveals no traces of carbon deposits or tarry materials. Although some small asperities may appear on the wall of the pyrolysis chamber, experience shows that the water screen is not "torn" by such asperities. The helical movement of the water screen is assurance in this respect.

Because the dimensions of the combustion chamber remain constant, the acetylene content in the pyrolysis gas also remains constant and relatively high.

A comparative operation, carried out under the same conditions and in the same apparatus, but without the water screen, choked up with carbon and other deposits to such an extent that operation of the plant had to be stopped after a run of a relatively few hours and the wall of the combustion chamber had to be cleaned each time before the operation continued.

Example II

4800 cubic meters per day of oxygen preheated to 450° C., 5200 cubic meters per day of coke oven gas having 59% of hydrogen and 25.5% of methane, also heated to 450° C. were introduced into the combustion chamber of the furnace represented in FIGURE 4 at the points indicated by the arrows **16** and **17**, respectively.

Into the superheated gas or vapor formed by the combustion of this gas, which has a temperature of approximately 1400° C., there is injected through the pipes 18 4,070 cubic meters per day of a propane-butane mixture, preheated to 350° C. and having the following composition:

	Percent by volume
Propane	82.3
Butane	15.3
Butene	2.4

At the same time, water at the rate of 21 cubic meters per day is introduced through the openings **7a** into the grooves **5a** to form a water curtain with helical flow along the wall of the chamber **3a** while the pyrolytic decomposition of the propane-butane mixture progresses at high temperature within the space surrounded by this liquid curtain.

The product gases are quenched by the spray **9**, and are found to contain 9.8% by volume of acetylene, and 11.2% of ethylene (calculated on a dry gas basis).

This furnace has been used for the simultaneous production of two tons per day of acetylene, and 25 tons per day of ethylene, such production being maintained constant during a very long period of operation without necessity to stop to clean the internal surfaces of the pyrolysis chamber.

By use of the jacketed chamber **3a**, the heat-exchange fluid passing from **8a** to **7a** through the jacket upwardly in counter-current to the downward flow of the liquid screen, helps to maintain a uniform screen by cooling it most where the liquid screen has been longest exposed to the reaction temperature. The heat-exchange fluid used need not be the same that is used as the screen fluid, but when a flow rate in the curtain is slow enough to allow substantial evaporation, in the example here given the pre-heating of the screen fluid in the jacket provides a greater vapor pressure of the screen liquid at the top of the chamber **3a**. This vapor then tends to flow down over the liquid screen and act as a barrier of relatively high humidity which tends to suppress evaporation from the liquid screen on the chamber wall and thus to keep the liquid screen more nearly uniform throughout. With water as the fluid, it enters the jacket through the pipes **8a** at the relatively low temperature of the water supply. It is warmed, but still well below the boiling point, as it reaches the grooves **5a** and is discharged onto the interior of the chamber **3a**. At this temperature, the water has a substantial vapor pressure which results in water vapor diffusing into the peripheral portion of the zones within the chamber **3a**. Because the chamber, at its top, is wider than the opening through the ring **4a**, this released vapor tends to fill in around the entering gases and to be dragged downward with them in laminar flow. The presence of this water vapor in the peripheral layer of gas which is in contact with the chamber walls, and the laminar gas flow which results from the design of the apparatus and the rate of flow, tends to suppress further evaporation so that a more uniform liquid screen is maintained than would be possible if turbulent flow were allowed to carry away the water vapor or if the water screen were allowed to heat excessively without external control.

In both examples, the pressure on the liquid as it is projected out along the surface of the chamber **3** or **3a**, and the rate of flow of the liquid thus supplied are most advantageously such that only a small proportion of the water is vaporized and it is still well below the boiling point when it reaches the point of its highest temperature in the reaction chamber. It is intended that the liquid screen should act as a heat screen for the chamber wall, but one which is replaced rapidly enough that the screen itself is never overheated.

We claim:

1. The method of carrying on gaseous reactions in which by-products tend to deposit which comprises flowing a mixture of reactants into a jacketed reaction chamber and establishing a reaction therein, forcing a screen liquid from the jacket onto the interior surface of the chamber near the top of the reaction zone therein, and forming thereby a continuous liquid screen around the reaction zone with descending helical flow, flowing additional screen liquid in heat-exchange relation to, but separated from the liquid screen around the reaction zone and controlling the temperature of said flowing screen, as it progresses along the reaction zone, by heat-exchange to said additional screen liquid, said liquid screen being injected through pressure jets inclined at an angle to the axis of said reaction zone for producing said descending helical flow.

2. The method as defined in claim 1 in which the flow in the screen and in the additional screen liquid is counter-current while they are in heat-exchange relation.

3. The method as defined in claim 1 in which the reactants pass through the reaction zone with substantially laminar flow.

4. Apparatus for carrying on pyrolysis reactions which comprises an upstanding tubular wall, a ring fitted into the top of the tube substantially against the inner face thereof, and having on its outer face toward said wall closely spaced helical grooves open at their lower interior end, and a header communicating with the upper exterior ends of said grooves to feed a liquid through them onto said inner face under substantial pressure for producing and maintaining a substantially continuous helically flowing liquid screen within said tubular wall.

5. Apparatus as defined in claim 4 which further comprises a substantially horizontal flange around the top of the tubular wall, and a distributor disc on the top thereof and the ring constitutes a skirt depending therefrom, fitting inside the tubular wall and externally grooved with said closely spaced helical grooves.

6. Apparatus as defined in claim 5 in which the top

of the tubular wall has a laterally extending flange and the disc has an annular channel on its bottom and fitted onto said flange, whereby the latter closes the channel except that it communicates with the upper ends of the grooves on the ring, whereby the channel serves as a header to feed the helical grooves.

7. Apparatus as defined in claim 6 in which the grooves extend at an angle of 45° to a plane normal to the axis of the tubular wall.

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