

Jan. 13, 1959

J. W. BEGLEY

2,868,855

CONVERSION OF HYDROCARBONS

Filed Oct. 18, 1954

3 Sheets-Sheet 1

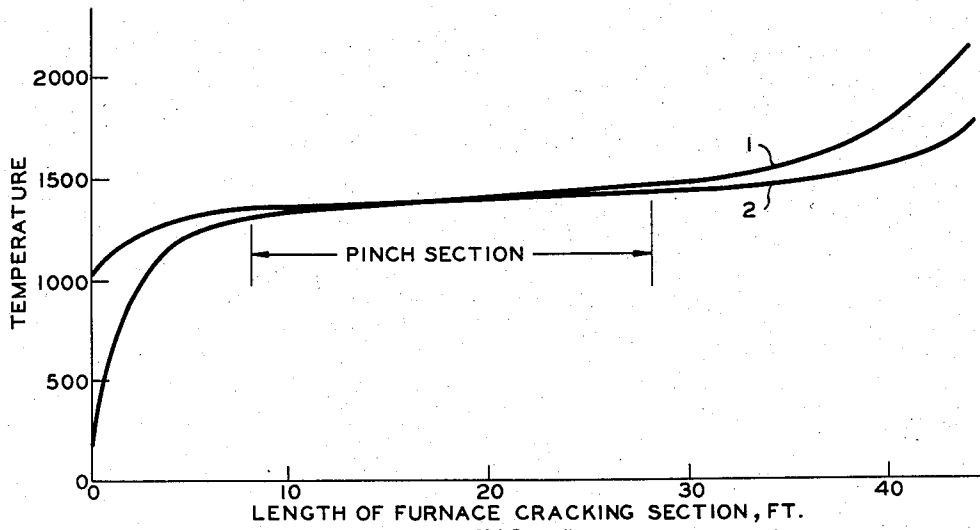


FIG. 1

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3 Sheets-Sheet 2

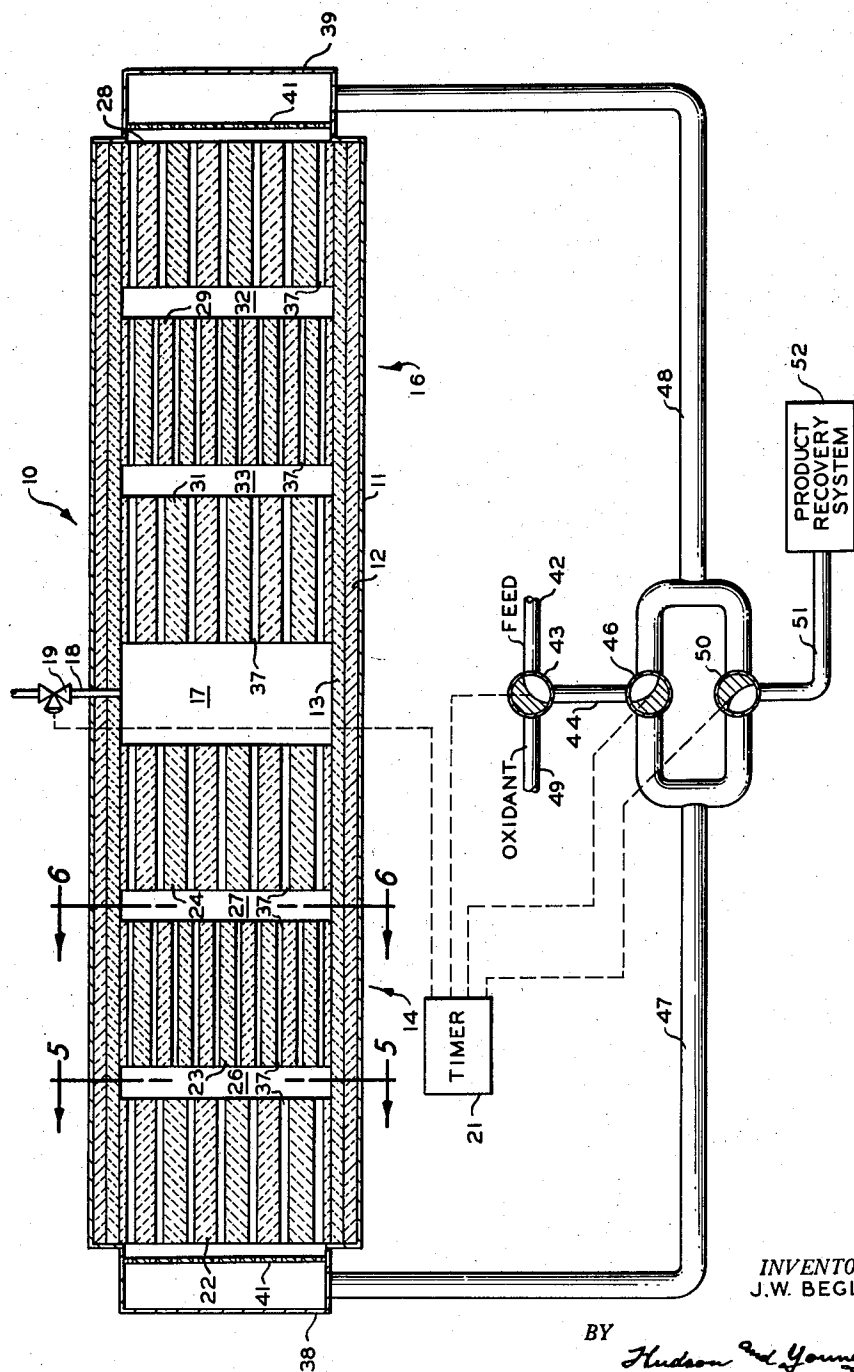


FIG. 2

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3 Sheets-Sheet 3

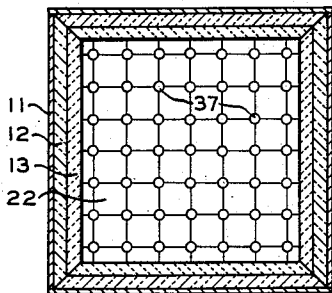


FIG. 4

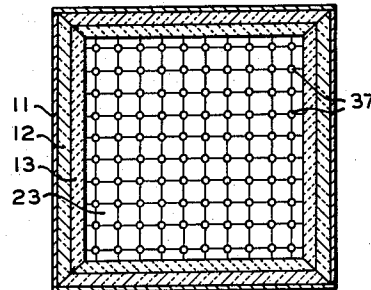


FIG. 5

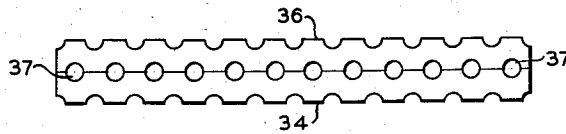


FIG. 3

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CONVERSION OF HYDROCARBONS

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6 Claims. (Cl. 260—679)

This invention relates to the conversion of hydrocarbons. In one of its more specific aspects, it relates to novel regenerative furnaces for use in the thermal cracking of hydrocarbons. In another of its more specific aspects, it relates to a process for the thermal conversion of hydrocarbons. In still another of its more specific aspects, it relates to a process for the production of unsaturated hydrocarbons.

During the early years of the petroleum industry, the possibility of producing unsaturated hydrocarbons by the cracking of low boiling hydrocarbons received comparatively little attention. Because of apparatus limitations imposed by the high reaction temperatures involved and the lack of understanding of the best manner of operation, early developments excluded the cracking of low boiling hydrocarbons. Still another deterrent in the development of successful processes was the availability of vast supplies of heavy naphthas which could be cracked by more easily manageable processes to form easily purifiable products in high yield. Recent advancements made in organic chemistry have resulted in such an increased demand for petro-chemical starting materials, such as acetylene and ethylene, that it is no longer possible to rely on the old sources of supply for these materials. The demand for ethylene has reached such proportions that it cannot be supplied from refinery streams without upsetting the balance in the production of motor and aviation fuels. Furthermore, commercial production of acetylene by reacting calcium carbide with water is too expensive and is limited to amounts far too low to satisfy the demand for acetylene as a chemical synthesis starting material. Accordingly, the development of successful processes for producing unsaturated hydrocarbons by the cracking of low boiling hydrocarbons has in recent years taken on added importance.

Various methods for the pyrolysis of gaseous hydrocarbons have been proposed which involve the use of a variety of heat sources, including externally heated tubes, electrical heated resistance elements, and spark or electrical discharges. The lack of cheap electric power has also drawn attention to other possible methods of heating, such as by the combustion of preheated natural gas with preheated compressed air. In such latter processes when utilizing regenerative furnaces, a stream of air and fuel gas is burned in, or hot combustion products passed through, a refractory checkerwork so as to heat it to a high temperature. After the hot gases have heated the checkerwork to the desired temperature, the flow of combustion gases is terminated, and thereafter the reactant materials to be treated are passed through the heated checkerwork in order to bring the materials to reaction temperature.

In a particularly useful regenerative furnace of this type, utilized for the thermal cracking of hydrocarbons, such as methane, ethane, propane or butane, to produce unsaturated hydrocarbons, such as ethylene or acetylene, an elongated checkerwork of refractory material is provided at either end of a central combustion chamber.

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Air is passed in one direction through one of the checkerwork structures while a fuel gas is introduced into the central combustion chamber. The fuel gas and air burn in the combustion chamber, and thereafter the resulting combustion gases flow through one of the refractory checkerworks. When this checkerwork has reached the desired temperature, the flow of air and fuel is terminated, and the materials to be cracked or otherwise converted are passed in the opposite direction through the heated refractory where the desired cracking or other reaction occurs.

After a timed reaction period, the flow of reactant materials is stopped, and air is passed through the furnace in a direction opposite to that of its first introduction. At the same time, fuel gas is introduced into the central combustion chamber to mix with the air and form a combustible mixture which is burned therein to form hot combustion gases to heat the refractory checkerwork downstream of the combustion chamber. When the checkerwork attains the desired temperature, the materials to be converted are passed through the heated refractory.

I have now discovered that when utilizing a regenerative furnace of the type described above, having similar refractory cracking sections, a very close temperature approach exists in the center of the cracking sections. The portion of the cracking sections in which the temperature of the gases, i. e., the combustion gases or the reaction products, and the refractory material, are substantially equal may be termed the "pinch section" and denotes that portion of the cracking section where substantially no net heat transfer occurs between the gases and the refractories. In a regenerative furnace, it is desirable that the length of the pinch section be as short as possible in order to reduce the overall length of the furnace. Figure 1 of the drawing illustrates graphically the temperature conditions existing in a cracking section of a regenerative furnace of the type described. Curves 1 and 2 represent, respectively, the temperature of the combustion gases and the temperature of the hydrocarbon reactant material as these materials pass through the refractory checkerwork. The combustion gases enter the checkerwork at a higher temperature and leave at a lower temperature while the hydrocarbons are introduced at a lower temperature and pass therefrom at a higher temperature. That portion of the curves in which the gases undergo substantially no change in temperature is labeled "pinch section" which designates that part of the furnace in which there is substantially no net transfer of heat between the gases and the refractory. It is noted that a major portion of the furnace is occupied by the pinch section. In order to decrease the length of the furnace, it is desirable to maintain the pinch section as short as possible, and in accordance with this invention, means are provided for attaining this result.

The following are objects of the invention.

It is an object of the invention to provide improved regenerative furnaces for use in the conversion of hydrocarbons.

Another object of the invention is to provide improved methods for the thermal conversion of hydrocarbons.

Still another object of the invention is to decrease the length of a regenerative furnace by decreasing the "pinch section" of the refractory masses.

Yet another object of the invention is to provide a regenerative furnace which includes means for distributing the gases evenly throughout the furnace so as to prevent channeling of the gases through any one portion of the furnace.

Still further objects and advantages of the invention will become apparent to one skilled in the art upon consideration of the following disclosure.

Broadly speaking, the present invention resides in novel regenerative furnaces and their use in processes for the conversion of hydrocarbons. In one modification of the invention, a furnace is provided which includes refractory masses having different sized openings or passageways therethrough for the flow of combustion gases and reaction products. By utilizing a larger number of smaller openings in a portion of the refractory, an increased surface area is presented to the gases, giving a corresponding increase in the heat transfer rate and thereby permitting a decrease in the overall furnace length.

A more complete understanding of the invention may be obtained by reference to the following description and the drawing, in which:

Figure 1 is a graph illustrating the "pinch section" existing in a conventional regenerative furnace;

Figure 2 is an elevation, partially in section, of a regenerative furnace constructed in accordance with one modification of the invention;

Figure 3 is an end view of refractory tiles suitable for use in the regenerative furnace of this invention;

Figures 4 and 5 are cross sectional views taken along lines 5-5 and 6-6 of Figure 3.

Referring now to the drawing, and in particular to Figures 2, 4 and 5, a regenerative furnace 10 is shown which comprises a shell 11 lined with insulating material, such as two layers 12 and 13 of fire brick. The inner layer 13 of insulating material is formed of a more refractory material than outer layer 12. Disposed within insulated shell 11 are two sets 14 and 16 of refractory masses separated by a combustion space or chamber 17 having a fuel introduction means 18 communicating therewith. Fuel introduction means 18 is provided with a flow control means 19 which is operatively connected to timer 21. A timer suitable for use in controlling the cycles of operation is manufactured by Taylor Instrument Companies, Rochester, New York. While only one means for introducing fuel has been shown, it is to be understood that a plurality of such means may be provided for injecting fuel into combustion space 17. One set 14 of the refractory masses comprises refractory masses 22, 23 and 24, which are spaced apart so as to provide gas redistribution zones 26 and 27 therebetween. The second set 16 of refractory masses is similar to set 14 and includes refractory masses 28, 29 and 31 separated by gas redistribution zones 32 and 33.

The refractory masses are formed of refractory tiles similar to tiles 34 and 36, as shown in Figure 3, which are arranged within the furnace with their longitudinal axis extending transversely thereof. The upper and lower faces of the tiles have spaced semi-circular portions formed therein which cooperate, when the tiles are placed on top of one another, to form a series of openings 37.

As shown in Figure 2, the openings 37 extend longitudinally through the refractory masses so as to provide passageways therethrough. The passageways in the center refractory masses 23 and 29 of each set of refractory masses are greater in number and have a smaller diameter than those in adjacent refractory masses, but the total open area of each of the refractory masses is substantially equal. The difference in the size and in the number of the openings through the center refractory masses and the masses adjacent thereto is further illustrated in Figures 4 and 5. The ratio of the number of openings of two different sizes but with the same total open area presented for gas flow can be represented by the formula:

$$\frac{No_1}{No_2} = \frac{1}{(f)^2}$$

where (f) is the ratio of the diameter of the larger openings to the diameter of the smaller openings and No_1 and No_2 refer, respectively, to the number of larger and smaller openings. Since the heat transfer coefficient

varies inversely with the diameter to the 0.2 power, the heat transfer rate is increased by factors of 2.30, 3.75 and 5.28, where the ratios (f) of diameters are 2, 3 and 4, respectively.

Plenum chambers 38 and 39, connected to either end of the regenerative furnace of Figure 2, provide means for introducing reactant materials into the furnace. Each of the plenum chambers may be provided with a perforated distributor plate 41 to ensure even distribution of the reactant materials across and through the cross-sectional area of the refractory masses.

Conduit 42, through which hydrocarbon feed material is introduced, is connected by a three-way valve 43 to a conduit 44. Conduit 44 in turn is connected through a three-way valve 46 to a conduit 47 which communicates with plenum chamber 38 or, alternatively, to a conduit 48 which communicates with plenum chamber 39. Valve 43 is also adapted to attach oxidant conduit 49 to conduit 44 and, thence, to conduits 47 and 48, as determined by the setting of valve 46. Conduits 47 and 48 are also selectively connected by a three-way valve 50 to an effluent conduit 51 which leads to a product recovery system 52, or other disposal, as desired. Timer 21, which is operatively connected, as previously mentioned, to flow control means 19 contained in fuel introduction means 18, is also operatively connected to three-way valves 43, 46 and 50, thereby providing means for sequentially changing the cycles of operation of the regenerative furnace.

The regenerative furnaces of this invention are especially adapted for carrying out processes for the production of unsaturated hydrocarbons, such as acetylene, ethylene, and mixtures of acetylene and ethylene. The reaction temperatures for such processes will vary in the approximate range of 1250° F. to 2700° F. More specifically, in the acetylene process, the reaction temperature is preferably maintained between about 2200° F. and 2700° F., in the process for the production of acetylene and ethylene, between about 1700° F. and 2200° F., and in the ethylene process, between about 1250° F. and 1700° F. The reaction times for the several processes are in the following approximate ranges: for acetylene, between 0.0001 and 0.2 second; for a mixture of acetylene and ethylene, between 0.01 and 0.2 second; and for ethylene, between 0.01 and 2 seconds. From this consideration of reaction temperatures and reaction times, it is apparent that the reaction times vary inversely with the reaction temperatures, i. e., the higher the reaction temperature, the shorter the reaction time.

A wide variety of hydrocarbon feed stocks can be used in the practice of the processes of this invention. Those which can be suitably used include methane, ethane, propane, butane and mixtures of these hydrocarbons and/or their corresponding olefins. It is to be understood, however, that any vaporizable or gaseous hydrocarbons can be advantageously employed as the feed. It is also within the contemplation of the invention to use a diluent such as steam with hydrocarbon feed in order to reduce the deposition of carbonaceous materials within the furnace.

Oxidants which can be used in the process of this invention include oxygen, air, and oxygen-enriched air. Any suitable fuel, preferably a clean burning fuel, can be utilized in the practice of this invention. Gaseous or liquid hydrocarbons are preferably used as fuels, and process off-gases from the process of this invention or other processes can be advantageously employed. When using a liquid hydrocarbon, the fuel is introduced into the furnace in vaporized form.

In the operation of the regenerative furnace of Figure 3, during the regeneration cycle valves 43 and 46 are in such a position that an oxidant, such as air, is forced by a blower (not shown) through conduits 49, 44 and 47 into plenum chamber 38, from which it passes into

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passageways 37 of refractory mass 22. Plenum chamber 38 and distributor plate 41 disposed therein provide for even distribution of air across the face of refractory mass 22 and assure even flow of the air therethrough. It is assumed that the furnace has been previously brought to operating temperature during a start-up cycle in which fuel and air introduced into the furnace are ignited by a suitable ignition means, e. g., a burning torch introduced into the combustion chamber. The resulting combustion products are then passed through the furnace until it is preheated to the desired temperature.

The air in passing successively through refractory masses 22, 23 and 24 is heated to a temperature at least as high as the ignition temperature of the fuel gas introduced into combustion chamber 17 through fuel inlet means 18. The fuel gas may be preheated prior to injection into the combustion chamber. The combustible mixture formed by the mixing of the air and fuel gas within the combustion chamber burns therein forming combustion products at a temperature in the approximate range of 2500° F. to 4000° F., depending upon the amount of air and the amount of fuel introduced through fuel inlet means 18. It is to be noted that the combustion of the fuel and air will not be confined to combustion chamber 17, but will also take place within the refractory masses downstream of that chamber and especially within refractory mass 31. The combustion products flow through refractory masses 31, 29 and 28, heating the refractories to the desired cracking temperature. The combustion products thereafter pass into plenum chamber 39 and, thence, through conduits 48 and 51 into product recovery system 52 where they may be used for heating or other purposes.

At the conclusion of a predetermined length of time, as determined by the setting of timer 21, valve 43 is actuated by timer 21 to transfer conduit 44 from its connection with conduit 49 to a connection with conduit 42. The timer also operates to close flow control means 19 and to reverse the settings of valves 46 and 50 so that conduit 44 is connected to conduit 48 and conduit 47 is connected to conduit 51. An interval of one minute is a suitable reaction period and regeneration period for the cracking of propane to form acetylene. The time interval will, in general, depend upon the particular process being carried out and the specific hydrocarbon feed stock being converted. As a result of the movement of valves 43 and 46, the process cycle commences and hydrocarbon feed and steam, if desired, now passes through conduits 42, 44 and 48 into plenum chamber 39. As previously noted, the combination of the plenum chamber and distributor plate 41 provides for even flow of gases through the refractory masses. On contacting hot refractory masses 28, 29 and 31, the hydrocarbon feed is raised to the desired cracking temperature and undergoes reaction. The cracked hydrocarbon feed thereafter passes immediately into combustion chamber 17 and through refractory masses 24, 23 and 22, which have previously been cooled by passage of air therethrough, for rapid quenching to a temperature in the range of about 400° F. to 1000° F. The reaction products then flow into plenum chamber 38 and are subsequently passed through conduits 47 and 51 to product recovery system 52 for separation of the product gas from the reaction products.

At the end of the predetermined time interval, timer 21 operates to change the setting of valve 43 so that air is now introduced into the regenerative furnace through conduit 48 to start the regeneration cycle. The timer functions also to open fuel flow control means 19, thereby allowing fuel to flow into combustion chamber 17. After the regeneration cycle is completed, the process cycle is begun by timer 21 operating to close flow control means 19 and change the settings of valves 43, 46 and 50, thereby permitting hydrocarbon feed to enter the furnace through conduit 48 and the effluent to pass to

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product recovery system 52 through conduits 47 and 51. The regeneration and process cycles are thereafter repeated at the predetermined time intervals to produce the desired product.

As previously mentioned in conjunction with the description of the regenerative furnace of Figure 3, center refractory masses 23 and 29 are provided with openings or passageways smaller in diameter than those in the other adjacent refractory masses. By forming the refractory masses in this manner, the heat transfer rate in the center refractory masses is increased, thereby substantially decreasing the pinch section in the cracking sections and making possible a regenerative furnace of decreased length.

It is to be noted also that gas distribution zones 26, 27, 33 and 32 are provided between the refractory masses. The utilization of such zones facilitates an even distribution of gases through the refractory masses, thereby preventing channeling of gases through a portion only of the refractory masses. By operating in this manner, it is possible to maintain a uniform temperature across the cross-section of the furnace, thereby preventing damage to the refractories and assuring an efficient and uniform cracking reaction.

A more comprehensive understanding of the invention may be obtained by referring to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

Example I

A regenerative furnace of a conventional type described herein as having similar refractory cracking sections separated by a central combustion chamber is utilized to convert ethane. The hydrocarbon feed rate is 72,450 pounds of ethane per day, the combustion temperature is about 2200° F., and the combustion gas outlet temperature is about 1040° F. In order to convert ninety percent of the ethane, refractory cracking sections each having a length of 44 feet are required. A very close temperature approach occurs in the center of the cracking sections, 20 feet being required in the "pinch sections".

Example II

A regenerative furnace similar to the one shown in Figure 3 is utilized to convert ethane. The hydrocarbon feed is charged to the furnace at the same rate as in Example I, and the combustion temperature and combustion gas outlet temperature are also approximately 2200° F. and 1040° F., respectively. By utilizing refractory cracking sections having different sized openings therethrough, the rate of heat transfer in the center of the sections is increased, thereby decreasing the length of the "pinch section" of conventional furnaces, and permitting use of shorter cracking sections. A ninety percent ethane conversion is obtained when using cracking sections each having a length of 20 feet.

Example III

A regenerative furnace similar to the one employed in Example I is utilized to convert ethane. The hydrocarbon feed rate is 72,450 pounds of ethane per day, the combustion temperature is about 2800° F., and the combustion gas outlet temperature is about 1000° F. The average temperature of the hydrocarbon during the cracking reaction is about 1700° F. The desired total conversion of eighty-three percent is obtained at a point about 1.5 feet downstream from the middle of the furnace with the result that the reaction period is greatly prolonged. At higher conversions, the point at which total conversion is obtained is moved even farther downstream from the middle of the furnace, e. g., at a total conversion of ninety-six percent about 3.5 feet. The yield of ethylene when 83 percent of the total feed is cracked is 70 pounds per 100 pounds of ethane cracked. Because of the long reaction time required to obtain the desired total con-

version, a considerable amount of product is consumed by secondary reactions.

It will be apparent that many advantages accrue from the utilization of the regenerative furnaces of this invention. Accordingly, by utilizing a furnace which provides for a more rapid heat transfer rate in the central portion of the cracking sections, it is possible to decrease the over-all length of the furnace.

As will be evident to those skilled in the art, various modifications of this invention can be made or followed without departing from the spirit or the scope of the disclosure.

I claim:

1. A regenerative furnace which comprises, in combination, an elongated shell; at least three regenerative masses disposed in said shell, said masses having passageways extending therethrough substantially parallel to the longitudinal axis of said shell and said masses being spaced apart and thereby forming chambers in said shell between said masses, which chambers are open to fluid flow only through said masses, so as to provide means for redistributing gases flowing therethrough; a combustion chamber formed of refractory insulating material communicating with the passageways of at least one of said regenerative masses; means for supplying fuel to said combustion chamber; and means for passing air and material to be converted through the passageways of said regenerative masses.

2. A regenerative furnace which comprises, in combination, a refractory checkerwork comprising first, second and third elongated refractory masses having a common longitudinal axis and spaced apart from one another so as to provide gas redistribution zones therebetween, each of said refractory masses having passageways extending therethrough substantially parallel to their common longitudinal axis, the cross-sectional area of each passageway through said second refractory mass being smaller than the cross-sectional area of each passageway through said first and third refractory masses and the total cross-sectional area of the passageways through each said first, second and third refractory masses being substantially equal; a combustion chamber formed of refractory insulating material communicating with one end of said refractory checkerwork; means for introducing fuel into said combustion chamber; means for passing air through said combustion chamber into said refractory checkerwork; and means for passing material to be converted through said checkerwork into said combustion chamber.

3. A regenerative furnace which comprises, in combination, a first refractory checkerwork comprising first, second and third elongated, refractory masses spaced apart from one another so as to provide gas redistribution zones therebetween; a second refractory checkerwork comprising fourth, fifth and sixth elongated refractory masses spaced apart so as to provide gas redistribution zones therebetween, said refractory masses having a common longitudinal axis and passageways extending therethrough substantially parallel to their common longitudinal axis, the cross-sectional area of each passageway through said second and fifth refractory masses being smaller than the cross-sectional area of each passageway through said first, third, fourth and sixth refractory masses and the total cross-sectional areas of the passageways through each said refractory masses being substantially equal; a combustion chamber formed of refractory insulating material positioned between said third and fourth refractory checkerworks and communicating with said third and fourth refractory masses; means for intro-

ducing fuel into said combustion chamber, and means for introducing air and material to be converted into the ends of said first and second refractory checkerworks remote from said combustion chamber.

4. A regenerative furnace which comprises, in combination, an elongated, closed shell; first, second and third refractory masses disposed in one end of said shell at spaced intervals so as to form gas redistribution zones therebetween; fourth, fifth and sixth refractory masses disposed in the other end of said shell at spaced intervals so as to form gas redistribution zones therebetween, each of said refractory masses having passageways extending therethrough substantially parallel to the longitudinal axis of said shell, the cross-sectional area of each said passageway through said second and fifth refractory masses being smaller than the cross-sectional area of each said passageway through said first, third, fourth and sixth refractory masses and the total cross-sectional areas of the passageways through each said refractory masses being substantially equal; a combustion chamber formed of refractory insulating material disposed in said shell between said third and fourth refractory mass and communicating with said third and fourth refractory masses; means for introducing fuel into said combustion chamber; and means for introducing air and material to be converted into the ends of said first and sixth refractory masses remote from said combustion chamber.

5. The regenerative furnace of claim 4 in which said means for introducing air and material to be converted comprises first and second plenum chambers each having a conduit attached thereto and each attached to and enclosing one of the ends of said shell.

6. A process for converting hydrocarbons which comprises passing air through a first refractory checkerwork into a combustion zone; introducing fuel gas into said combustion zone, thereby forming a combustible mixture; burning said combustible mixture; passing the resulting combustion products into a second refractory checkerwork; transferring heat from said combustion products to said second refractory checkerwork; increasing the rate of heat transfer in a central portion of said second refractory checkerwork; terminating the supply of air and fuel gas; passing hydrocarbon feed into said second refractory checkerwork; transferring heat from said second refractory checkerwork to said hydrocarbon feed; increasing the rate of heat transfer in a central portion of said second refractory checkerwork; passing the resulting reaction products from said second refractory checkerwork into and through said first refractory checkerwork, thereby quenching said products to a temperature at which they are comparatively stable; and removing said reaction products from said first refractory checkerwork.

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