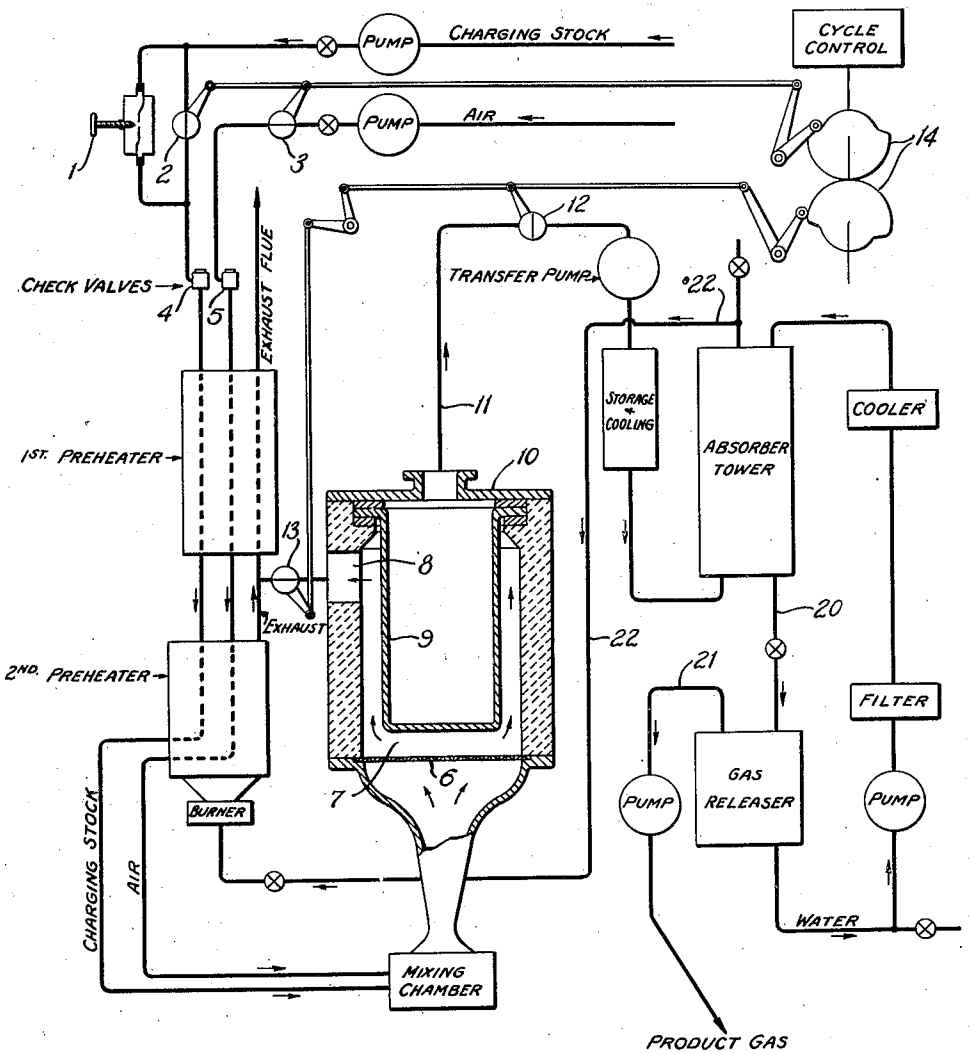
Feb. 27, 1940. B. W. WHITEHURST 2,191,510

MANUFACTURE OF HYDROCARBONS

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Fig. 1



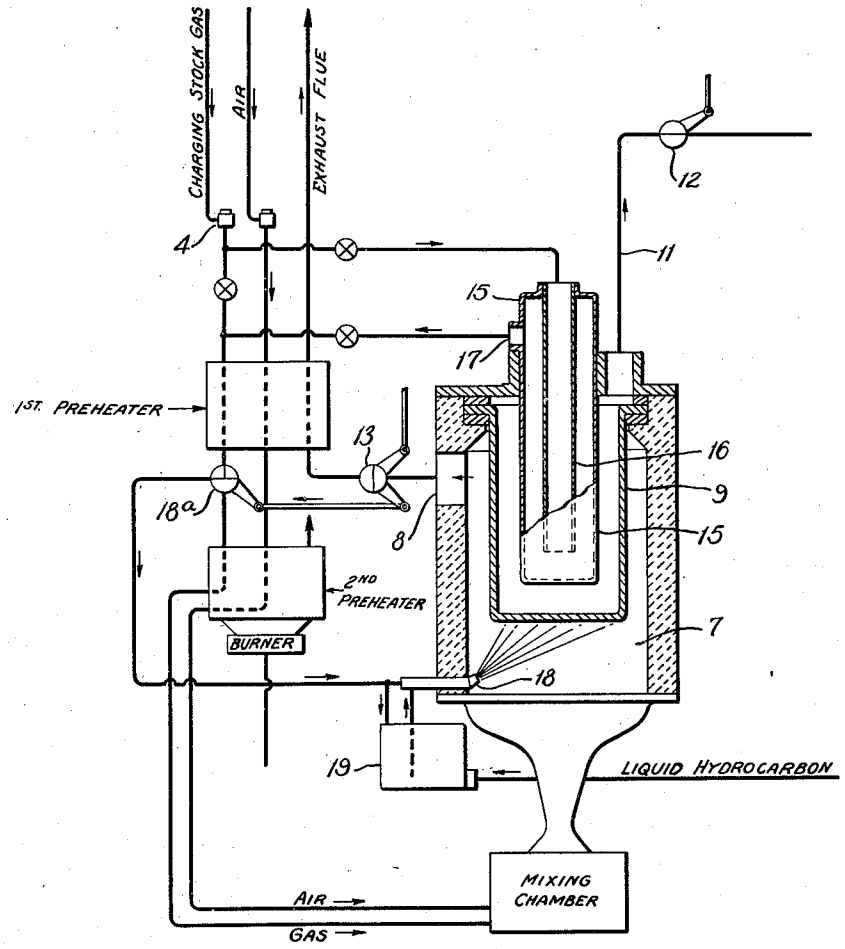
INVENTOR
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MANUFACTURE OF HYDROCARBONS

Filed Sept. 25, 1935 3 Sheets-Sheet 2

Fig. 2



Bert W. Whitehurst INVENTOR

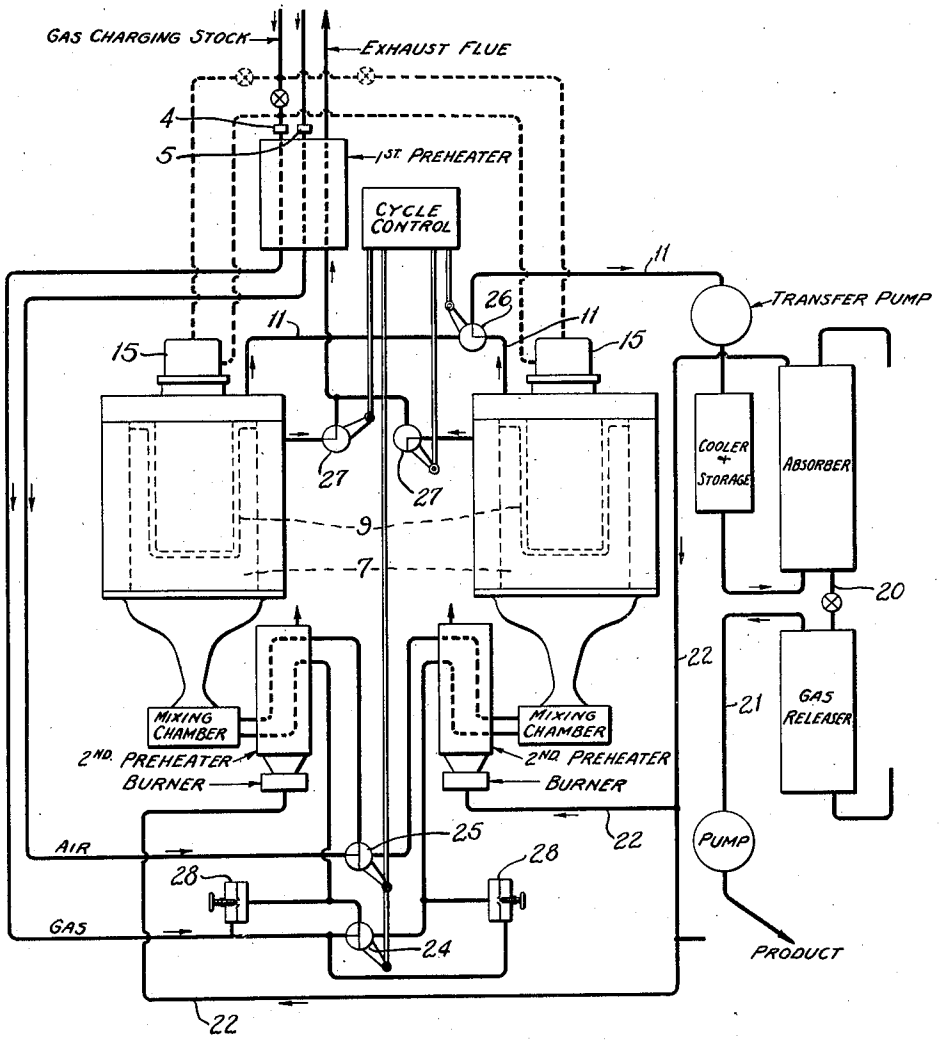
Jeffery, Kimball & Eggleston BY his ATTORNEYS

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MANUFACTURE OF HYDROCARBONS

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Fig. 3



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UNITED STATES PATENT OFFICE

2,191,510

MANUFACTURE OF HYDROCARBONS

Bert W. Whitehurst, New London, Conn., assignor to Whitehurst Research Corporation, a corporation of New Jersey

Application September 25, 1935, Serial No. 41,961

16 Claims. (Cl. 260—679)

My invention relates to the treatment of gases, especially hydrocarbons, for the manufacture of other products therefrom, and consists of a new system and process and a new conversion element useful in such treatments, being more directly concerned with the thermal decomposition or reformation of hydrocarbons to reduce the saturation thereof and being described herein for the manufacture of acetylene, etc., out of natural gas or methane, but without limitation to acetylene or any particular product except as specified by the claims.

For the manufacture of acetylene the invention affords high yields and high overall efficiency resulting from the use of combustion heat and the avoidance of obstructive deposits of carbon and the like which hitherto are believed to have been the barrier to commercial manufacture of acetylene from hydrocarbons. Instead of natural gas similar gases or vapors of the paraffin series, illuminating gas, olefines of the ethylene series, etc., may be used as the charging stock. Crude oils, waste lubrication oils and other heavy hydrocarbons may also be used under proper conditions.

In the drawings Fig. 1 illustrates the system in diagram and the new conversion element in axial section; Fig. 2 illustrates modifications, and Fig. 3 a duplex system giving a continuous delivery of product gas.

Referring to Fig. 1, the system is governed by a suitable motor-driven cycle-control which periodically sets certain valves or switches in alternate positions producing respectively the combustion and conversion stages which together constitute one cycle of the process. In Fig. 1 they are set for the combustion stage.

Charging stock, which can be understood to be natural gas containing about 83% methane, and air from atmosphere are caused to flow by the pipe lines marked "Charging stock" and "Air", respectively, through the open valves marked 1, 2 and 3, and check valves 4 and 5, and then through two stages of preheat, marked "1st preheater" and "2nd preheater", respectively, and thence to a mixing chamber, so marked, where the two are homogeneously mixed, the relative proportions being about 1:10 or so as to give complete combustion with a slight excess of oxygen for a purpose presently referred to.

The flow is produced by any suitable means, pumps being indicated and at a pressure ordinarily about 4 to 5 lbs. per sq. in. measured at the entrance to the first preheater. Regulation is by manual valves which will be understood to be present wherever necessary or convenient though not indicated; also meters and gauges are ordinarily included in the two lines though not indicated. During the combustion stage charging gas flows through the manually adjusted valve 1 and through the automatic valve 2, in parallel with it, and this latter valve is open during the combustion stage but closed during the conversion stage, as presently explained. By the preheating the temperature of the gas and air is raised to at least about 300° C. and preferably higher, up to a safe margin below the ignition point, the efficiency of the conversion being promoted by the degree of preheat applied. A preheat of about 350° C. to 500° C. is sufficient for the case in hand.

From the mixing chamber the preheated air and gas pass through a guard screen 6 to the combustion chamber 7 wherein they are ignited and burned and the combustion products escape by outlet 8 to atmosphere through the exhaust flue which traverses the first preheater and serves as the heat source therefor. The chamber 7 is heavily heat-insulated. Initial ignition is by electric resistance, spark or otherwise, but later is automatic by the heat of the chamber.

In the combustion chamber the flame is directly in contact with the conversion element 9 which is the device whereby or wherein the cracking or converting of the hydrocarbon is to occur, and the combustion is continued until this element attains an appropriate reactive temperature. This varies with different hydrocarbons, but for the case in hand, that is to say, for the manufacture of acetylene from natural gas of the kind stated, should be above 950° C.

While any known or suitable type of conversion device might be used in the apparatus under description and within this invention, the particular element shown constitutes a further and independent part of the invention. It consists essentially of a heat-resistant membrane or thin wall, which is preferably given the shape of a pot or cup and provided with a flange for supporting it on or in the combustion chamber or so as to constitute in effect one of the walls of that chamber. The cup, or at least the part of it exposed to the combustion, is made of a refractory material that is permeable to gas, if under sufficient pressure, as presently described. The side of the cup wall not in contact with the flame and which is the interior of the cup in the present case is in communication through its clamp cover 10, with the suction line 11 of a suitable transfer pump by which gases which have been

passed or forced through the wall of the element are transferred to a place of storage or to the recovery system in which the acetylene or product gas is separated out, as described below.

When the conversion cell has reached the appropriate temperature, the cycle control mechanism changes the system over to its conversion-stage setting, according to which the air flow is immediately stopped by the closure of air valve 3, the suction line 11 is opened by the transfer valve 12 and, when necessary, the exhaust flue is closed by the closure of valve 13. The control mechanism will be clear from the drawing, and it will be understood that the links and the cams 14 represent any suitable automatic gearing for throwing the valves at the required intervals, being preferably adjustable as to timing though not so shown.

By the shift of the valve system the flow of charging stock gas is not interrupted and continues as before (through the valve 1) and on arriving at the combustion chamber, now without air, passes through the hot wall of the porous cup or cell 9 and by such passage, from one side to the other of the cell wall, becomes cracked or converted to less saturated compounds containing a relatively large percentage of acetylene, which are promptly removed by the action of the transfer pump. The reaction occurs quickly, in the brief period required for the gas to traverse the hot thin wall of the cell, and owing to the resistance to flow offered by the latter occurs coincidently with a sharp pressure drop and with an attendant expansion-cooling as will be apparent both of which conditions will be recognized as intimately concerned with the fixation of the atomic structure in the acetylene relation.

It is practical to adjust the system to the resistance to flow that is offered by the cell wall so that the pressure in the combustion chamber will approximate atmospheric and the valve 13 will not then be necessary, but with some forms of the conversion element positive pressures are required for the conversion stage, in which case such valve is necessary. In the manufacture of acetylene from natural gas, it is preferred to operate the system with the combustion chamber at about atmospheric pressure, or only slightly above, running the transfer pump at a rate to give a negative pressure inside the cell and a pressure difference on opposite sides of the cell wall of several pounds, say 4 or 5 lbs. per sq. in.

The pressure in the combustion chamber is subject to some disturbance by the abrupt cessation and resumption of the air flow and it is to compensate this effect that the automatic gas valve 2, above mentioned, is provided. Such valve, as stated, closes when the air is turned off and opens when it is turned on and thereby insures a prompt establishment of the chamber pressure that is desired for the conversion stage. By appropriate adjustment or modification of the valves and their controls the pressure in the combustion chamber for each stage can be made as desired. Preferably it is the same for both stages, that is, constant, and the charging stock therefore flows to the chamber at a constant rate through the whole cycle.

The cycle is so ordered as to hold the system in the combustion stage long enough to create an efficient reactive temperature in the cell wall, then shifting and holding it in the conversion stage for as long as the reaction continues with satisfactorily high efficiency, then shifting back again to the combustion stage at which time the heat of the combustion space produces ignition automatically. Since the cracking reactions with different hydrocarbons are endothermic to different degrees, the relative time periods of the two stages of the cycle are to be determined according to conditions, as well as to the degree of preheat that can be conveniently applied. For making acetylene from natural gas under the conditions indicated, a combustion stage of 5 seconds and a conversion stage of 4 seconds gives a high efficiency and suffices to keep the cell at all times above a predetermined minimum temperature suited for maximum production of acetylene, but the stages may be equal as later explained, and by adjusting the timing it is apparent that the average cell temperature can also be controlled as desired.

The following observations may be made: The thin porous wall and the pressure difference to which it is subjected combine to produce an extremely short and nearly instantaneous application of the reaction temperature to the gas and while the latter is in a state of extremely fine subdivision in passing through the fine pores of the wall, and therefore while it is well adapted to be uniformly affected by the heat. The reaction time is determined by the wall thickness and the gas velocity through it, both of which can be adjusted, but the least thickness consistent with durability at high temperature is desirable. As the wall is made thinner it tends to lose its temperature more quickly but at the same time its temperature can also be restored quickly and without loss because, as will be apparent, the cycle frequency has little or no effect on the overall efficiency, the various switch valves being in any event of the quick action type. The cell wall therefore defines an extremely short and sufficiently heated reaction zone through which the gases pass at a desired high velocity and from which they expand abruptly as they emerge from or leave its delivery surface, and such conditions broadly characterize this part of my invention.

Since the flow of charging gas to the porous wall is continuous, the air supply only being intermittent, there is no time loss in shifting from one stage to the other and there is little or no residuum of gas left in the apparatus between stages to affect or mix with the gases involved in the next stage, such as occurs for instance, in the flow-reversing systems heretofore proposed for making hydrocarbon products. More especially at the end of the combustion stage there is no residuum of combustion products to flow ahead of the converted gases into the receiver for the product to dilute the latter. In order to forestall the possibility of the passage of any such products through the cell wall, the transfer valve 12 is preferably opened with a slight lag behind the closing of the air valve 3 enough to afford an opportunity for the chamber 7 to clear itself and fill with pure charging gas before transfer through the wall commences. This can be so adjusted as to avoid any appreciable wastage of the pure charging gas through the exhaust flue. Combustion products cannot enter the cell wall during the combustion stage because the porosity is too fine and because there is then no pressure difference to cause the movement.

The formation of free carbon, more or less inseparable from ordinary methods of cracking natural gas, is negligible and unobjectionable in this process because such carbon as is formed

lodges on the surface of the cell, where it is quickly and usefully consumed on the next combustion stage due to the excess of oxygen in the burning fuel mixture. It does not enter the fine pores of the cell wall, nor does carbon appear to form in the interior of the wall as might perhaps be expected from the fact that some hydrocarbon must be present in the wall and stagnant therein during the combustion stage. On the contrary, if the wall be fractured and the fracture examined, no carbon is observable in its interior. The cell appears to function indefinitely without diminished efficiency and without need of cleaning.

Inasmuch as the carbon is thus easily disposed of it will be apparent that the process and the apparatus are well adapted to those cracking reactions which proceed with a greater liberation of elemental carbon than occurs in converting to acetylene, for instance when the process is adjusted to the manufacture of hydrogen as the preferred product.

The conversion cell can be made of any material sufficiently refractory; for example, granular alumina, known as electrically-fused alumina, Al_2O_3, or silicon carbide, SiC, quartz, SiO_2, etc. Alumina is preferred, being obtained in form resembling flour or fine meal. It is thoroughly mixed with a suitable ceramic binder and molded into cup shape and fired at a temperature sufficient to cause the mass to sinter, producing an integral structure, as customary in the manufacture of ceramic ware. The cell resembles unglazed china. By grading and adjusting the size of the flour grains with reference to the wall thickness desired, the degree of gas-permeability can be made as required. Degrees of permeability can be conveniently expressed by reference to the volume of a gas, for instance air, that will pass at a given temperature and under a constant pressure difference through a constant thickness of wall in unit time, and expressed on this basis, I have found that a cell wall 5 mm. thick which will permit not more than 960 cc. of atmospheric air, at room temperature (22° C.) to pass through it per minute per square centimeter under a pressure difference of 2 atmospheres absolute, produces results in the conversion of methane to acetylene, by this process, which are notably superior to the elongated conversion tubes heretofore proposed for this reaction. I have further found that the acetylene yield increases as the gas-permeability rating is decreased toward a certain practical minimum, and according to the preferred practice of this invention the permeability is therefore made as low as consistent with the temperature and pressure conditions. A cell wall about 5 mm. thick with a permeability rating on the above basis of about 100 cc., functions well under a pressure difference of about 4 or 5 lbs. for making acetylene from natural gas and that rating is preferred.

The efficiency of the reaction is promoted by the use of a catalyst which is applied to the cell preferably on the surface that is exposed to the combustion. Metals of group VIII, of the periodic table of elements according to Mendelyeev have been found practical, especially platinum, palladium and platinum-palladium mixtures. They may be applied to the cell by coating it with a solution of the chloride of the metal, such chloride being subsequently reduced in the flame so that the metal is left in the form of a porous coating on the cell surface. A particular effect of the catalyst thus applied, or otherwise applied to, or associated with, the outside surface of the cup, is to stimulate or quicken the combustion and spread it over the entire cell surface apparently resulting in a more uniform temperature in all parts thereof irrespective of the conditions of flame path in the chamber. The importance of such uniformity will be apparent.

Inasmuch as efficiency of the process depends in some measure in the prompt removal and cooling of the cracked gases as they emerge from the surface of the cell wall it is desirable, in the larger sizes of cells particularly, that the interior volume of the cell be reduced as much as possible and to this end it is preferred to install a filler in the cell concentric thereto and about as shown in Fig. 2 wherein the filler is marked 15. This increases the gas velocity through the cup space and reduces the volume of gases left inside it during the combustion stage. Advantage can be taken of such a filler to aid in cooling the freshly cracked gases as by making it hollow and including its interior in a cooling gas or air flow thereby obviously also conserving heat. In such case the charging stock gas is led into the hollow body of the filler through a central dip tube 16 and out through a lateral outlet 17 and thence to the preheater, etc., as before. The flow is under the control of valves as indicated in the diagram.

Such a cooling filler can be used in the cell represented in Fig. 1 where the charging stock is natural gas only, but it is shown in Fig. 2 as applied to the conversion unit when modified to utilize liquid hydrocarbons also as charging stock. In this case the gaseous charging stock, such as natural gas is supplied under appropriate pressure and through an automatic valve 18^a to an ejector type atomizer 18 which is mounted in the base of the combustion chamber 7 and connected with a liquid hydrocarbon supply through a constant level or float chamber 19. The gaseous charging stock flows to the mixing chamber and burns with the hot air during the combustion stage to heat the conversion cell as before. On the shift to the reaction stage it is diverted by valve 18^a to the atomizer 18 producing a fine and preferably nebulized liquid spray directed to impinge on the cell, being promptly converted to gaseous phase in which it passes through the cell wall. Otherwise the action of the system may be the same as already described.

According to a further part of this invention, the acetylene contained in the product gases removed by the transfer pump and delivered to the storage and cooling tank, is recovered by washing such gases in water under pressure and at a low temperature, say just above 0° C. Under such conditions the acetylene dissolves readily in the water, whereas the other gases present do not. At a temperature of 0° C. for example, 1.73 volumes of acetylene dissolve in one volume of water, whereas only .056 volume of methane and .022 volume of hydrogen will go into solution. When a freeze-point depressant has been added to the water lower temperatures can be used with still greater gas absorption. Any suitable absorber tower providing counterflows of gas and water will suffice. As acetylene is liable to explode when subjected to a pressure greater than 4 atmospheres, the allowable pressure in the tower is governed by the percentage of acetylene contained in the gases. At a 10% concentration, the allowable pressure inside the absorber

tower would be in the neighborhood of 40 atmospheres, but at a temperature of just above 0° C. a pressure of only 15 atmospheres is sufficient to give good absorption.

The water from the tower, containing acetylene dissolved therein, is led through a pipe 20 and a suitable valve to the gas releaser, where a sufficient vacuum is maintained to cause the gas to escape from the water. A pressure drop to 5 lbs. or less, absolute, is sufficient to produce a vigorous degasification of the water and a substantially complete release of the dissolved acetylene, which is then conducted out of the system by pump and pipe line 21, as the primary product of the process, while the water is pumped back to the absorber tower through a filter and a cooler as indicated. Under these conditions an absorption efficiency of 97% has been obtained and a reclamation efficiency of 93%, giving an overall efficiency of about 90%. Other methods of recovering the acetylene from the decomposition gases leaving the conversion cell may of course be employed, but the method described offers a superior economy when acetylene by itself represents the principal product.

The residuary gases not absorbed by the water and being the by-product gases in the present case, consisting mainly of hydrogen with some methane, ethylene, etc., are led off from the top of the tower by pipe 22 to be utilized to supply energy for driving the pumps, or it is used as indicated in the diagram for firing the 2nd preheater with or without additional fuel as circumstances may require.

Figure 3 represents the system organized with plural units to deliver the reformed gases continuously to the recovery system. In this form two conversion units are employed so connected and controlled that while one is in the combustion stage, the other is in the reaction stage and vice versa. The pipe and valve system will be apparent in the diagram.

The automatic gas and air valves 24 and 25 and the discharge valve 26, corresponding respectively in function to the valves 2 and 3, and 12 of Fig. 1, are now two-way valves shifted periodically by the cycle controller as before, and they are shifted at equal intervals so that the two stages are equal, except that in order to provide for the purging of the combustion chambers between stages the discharge valve 26 is operated with a relatively slower or delayed action so that suction is not applied to the particular conversion unit until a moment after the air supply thereto has been cut off. For the same reason the two exhaust-flue valves 27, 27, are so separately governed as not to close their respective units until the instant the suction or transfer valve has been opened thereto. Thereby each combustion chamber is properly purged in alternation. The adjustable valves 28, 28 correspond to the adjustable valve 1 in Fig. 1 and have the same function with reference to their respective units. A single first preheater suffices for both units but a separate second preheater is provided for each of them and the valves 24, 25 and 28 are located after the first preheater and before the second, where they are not subject to injurious temperatures.

Obviously more than two units could be similarly organized into one system following the plan above described to deliver to a common recovery system and it will be understood that various other departures from the particular form of system and process above described may be resorted to within this invention and are intended to be included in the claims hereto appended.

I claim:

1. The process of reforming gases which comprises maintaining a gas-permeable wall at a reactive temperature by intermittently subjecting one side only to contact with a burning mixture and passing the gas to be treated through the wall in the intervals between the heatings thereof.

2. The process of reforming hydrocarbon gases which consists in first burning a fuel-air mixture in contact with a thin close-grained porous wall having a combustion-promoting catalyst associated with its flame-exposed surface and establishing a reactive temperature therein, and then passing the hydrocarbon gas through the wall while at that temperature.

3. The process of reforming hydrocarbons which comprises heating a gas-permeable wall of extended area to reaction temperature by passing a burning mixture of the hydrocarbon and air over but not through it, then depriving the mixture of its air supply and passing said hydrocarbon without air through such wall.

4. The process of reforming hydrocarbons, which comprises directing flows of hydrocarbon and air into a combustion chamber and over but not through a gas permeable wall thereof, burning the same therein to establish a reactive temperature in said wall, stopping the air flow while continuing the hydrocarbon flow and, after a purging interval, passing the hydrocarbon flow through said wall, then stopping the flow through the wall and reinstating the air flow to the chamber.

5. The process of making acetylene by thermally decomposing hydrocarbons, which consists in heating a close-grained porous wall to an acetylene-forming temperature, preheating and supplying the hydrocarbon to one side of said wall at a pressure approximating atmospheric and withdrawing decomposed gases containing acetylene from the other side at less than atmospheric pressure.

6. The process of making acetylene from methane-containing gases which consists in heating a close-grained, porous catalyst-covered wall to an acetylene-forming temperature, preheating such gas to at least 300° C. and passing it through such heated wall at a pressure difference of several pounds while removing decomposition gases containing acetylene from the low pressure side of said wall.

7. The process of making acetylene and the like from natural gas which consists in preheating and continuously passing such gas to a combustion chamber, preheating and intermittently passing air to said chamber for combustion therewith, heating a fine porous wall of said chamber to cracking temperature by such combustion, and in the intervals between heatings, forcing the preheated gas alone from said chamber through said wall under conditions establishing a pressure drop of several pounds in its passage from one side of the wall to the other, and in the presence of a catalyst associated with said wall.

8. A process of the kind described, which comprises alternately passing a burning mixture of air and a gas to be reformed over but not through each of two finely porous gas-permeable walls

to establish reaction temperature therein, and in the intervals passing said gas without the air through said walls and removing the conversion products emerging from the surfaces of said walls.

9. A process of the kind described comprising heating a finely porous wall to reacting temperature by passing a burning air and gas mixture in contact with but not through said wall, then discontinuing the supply of the air component of the mixture and continuing the supply of the gas component while commingling liquid hydrocarbon with it and passing the latter through said wall, said wall having such fineness of porosity as to preclude entry of deposited carbon into the pores thereof.

10. The process of claim 9 in which the gas supply that is continued after cessation of the air supply serves to atomize and project the liquid hydrocarbon toward said porous wall.

11. The process of thermally synthesizing hydrocarbons which comprises heating to a temperature in the order of 950° C., or above, a porous wall of such close texture as to exclude carbon deposit in its interior structure, preheating and forcing the hydrocarbon to be synthesized in gas-phase through the fine pores of such wall at such temperature, removing the synthesized product from the delivery surface of said wall in the absence of free oxygen and admitting free oxygen to the entrance surface of said wall to the extent necessary to burn off any carbon deposit thereon.

12. The process of claim 11 wherein the hydrocarbon comprises methane and is preheated to a temperature of between 350° C. and 500° C. and the converted product removed from the delivery surface of said wall contains free acetylene.

13. The process of synthesizing acetylene and the like which comprises heating a porous wall to a temperature of the order of 950° C., or above, and forcing methane through such wall at that temperature, said wall having a permeability rating of less than 960 according to a scale wherein the rating represents the number of cubic centimeters of air at 22° C. and under a pressure of two atmospheres absolute, that will pass per minute per square centimeter through a wall of 5 mm. thickness.

14. The process of thermally converting hydrocarbons which comprises heating a porous wall to a temperature of the order of 950° C. or above, and forcing the hydrocarbon through the pores of such wall while at that temperature, said wall having a permeability rating of about 100 according to the scale wherein the rating represents the number of cubic centimeters of air at 22° C. and under a pressure of two atmospheres absolute, that will pass per minute per square centimeter through a wall of 5 mm. thickness.

15. The process of synthesizing acetylene from hydrocarbons which comprises forcing the hydrocarbon in gas phase through a porous wall heated to a temperature of at least 950° C. and having a permeability rating of about 100 according to the scale wherein the rating represents the number of cubic centimeters of air at 22° C. and under a pressure of two atmospheres absolute, that will pass per minute per square centimeter through a wall of 5 mm. thickness, removing the synthesized gaseous product containing acetylene without further change from the delivery surface of said wall and removing carbon from the entrance surface of said wall.

16. In the process of converting hydrocarbons which consists in alternately passing a mixture of hydrocarbon gas and air in process of combustion through a chamber containing a highly flow resistant conversion element and out through a closable outlet from such chamber, and then closing said outlet and passing only gas alone into such chamber and out through the conversion element, the step of maintaining substantially constant pressure in such chamber which comprises enlarging the gas supply when the gas and air are passing through the chamber and reducing the rate of gas supply when gas alone passes through said chamber.

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