

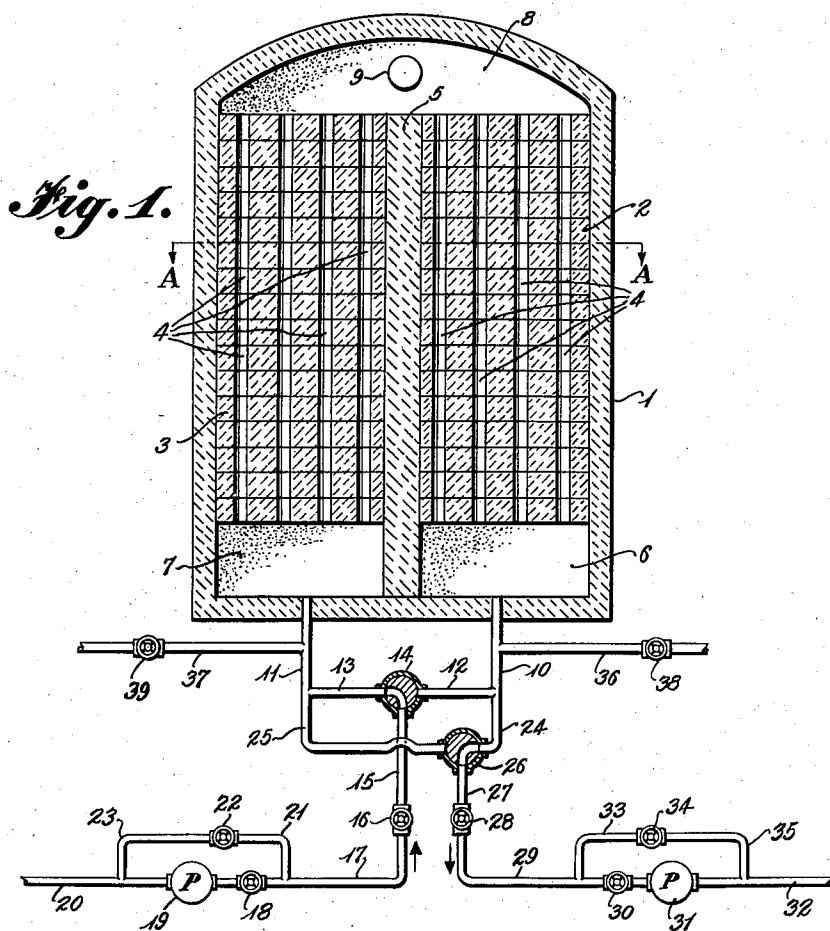
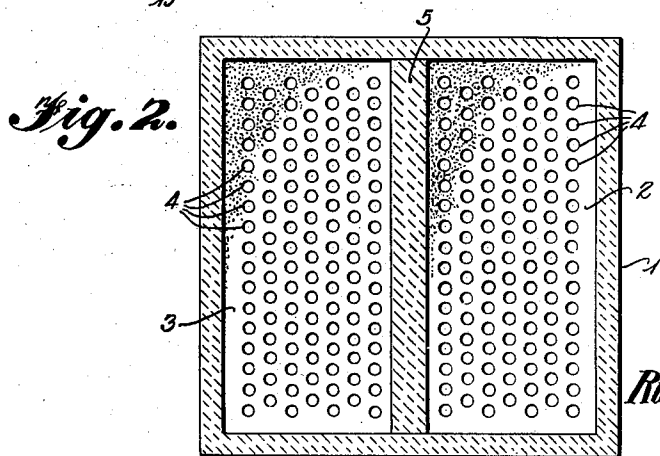
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SELF-SUSTAINING REGENERATIVE PROCESS

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SELF-SUSTAINING REGENERATIVE PROCESS

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6 Claims. (Cl. 48—196)

This invention relates to gas reactions and more particularly to novel regenerative apparatus and processes whereby a combination of endothermic and exothermic gas reactions may be effected at high thermal efficiency. A primary object of the invention is the provision of a continuous method for the production of low density heating gases, acetylene, olefins, aromatics and other endothermic gas reaction products by the partial combustion of exothermically combustible starting materials such as hydrocarbons and ammonia.

Methods known to the prior art for the production of endothermic reaction products and heating gases of the aforementioned type are thermodynamically inefficient and of restricted commercial feasibility. Conventional prior art processes entail the use of regenerative furnaces in conjunction with intermittent heating and production cycles with attendant interruptions of heating gas production. Modifications of this conventional regenerative process involve the continuous relocation of heating zones within a regenerative mass as well as frequent interruptions in gas production necessitated by the cooling and required reheating of the refractory. Other conventional practices require long heating periods for the hydrocarbon starting materials and yield an inferior product containing predominantly carbon monoxide, carbon dioxide and hydrogen.

It has now been discovered that low density heating gases, unsaturated hydrocarbons including acetylene and other endothermic gas reaction products may continuously and substantially isothermally be produced by heating a nonflammable first mixture of an exothermically combustible material and oxygen to effect incipient endothermic thermal alteration of the combustible material, thereby producing a flammable second mixture, the so initiated endothermic reaction being propagated by the resulting exothermic combustion reaction, said combustion reaction being controlled by the limited amount of oxygen present; and thereafter rapidly cooling the product so obtained, the heat resulting from said cooling being employed to raise additional quantities of combustible material and oxygen to incipient cracking temperature.

For example, in those instances where a hydrocarbon is employed as a starting material for the production of a heating gas, acetylene, or the like, the hydrocarbon is first mixed in non-flammable proportions with air or other oxygen containing gas, and the mixture heated to the incipient thermal cracking temperature of the hydrocarbon. There is produced in this manner a flammable second mixture containing carbon and hydrogen in addition to the hydrocarbon starting material. The combustion of this carbon and hydrogen together with a minor portion of the original hydrocarbon provides the heat required to propagate the endothermic cracking reaction. Heat released by the quenching of the product so obtained is utilized to heat additional quantities of the starting mixture to the incipient cracking temperature of the hydrocarbon.

It will be appreciated that only a relatively small por-

tion of the hydrocarbon or other combustible starting material, normally not more than about 15% to about 40% thereof, will be consumed by the limited combustion reaction. The balance of the starting material will be efficiently cracked or otherwise thermally altered by the heat released by such combustion. The sensible heat of the entire gas mixture will accordingly be raised to the flame temperature of the combustion reaction which is above that necessary to initiate thermal alteration of the starting material. Hence additional quantities of starting material and oxygen may be raised to the incipient thermal alteration temperature of the starting material through utilization of the heat released by the cooling of the product.

In the preferred embodiment of the invention the process is carried out in a continuous regenerative manner by passing a non-flammable first mixture containing an exothermically combustible starting material and oxygen through the channels of a first refractory regenerative mass from the cooler to the hotter ends thereof, thereby effecting incipient thermal alteration of the combustible starting material and producing a flammable second mixture, passing said second mixture into a combustion and thermal alteration zone wherein the previously initiated endothermic thermal alteration reaction is propagated by the simultaneously occurring combustion reaction, thereby producing a third gaseous mixture hotter than the hottest portions of said first regenerative mass, and thereafter quenching said third gaseous mixture by passing the same through the channels of a second regenerative mass from the hotter to the cooler end thereof, the direction of flow of gases through said first and second regenerative masses being reversed at suitable intervals whereby a continuous yield of product is obtained.

The above described continuous regenerative process differs radically from the methods of the prior art which entail alternate heating and production steps which result in an intermittent flow of desired product. Furthermore, the prior art teaches that the regenerative masses employed to effect the thermal cracking of hydrocarbons and the like must be preheated to a temperature in excess of that required to initiate cracking, that is, that the regenerative mass must be at least as hot as the gases produced and that the mass must alone supply the heat requisite not only to initiate but also to propagate the exothermic cracking reaction. Such processes are necessarily attended by excessive heat loss and therefore of intermittent character occasioned by the constantly recurring necessity of reheating the regenerative mass.

In contrast to such prior art processes, in this invention the product gases when produced are substantially hotter than the regenerative masses with which they come in contact. That is, the regenerative mass is always at a temperature substantially lower than the maximum gas temperature. Furthermore, in the actual cracking or thermal alteration phase the endothermic and exothermic reactions which occur are substantially in balance. Hence, there is no significant heat loss in the system and the entire process is essentially isothermal. Operation at high temperatures without serious adverse effect upon the refractory of the regenerative mass is thus made possible.

The continuous refractory regenerative process of this invention is admirably suited by virtue of its continuous nature, both with respect to the introduction of starting materials and to the flow of the product obtained to operation under sub-atmospheric or super-atmospheric conditions. Accordingly, the process of the invention is appropriate for the production not only of heating gas and unsaturated hydrocarbons from more saturated starting materials, but also may be employed to advantage in effecting other reactions involving the formation of endo-

thermic reaction products by simultaneous exothermic combustion and endothermic product producing reactions. Thus, sub-atmospheric pressure may appropriately be employed for the production of acetylene, of hydrazine from ammonia, of nitric oxide from air and of other products which require extremely rapid quenching to prevent destruction thereof. Such reactions are preferably carried out at a pressure of from about 0.2 atmosphere absolute to about 0.8 atmosphere absolute. It will be obvious that both the residence period and the quenching time of the gases in the furnace can be reduced in direct proportion to the reduction in pressure below atmospheric of the gases undergoing treatment.

Similarly, operation at super-atmospheric pressure is desirably employed for the production of higher olefins and liquid fuels from higher molecular weight starting materials. Through the utilization of such super-atmospheric pressure the longer reaction and quenching periods which are of significance in the production of these materials may be achieved.

Certain critical limitations must be observed with respect to this process. It is required that the original mixture contain hydrocarbon or other starting material and oxygen in non-flammable proportions to preclude excessive consumption of the starting material by combustion. Furthermore, only so much oxygen is desirably employed as is required to obtain the heat requisite to the production of the desired pyrolysis product. Air, oxygen or oxygen in admixture with gases inert under the conditions may be employed. Air is preferred.

These limits of combustible proportions of the various hydrocarbons and other combustible gases with oxygen are well known to the art. Such data may be found for example in "Handbook of Chemistry and Physics," 30th edition, 1947, p. 1506. The proportions of oxygen or air required to form a combustible mixture with the preferred hydrocarbons for use in this invention and the preferred proportions for use with these starting materials are set forth in Table I, for operations at atmospheric pressure.

Table I

Hydrocarbon	Required for Combustion ¹		Preferred Range	
	Oxygen	Air	Oxygen	Air
Methane.....	2.0	9.52	0.2-0.7	1.0-3.5
Ethane.....	3.5	16.67	0.15-0.7	0.75-3.5
Propane.....	5.0	23.80	0.2-1.0	1.0-5.0
Butane.....	6.5	30.95	0.3-1.5	1.5-6.5
Ethylene.....	3.0	14.29	0.1-0.5	0.5-2.5
Propylene.....	4.5	21.43	0.15-0.8	0.75-4.0
Butylene.....	6.0	28.58	0.2-1.0	1.0-5.0
Natural Gas.....			0.2-0.7	1.0-3.5

¹ Parts by volume of oxygen or air per part by volume of hydrocarbon

It is also essential to the success of the process that both the hydrocarbon or other starting material and the oxygen be preheated to the incipient cracking or thermal alteration temperature. The addition of unpreheated oxygen or oxygen containing gas to the starting material raised to the thermal alteration temperature is unsatisfactory.

The hydrocarbon employed may be any hydrocarbon which is gaseous or may be vaporized under the conditions and which is subject to thermal cracking. Thus low molecular weight compounds such as methane, ethane and the various isomeric propanes, butanes, hexanes, and mixtures thereof may be employed as well as higher molecular weight materials such as the octanes and decanes and petroleum naphtha. Unsaturated materials may be employed. Low molecular weight, saturated, normally gaseous hydrocarbons such as propane and butane are preferred. However, liquid hydrocarbons may be preheated or atomized and introduced with air to produce good yields of the higher liquid olefins.

The continuous regenerative embodiment of the process of this invention is attended by a number of unique and outstanding advantages. As previously mentioned, the process may be carried out at high temperature without serious adverse effect upon the refractory of the regenerative masses utilized for the reason that such masses are always at a temperature substantially lower than the maximum gas temperature. Furthermore, the cracking of hydrocarbons may be effected at extremely high temperatures without the formation of appreciable quantities of carbon, thus obviating a serious problem inherent in the processes of the prior art. An additional outstanding advantage of the process resides in the fact that the temperature of operation may automatically be controlled merely by controlling the composition of feed mixture of oxygen containing gas and combustible starting material employed. Furthermore, the process of this invention represents an advance over the prior art in that there is a remarkably low pressure drop, generally not more than about 2.5 pounds per square inch therefrom.

It will be apparent that the above described process may be carried out in a plurality of types of apparatus. For example, hydrocarbon and oxygen might be introduced into coils and preheated to incipient cracking temperature, the hot gases mixed and the combined cracking and combustion permitted to take place in a cracking zone and the hot products cooled by passage in heat exchange relationship with the aforementioned preheating coils. This mode of operation is inexpedient in that it entails the use of expensive equipment and temperatures attained are limited to those possible with alloy metal tubes and coils.

The process of the invention is preferably carried out however in a refractory regenerative furnace structure. It is essential however when such a structure is employed at substantially atmospheric pressure that the period of residence of the gases undergoing treatment in that portion of the regenerative mass wherein the gases are heated to the cracking temperature of the starting material not exceed about 0.3 second. A preferable range for this residence period is from about 0.05 second to about 0.1 second. It is likewise necessary that the period of residence of the gases undergoing treatment in that portion of the regenerative furnace wherein the simultaneous combustion and cracking reaction occurs not exceed about 0.05 second. A preferable range for this period of residence is from about 0.01 second to about 0.03 second. As the product gases are quenched by passage through a second regenerative mass, the same limits of residence time obtain as those previously defined with respect to the initial heating step.

The foregoing limits with respect to residence time apply to operations conducted at atmospheric pressure which are suitable for the production of heating gas, lower olefinic hydrocarbons and the like. When it is desired to produce acetylene, nitric oxide, hydrazine, hydrocyanic acid and the like, which products require very short residence time in the regenerative masses and extremely rapid quenching, the process of the invention is effected at sub-atmospheric pressure. The foregoing limits will in such cases be reduced to an extent corresponding to the reduction in pressure of operation. For example, if the process is effected at a pressure of about one-third atmosphere absolute, the residence time and quenching time can preferably be reduced to below 0.01 second. Likewise, when operating at super-atmospheric pressure for the production of higher liquid olefins, aromatics and the like, correspondingly longer residence periods which favor the reactions yielding such products are employed. Thus, at a pressure of two atmospheres residence times as great as about 0.3 second may be employed. Similarly, when oxygen is utilized in lieu of air, the residence time in the furnace may be reduced to about one-half of that required with analogous operations conducted with air. Thus, the residence time when oxygen is utilized may be reduced to

a few thousandths of a second. It will be obvious that the reduction of residence and quenching periods by the reduction in pressure in the system can be accomplished without appreciable change in pressure drop through the regenerative mass because only the lineal gas velocity is increased, not the mass velocity. This feature of restricted pressure drop constitutes one of the salient advantages of this invention.

It is also necessary when a refractory regenerative furnace structure is employed that the pressure drop in the apparatus not exceed about 5 pounds per square inch. A preferable range is from about 1 pound per square inch to about 2.5 pounds per square inch.

The provision of one type of novel regenerative furnace structure in which this process may be carried out is one of the salient and primary features of this invention. Briefly stated, the furnace of the invention comprises two regenerative masses having a plurality of uninterrupted flues or slots passing therethrough. Each of said regenerative masses is provided with a free space at one extremity of the flues for the introduction or withdrawal of gases. The opposite extremities of the regenerative masses are interconnected with an insulated combustion chamber which is provided with a heating means. Each of the aforementioned free spaces is provided with gas admission and withdrawal means which are in turn associated with means for causing a gas to flow from the aforementioned free space of one regenerative mass through the flues or slots thereof into and through the combustion chamber and thence through the flues of the second regenerative mass. Means for the reversing of this gas flow are also provided.

This novel furnace structure will now be described in detail with reference to the accompanying drawings in which:

Figure 1 represents partly in vertical section, partly diagrammatically a complete apparatus in accordance with the present invention, and

Figure 2 represents a horizontal section taken on the line A—A of Figure 1.

In Figure 1 there is shown a refractory insulated chamber 1 containing two contiguous regenerative checkerworks 2 and 3 both of which are provided with straight, uninterrupted flues 4. Checkerworks 2 and 3 are separated by gas-tight wall 5 and respectively provided with gas inlet and withdrawal spaces 6 and 7, which are in communication with flues 4. Above the regenerative checkerworks 2 and 3 there is provided an interconnecting chamber 8 which is in communication with the upper extremities of flues 4 of both regenerative checkerworks 2 and 3. Chamber 8 is provided with heating means 9, normally a burner for gaseous or liquid fuel. Gas inlet and withdrawal lines 10 and 11 connected respectively with gas inlet and withdrawal spaces 6 and 7 are connected through lines 12 and 13 respectively and three-way valve 14 to line 15 which in turn leads through valve 16, line 17, valve 18, pump 19, and line 20 to a source of hydrocarbon and oxygen containing gas not shown. Valve 18 and pump 19 may be bypassed through line 21, valve 22 and line 23. Likewise, gas inlet and withdrawal lines 10 and 11 are connected through lines 24 and 25 respectively to three-way valve 26 and withdrawal line 27 which in turn leads through valve 28, line 29, valve 30, pump 31 and lines 32, to storage means not shown. Valve 30 and pump 31 may be bypassed by line 33, valve 34 and line 35.

Lines 10 and 11 are also connected respectively to lines 36 and 37 which function as chimneys during the initial heating of the furnace. Lines 36 and 37 are respectively provided with valves 38 and 39.

Very high heat transfer, short residence periods, and low pressure drop in the regenerative furnace are absolutely essential to the successful practice of the previously mentioned process for the production of low density heating gas as well as acetylene, other unsaturated hydro-

carbons and other endothermic reaction products. To this end it is necessary that the above described furnace structure and modifications thereof embraced by this invention conform to certain definite structural limitations.

It is critical and essential that the length of the regenerative checkerworks 2 and 3 not exceed about fifteen feet in length. Likewise regenerative checkerworks of less than about four feet in length are impractical although the lower limit is not critical. A preferred length for the regenerative checkerworks is from about six feet to about ten feet.

It is also essential that the gas passageways or flues 4 in the regenerative checkerwork not exceed about 0.75 inch in maximum width or diameter. The lower limit of operable width or diameter of such flues is not necessarily critical but must not be so small that excess pressure drop in the furnace occurs as a consequence thereof. Generally, flues of maximum width or diameter of from about 0.75 inch to about 0.25 inch may feasibly be employed. Flues of maximum width or diameter of from about 0.375 inch to about 0.5 inch are preferred. It will be apparent that mere masses of promiscuously deposited heat absorbing solids are unsatisfactory regenerative masses for the furnace of this invention.

It is also essential that the ratio of the total volume of the flues 4 in each regenerative checkerwork 2 or 3 to the total volume of the checkerwork in which the flues are located not exceed about 1:3. A preferred range for this ratio is from about 1:4 to about 1:10, and a practical lower limit is about 1:20. This lower limit, however, is not critical except insofar as pressure drop is concerned.

A particularly appropriate type of checker brick for use in the construction of the regenerative checkerwork of the furnace of this invention is that described and claimed in my copending application Serial No. 129,969, entitled Regenerative Packing Construction, filed November 29, 1949, and now abandoned. These checker bricks are prepared from any conventional refractory material such as the various calcium, magnesium aluminum silicon, iron, chromium, etc. oxides and mixtures thereof. Furthermore, as a consequence of the thermodynamic advantages of the process of this invention in the lower or cooler portions of the regenerative masses, a checkerwork metal such as iron or copper or a checkerwork graphite may be employed. Preferably the bricks are prepared from a material having a high alumina content to obtain maximum heat capacity, high refractoriness, high thermal stability and inertness toward the gases undergoing treatment.

The novel placement of the flues or gas passages 4 in this checker brick is diagrammatically shown in Figure 2. It will be observed that all of the flues are equidistantly spaced from all the next closest adjoining flues and that accordingly the thickness of the walls between each flue and the next adjoining flue is uniform. As shown in the drawing, for example, each flue is circular in shape and has a diameter of about $\frac{3}{8}$ inch. Furthermore, it is approximately $\frac{1}{16}$ from the center of each flue to the center of each of the next most closely adjoining flues. Obvious variations in relative size and shape of the flues and interwall thickness are operable within the previously defined limits with respect to maximum slot size and volume. Conventional checker bricks of other types than those described in aforementioned application Ser. No. 129,969 may of course be employed if the aforementioned limits are observed.

It is further required that the volume of the combustion chamber 8 not exceed about 60% of the combined volume of the flues 4 in both of the regenerative checkerworks 2 and 3. It is preferred that the volume of the combustion chamber 8 be equal to from about 20% to about 40% of the aforementioned combined volume of the flues 4.

Operation of the furnace and process of the invention to produce a low density heating gas from propane and

air will be described by reference to Figure 1. Prior to initiating the cracking reaction the furnace must be preheated. To this end, valves 38 and 39 are opened and valves 16 and 28 are closed. Heating means 9 is then actuated in chamber 8 whereby hot combustion gases are caused to pass downwardly in parallel streams through flues 4 of regenerative checkerworks 2 and 3 into chambers 6 and 7 and thence out of the furnace through lines 10 and 36 and 11 and 37 respectively. During passage through flues 4 the hot combustion gases produced by heating means 9 give up heat to regenerative checkerworks 2 and 3. The heat transfer efficiency resultant from the construction and dimensions of the regenerative checkerworks 2 and 3, previously described, is such that the combustion gases leave the furnace at a temperature of about 100° C. This procedure is continued until the top of the regenerative checkerwork is in excess of 1000° C., preferably within the range of 1100° C. to about 1300° C. There is thus provided a temperature gradient in the mass ranging from about 100° C. at the bottom to the temperatures in excess of 1000° C. in the top thereof.

Alternatively, the heating means 9 may be turned off after the top of regenerative checkerworks 2 and 3 has reached a temperature above the ignition temperature of the fuel employed, generally, about 550° to 650° C., valves 18, 30, 38 and 39 closed and valves 16, 22, 28 and 34 opened. Combustible material is then introduced through lines 20 and 23, valve 22, lines 21 and 17, valve 16, line 15, valve 14 and lines 13 and 11 to gas inlet 7 from which it passes upwardly through flues 4 of regenerative checkerwork 3 wherein it is heated to ignition temperature. The heated combustible material then passes into combustion space 8 where it burns. The combustion products then pass down through flues 4 of regenerative checkerwork 2 into gas withdrawal space 6 and thence out of the furnace through lines 10 and 24, valve 26, line 27, valve 28, lines 29 and 33, valve 34 and lines 35 and 32. This gas flow is reversed at suitable intervals by reversing three-way valves 14 and 26. The temperature conditions so obtained in the mass correspond to those previously described.

This alternative method of heating is particularly advantageous in that a very high flame temperature is obtained in chamber 8 with attendant decrease in the time required to heat the furnace. Furthermore, the high temperature zone at the top of regenerative checkerworks 2 and 3 is shorter in length than that resulting from the first described heating method. This result is particularly advantageous when it is desired to produce a maximum quantity of unsaturated hydrocarbons in a short residence time at high temperature.

The operation of the heated furnace to produce low density heating gas by the partial combustion of hydrocarbons is much the same as the last described heating method. A mixture containing hydrocarbons consisting predominantly of propane and air in non-combustible proportions of about one to two is introduced through lines 20 and 23, valve 22, lines 21 and 17, valve 16, line 15, valve 14, and line 11 into gas inlet space 7. The mixture is then passed upward through flues 4 of checkerwork 3. In the course of such passage the temperature of the propane is raised until near the top of checkerwork sufficient cracking has occurred to render the gas mixture flammable. It will be appreciated that carbon and hydrogen will be formed by the cracking and that the materials will be flammable even with the limited amount of oxygen present. Since there is a deficiency of oxygen, however, only a portion of the combustible materials will be consumed. However, only about 15% to about 40% of original hydrocarbon employed is so dissipated. The balance of the hydrocarbon in the case under consideration, predominantly propane, is efficiently cracked by the heat released by the aforementioned combustion reaction. The combustion and cracking reactions predominantly

occur in combustion chamber 8 where it will be noted the endothermic and exothermic heat are substantially equally balanced. It will be obvious that the exothermic heat from the combustion will be absorbed by the endothermic cracking reactions. Furthermore, the sensible heat of the entire gas mixture is raised to the flame temperature of the combustion reaction.

By virtue of the type and dimensions of the checkerworks 2 and 3 and chamber 8 of the furnace of this invention, the contact time of the gases in chamber 8 is extremely short, i. e., less than about 0.025 second with the result that extremely high yields of unsaturated hydrocarbons are obtained.

Subsequent to the combustion and cracking reaction which predominantly occurs in chamber 8, the gas mixture produced passes downwardly through flues 4 of checkerworks 2 and gives up heat thereto. The mixture then passes out through chamber 6, lines 10 and 24, valve 26, line 27, valve 28, lines 29 and 33, valve 34 and lines 35 and 32 to storage. The temperature of the gas leaving the furnace will be about 100° C.-150° C., which evidences high thermal efficiency.

The gas flow through the furnace is continued in the manner specified for approximately one minute and three-way valves 14 and 26 are then simultaneously reversed. This reversal is preferably accomplished in a fraction of a second, in fact so quickly that the continuous flow of product gas passing through line 25 is not interrupted. The reversal of flow transfers the stream of inlet gas through valve 14, lines 12 and 10 and chamber 6 into flues 4 of checkerwork 2. The gas passes upward through flues 4, checkerworks 2, is heated to partial cracking, undergoes simultaneous cracking and combustion in chamber 8, is quenched in checkerworks 3 and passes out through chamber 7, lines 11 and 25, valve 26, line 27 and valve 28, lines 29 and 33, valve 34 and lines 35 and 32 to storage. The gas flow is again quickly reversed after operation for one minute and the process so operated continuously. After a period of such continuous operation, the maximum temperature of the regenerative checkerworks levels off at about 800° C. to 900° C., normally 850° C.

The gas product obtained had the following composition in percent by volume:

Carbon dioxide	1.8
Acetylene	0.9
Ethylene	15.6
Propylene	3.0
Hydrogen	11.3
Carbon monoxide	7.8
Methane	17.5
Propane	3.0
Nitrogen	39.1
	100.0

The volume of the product gas as compared with the inlet mixture is 1.37. The heating value of the constituents of the product gas per unit volume is 97% of that of the propane contained in a unit volume of the feed.

It will be apparent from the foregoing that this invention embraces a continuous regenerative process for the production of heating gas containing unsaturated hydrocarbons. This process operates at very high thermal efficiency by supplying heat internally and by combustion and heat transfer. The exothermic heat is generated by combustion of a portion of the cracked hydrocarbons in a restricted combustion chamber located immediately above the checker sections.

The process is completely reversible and establishes a steady state which continues indefinitely. It is particularly advantageous in that no reheating, relocation or condensation heating zones in the regenerative mass is

required other than that resultant from the simple reversal of gas flues herein discussed. Furthermore, the absence of rapid and extreme temperature changes greatly prolongs the life of the regenerative checkerwork and thereby effects substantial economy.

The operation of the furnace in the manner above described results in the continuous production of low density heating gas containing a high proportion of olefinic hydrocarbons. This mode of operation, while admirably suited to the production of such heating gas is not adapted to the production of acetylene in high yields for the reason that operation under reduced pressure and a more rapid quenching is necessary to prevent decomposition of that product.

Operation at sub-atmospheric pressure may be effected in the apparatus of this invention through utilization of vacuum pump 31. To obtain the benefits of pump 31, valve 30 is opened and valve 34 is closed. Valve 22 or 16 may be throttled to maintain the desired vacuum. The apparatus is otherwise operated in the same manner as that previously described for operation at atmospheric pressure. A vacuum as great as about 0.2 atmosphere absolute may be obtained. Such reduced pressure operations are particularly suitable for the production of acetylene, hydrazine and other products which require rapid quenching to prevent decomposition for the reason that the residence time of the gases undergoing treatment in the refractory regenerative furnace can be reduced in proportion to the reduction in pressure below atmospheric. Likewise, yields of acetylene and the like are increased by the low partial pressure of such product gases in the reaction mixture.

Different ratios of hydrocarbon to oxygen or oxygen containing gas are employed when it is desired to produce acetylene, than when heating gas is the desired product. Table II indicates the preferred ranges in parts by volume of air and oxygen to one volume of methane, ethane, propane, and natural gas for the production of acetylene by operation at sub-atmospheric pressures.

Table II

Starting Material	Oxygen	Air
Methane.....	0.2-6	1-3
Ethane.....	0.4-8	2-4
Propane.....	0.6-1	3-5
Natural Gas.....	0.2-6	1-3

Operation of the apparatus in this invention under a reduced pressure of about 0.2 atmosphere absolute utilizing a starting material comprising a mixture of air and natural gas in the ratio of about 2.75 volumes of air per volume of natural gas, yielded a product having the following composition in percent by volume.

Carbon dioxide	1.4
Acetylene	7.5
Carbon monoxide	6.2
Hydrogen	28.0
Methane	2.4
Nitrogen	54.5

It will be observed that the yield of acetylene obtained is more than 60% of theoretical, a higher yield than has heretofore been reported by any commercial pyrolysis operation. Thus, the novel apparatus and process of this invention makes possible a continuous method for the production of acetylene under reduced pressure and under the optimum conditions of extremely short residence time, i. e., 0.01 second or less, in the reaction zone combined with extremely rapid quenching. Accordingly, there has been developed for the first time a continuous regenerative furnace operation for the production of acetylene which is operable under a wide range of pressures and which is attended by no disturbing pressure changes or

other adverse effects. An additional result which has been achieved by this invention is the production of acetylene in excellent yield which contains no appreciable contamination of carbon particles. Hence, the difficulties of separation of carbon from the product acetylene is largely obviated.

It will be appreciated that the method and apparatus of this invention is equally adapted to continuous operation at super-atmospheric pressures and may be employed to effect endothermic gas reactions which are favored by such conditions. To achieve this purpose, valve 30 is closed, valve 34 is opened, valve 22 is closed, and valve 18 is opened. The starting materials are introduced through line 20, in pump 19, the process otherwise being conducted in the manner previously described for operations at atmospheric pressure. Valves 28 and 34 may be throttled to maintain the desired pressure in the system.

The novel process and regenerative furnace of this invention constitute a significant advance in the art typified by many advantages such as those hereinbefore described. Obvious modifications of the process and apparatus may be made. Thus, if desired, the furnace might be operated intermittently. Such a mode of operation however, would dissipate the advantages of continuous production of product gases which constitute one of the salient features of the invention.

The apparatus of this invention may also be operated by the continuous addition of a portion of the product to be pyrolyzed through openings in heating means 9. As previously pointed out, however, such a mode of operation reduces the thermal efficiency of the furnace and negatives the advantages of the unique structure of the furnace.

Obvious modifications of the apparatus and process of this invention will be apparent to those skilled in the art. It will be understood that the scope of the invention is restricted only by the sub-joined claims.

What I claim is:

1. A self-sustaining regenerative process for continuously effecting endothermic reactions with fluid reactants which comprises flowing a non-flammable mixture containing hydrocarbon and air through continuous channels of a regenerative mass progressively hotter in the direction of gas flow to pre-heat said mixture and effect incipient endothermic cracking of the hydrocarbon in the regenerative mass to produce a flammable mixture, flowing the flammable mixture through a combustion and endothermic alteration zone simultaneously to burn a portion of the hydrocarbon and endothermically to alter substantially all of the remainder of said hydrocarbon, said burning supplying all of the required heat for said endothermic alteration and producing a gaseous effluent having a temperature higher than that of the regenerative mass, flowing the said effluent through continuous channels of a second regenerative mass progressively cooler in the direction of flow to quench said effluent and to transfer the sensible heat thereof to the second regenerative mass in an amount substantially equivalent to the amount of sensible heat removed from the first regenerative mass in the pre-heating step, rapidly reversing the flow of non-flammable gaseous feed mixture when the temperature of the first regenerative mass falls below that effective to pre-heat the said gas and by incipient cracking produce a flammable mixture and the temperature of the second regenerative mass rises above that effective to quench the effluent; the period of residence of the gases undergoing treatment in each of the regenerative masses not exceeding about 0.3 second, the period of residences of the gases undergoing treatment in said combustion and thermal alteration zone not exceeding about 0.05 second, said residence periods being calculated at atmospheric pressure, the pressure drop of the gases passing through said regenerative masses not exceeding about five pounds per square inch.

2. A process according to claim 1 for producing a heating gas in which the feed gas comprises a non-flammable mixture of air and methane, the ratio of air to methane being about 1-3.5:1.

3. A process according to claim 1 for producing a heating gas in which the feed gas comprises a non-flammable mixture of air and a gaseous hydrocarbon having at least two carbon atoms.

4. A process according to claim 1 for producing a heating gas in which the feed gas comprises a non-flammable mixture of air and propane, the ratio of air to propane being about 1-5:1.

5. A process according to claim 1 for producing a heating gas in which the feed gas comprises a non-flammable mixture of air and butane, the ratio of air to butane being about 1.5-6.5:1.

6. A self-sustaining regenerative process for continuously effecting endothermic reactions with fluid reactants which comprises initially burning a gaseous fuel with substantially complete combustion in a combustion zone disposed between two regenerative masses having continuous channels therethrough, flowing the hot products of combustion simultaneously through the channels of the regenerative masses until a temperature gradient is established in each of the masses ranging from a temperature in excess of 1000° C. at the ends thereof adjacent the combustion zone to a temperature of 100° C. at the opposite ends thereof, discontinuing said burning when said gradient is established, flowing a non-flammable mixture containing hydrocarbon and air through the continuous channels of the first regenerative mass progressively hotter in the direction of gas flow to pre-heat said mixture and effect incipient endothermic cracking of the hydrocarbon in the generative mass to produce a flammable mixture, flowing the flammable mixture through the combustion zone simultaneously to burn a portion of the hydrocarbon and endothermically to alter substantially all of the remainder of said hydrocarbon, said partial burning sup-

plying heat losses of the system and all of the required heat for said endothermic alteration and producing a gaseous effluent having a temperature higher than that of the regenerative mass, flowing the said effluent through the continuous channels of the second regenerative mass progressively cooler in the direction of flow to quench said effluent and to transfer the sensible heat thereof to the second regenerative mass in an amount substantially equivalent to the amount of sensible heat removed from the first regenerative mass in the pre-heating step, rapidly reversing the flow of non-flammable gaseous feed mixture when the temperature of the first regenerative mass falls below that effective to preheat the said gas and by incipient cracking produce a flammable mixture and the temperature of the second regenerative mass rises about that effective to quench the effluent; the period of residence of the gases undergoing treatment in each of the regenerative masses not exceeding about 0.3 second, the period of residence of the gases undergoing treatment in said combustion and thermal alteration zone not exceeding about 0.05 second, said residence periods being calculated at atmospheric pressure, and said process having a thermal efficiency of at least about 90%.

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