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MEANS AND METHOD FOR PRODUCING FUEL GAS

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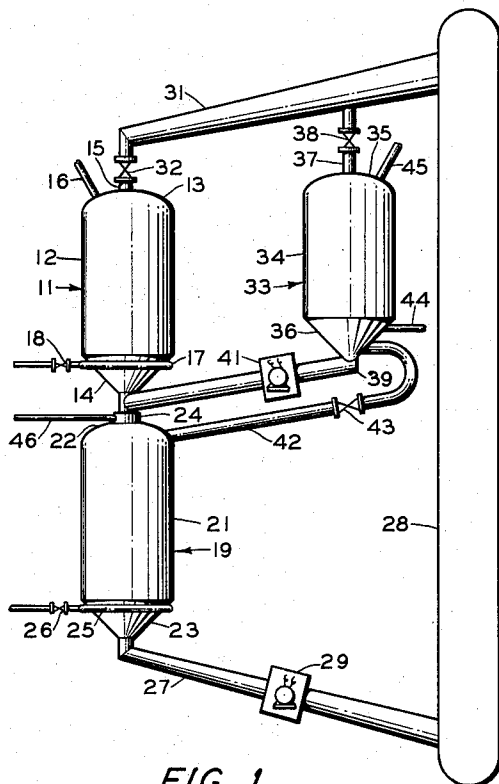


FIG. 1.

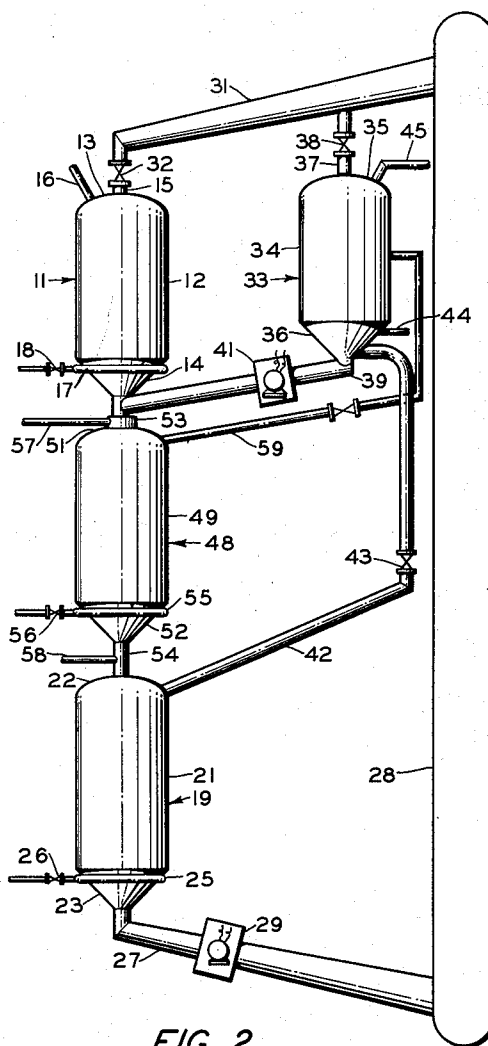


FIG. 2.

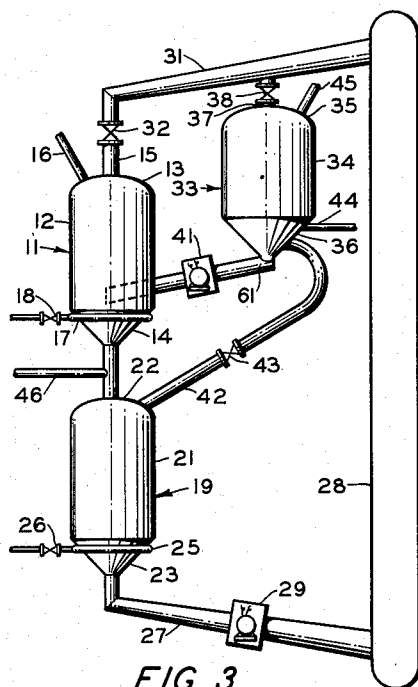


FIG. 3.

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2,714,059

MEANS AND METHOD FOR PRODUCING FUEL GAS

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14 Claims. (Cl. 48—197)

This invention relates to processes of cracking hydrocarbons in pebble heater apparatus. In one of its more specific aspects it relates to pebble heater type apparatus wherein heat required for heating the hydrocarbons to a cracking temperature is supplied by superheated steam or by steam and air, and sensible heat is removed from resulting reaction products by a mass of cool pebbles. In another of its more specific aspects it relates to processes of converting normally gaseous hydrocarbons, predominantly having at least three carbon atoms per molecule, to water gas and blending the water gas with additional gaseous hydrocarbon.

In thermally cracking hydrocarbon gases which are predominantly in the C₃ and C₄ range it is conventional to contact the feed gases with hot solid materials such as hot refractory checker work, hot flue walls, or hot flowing pebbles. In such procedures carbon resulting from the cracking reaction is deposited on the hot solid material and it is necessary to alternate the cracking step with a burning step or, in the case of the flowing pebbles, to pass the carbon bearing pebbles through a heating zone and burn the carbon therein.

When liquefied petroleum gas is converted to water gas for commercial gas systems it is economically desirable to waste as little of the products of the reaction as possible because of the relatively high cost of that gas. In conventional thermal cracking of hydrocarbon gases which are predominantly in the C₃ and C₄ range, temperatures which are ordinarily used are too low to produce a gas of the low heating value usually employed in established domestic gas systems. Such commercial gas systems usually require a gas having a heating value of between about 500 and 700 B. t. u. per cubic foot and a relatively low specific gravity, such as below about 0.5 as compared to a value of 1.0 for air. As far as is known, conventional propane cracking procedures result in a product gas having a B. t. u. value per cubic foot of at least about 775 and a specific gravity of at least 0.386 as compared to a value of 1.0 for air. In order to produce a low specific gravity gas of the required B. t. u. rating, it is necessary to operate at sufficiently high temperatures to thoroughly crack the primary decomposition products. Considerably greater amounts of carbon are deposited on the solid materials at the higher temperatures than at the lower temperatures.

Broadly speaking this invention comprises superheating a stream of steam, with or without air or oxygen, in a heating chamber of pebble heater apparatus. The superheated gas stream is introduced into the lower portion of a reaction chamber containing a cool flowing mass of pebbles, together with a stream of the normally gaseous hydrocarbons to be converted. The superheated gas stream furnishes the heat required for heating the gaseous hydrocarbons to reaction temperature, and supplies the heat of reaction. Resulting reaction products are quenched in direct heat exchange with the cool pebbles in the reaction chamber.

An object of this invention is to provide a method for

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producing a gas suitable for mixing with or supplementing a domestic gas system supply by converting C₃ and/or C₄ rich hydrocarbon gases to water gas. Another object of the invention is to provide a process of converting hydrocarbon materials to water gas of a desired heating value and specific gravity without substantial loss of carbon or tar material. Another object of this invention is to recover carbon or tar material formed in the conversion of C₃ and/or C₄ rich hydrocarbon gases to water gas for ultimate conversion to further water gas. Another object of this invention is to provide a process for producing a fuel gas of a desired B. t. u. and specific gravity by conversion and blending of hydrocarbons. Other and further objects and advantages of this invention will be apparent to those skilled in the art upon study of the accompanying disclosure.

Solid heat exchange material which may be utilized in the gasification system of this invention may be generally termed "pebbles." The term "pebbles" as used herein denotes any substantially solid material of flowable size and form which has sufficient strength to withstand mechanical pressures and the temperatures encountered within the gasification system. These pebbles must be of such structure that they can carry large amounts of heat from one chamber to another without rapid deterioration or substantial breakage. Pebbles which may be satisfactorily used in this gasification system may be substantially spherical in shape and range from about 1/8 inch to about 1 inch in diameter. The pebbles are preferably of a size within the range of from 1/8 inch to 3/8 inch in diameter. Materials which may be used singly or in combination in the formation of such pebbles include among others alumina, silicon carbide, periclase, beryllia, mullite, nickel, cobalt, copper, iron, magnesia, and zirconia.

More complete understanding of the invention will be obtained upon reference to the schematic drawings in which Figure 1 is a diagrammatic elevation of the pebble heater apparatus of this invention. Figure 2 is another diagrammatic elevation in the form of a preferred modification of this invention. Figure 3 is also a diagrammatic elevation of another modification of the invention.

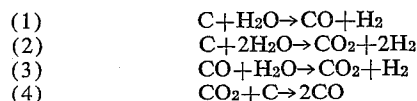
Referring particularly to the device shown in Figure 1 of the drawings, pebble heater chamber 11 comprises upright shell 12 which is closed at its upper and lower ends by closure members 13 and 14. Pebble inlet conduit 15 and effluent outlet conduit 16 are provided in closure member 13. Heating material inlet conduit 17 extends in a preferred form about the lower portion of chamber 11, preferably about at least a portion of closure member 14 and communicates with the interior of chamber 11 through that closure member. Flow control member or valve 18 is provided in inlet conduit 17. Chamber 19 comprises upright shell 21 disposed below chamber 11 and is closed at its upper and lower ends by closure members 22 and 23, respectively. Conduit 24 extends between closure member 14 of chamber 11 and closure member 22 of chamber 19. Gaseous material inlet conduit 25 extends in a preferred form about at least a portion of closure member 23 in chamber 19. Flow control means which is in the form of valve 26 is provided in conduit 25. Conduit 25 preferably communicates with the interior of chamber 19 through closure member 23. Pebble conduit 27 extends from closure member 23 to the lower end portion of elevator 28. Pebble flow controller 29, which may be in the form of a table or vibratory feeder, is provided intermediate the ends of conduit 27. Elevator 28 is connected at its upper end portion with the upper end portion of pebble conduit 31 which extends to pebble inlet conduit 15. Pebble flow control means 32 which may be a conventional star or gate valve may be, though it is not necessarily provided in inlet conduit 15. Chamber 33 which comprises upright shell 34, closed at its upper and

lower ends by closure members 35 and 36, respectively, is connected by pebble conduit 37 to a point intermediate the ends of conduit 31. Pebble flow controller 38 which may be in the form of a star or gate valve may be, though it is not necessarily provided in conduit 37. Pebble outlet conduit 39 extends between closure member 36 in chamber 33 and conduit 24 which extends between chambers 11 and 19. Pebble flow control means 41, which may be a table or vibratory feeder, is provided intermediate the ends of conduit 39. Effluent conduit 42 extends between closure member 22 in chamber 19 and closure member 36 in chamber 33. Flow control member 43 which may be a conventional valve is provided intermediate the ends of conduit 42. Reactant material inlet conduit 44 extends into closure member 36 in chamber 33 at a point adjacent the inlet of conduit 42 thereto. Effluent outlet conduit 45 is provided in the upper end portion of chamber 33, preferably in closure member 35. Sealing fluid inlet conduit 46 extends into pebble conduit 24 between chambers 11 and 19.

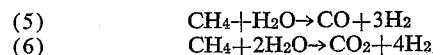
In the operation of the device shown as Figure 1 of the drawings, pebbles are introduced into the upper portion of chamber 11 through pebble inlet conduit 15. The pebbles form a flowing contiguous mass within chamber 11 and hot combustion gas or a fuel air mixture or a combination of the two is introduced into the lower portion of chamber 11 through heating material inlet conduit 17. If a fuel is introduced into the chamber through conduit 17, that fuel is burned in the presence of the pebbles, thereby heating the pebbles to a high temperature. Resulting combustion gas or any other hot gas utilized as the heating medium is passed upwardly countercurrent to the flow of pebbles through chamber 11 and is removed from that chamber through effluent outlet conduit 16. The heated pebbles are gravitated from chamber 11 through conduit 24 into chamber 19 forming a flowing contiguous mass within the latter chamber. Steam or steam and air are introduced into the lower portion of chamber 19 through inlet conduit 25 and flow upwardly through the hot contiguous mass of pebbles countercurrent to the pebble flow. The steam or steam and air are superheated in the direct heat exchange with the hot pebbles, are removed from the upper portion of chamber 19, and are transmitted at the high temperature to the lower portion of chamber 33. Pebbles which are cooled in the direct heat exchange within chamber 19 are gravitated from that chamber through conduit 27 and are fed by means of pebble feeder 29 to the lower portion of elevator 28 by which they are elevated to pebble conduit 31. A first portion of the cooled pebbles is passed by means of inlet conduit 37 and pebble flow control member 38 into the upper portion of chamber 33 in which they form a contiguous flowing mass. Hydrocarbon materials which may be predominantly C₃ or C₄ hydrocarbons or which may be heavier material such as natural gasoline or heavier are introduced into the lower portion of chamber 33 through inlet conduit 44 at a point adjacent the inlet of conduit 42. The hydrocarbon material is reformed in the presence of the superheated gas stream from chamber 19, the superheated gas stream providing the heat required to raise the hydrocarbon material to conversion temperatures. A portion of the hydrocarbon material is converted to carbon in the reaction. The carbon formation is in the neighborhood of about 15 per cent by weight of the feed. The second or remaining portion of the pebbles from conduit 31 is introduced into chamber 11 through inlet conduit 15 and pebble flow control means 32.

In the process of this invention the steam and air streams are admitted to the reaction zone with the hydrocarbon feed in such quantities that some of the carbon produced is substantially converted to CO and CO₂ by the well known water gas reaction. The following

reactions take place upon passing steam over carbon at various temperature levels.



When steam is present during the thermal cracking of the hydrocarbon material, the above reactions are important along with reactions of hydrocarbons and steam. The reactions of methane and steam may be represented as follows:



Although the Reaction 1 takes place below 1650° F., the velocity of the reaction at such temperatures is quite low. At temperatures above 1650° F., however, the velocity of the reaction is relatively rapid. The velocity of Reaction 2 is rapid as compared to Reaction 1 up to a temperature of 1650° F., but above this temperature the reaction rates of (1) and (2) are about equal. The velocity of Reaction 4 is more than twice that of Reaction 1 at temperatures above 1650° F.

While temperatures within the range of between 1650° F. and 2500° F. are required in the reaction zone, the preferred range of temperature in which the process operates most efficiently is within the range of 1900° F. to 2400° F. Temperatures of about 1850° F. to 2900° F. in the pebble heating zone will result in the desired temperature in the reaction zone. That temperature may be lowered, however, as air is introduced into the system. The reaction products resulting from the conversion of the carbonaceous material in the water gas reaction pass upwardly through the cool pebbles within chamber 33 giving up their sensible heat to the pebbles, thus being quenched below reaction temperature. The quenched reaction products are removed from chamber 33 through effluent outlet conduit 45. The major portion of carbon which is deposited upon the surface of the pebbles during the conversion of the hydrocarbon remains unconverted in chamber 33. The carbon bearing pebbles are gravitated from chamber 33 through conduit 39, pebble feeder 41, and conduit 24 into the upper portion of chamber 19. The carbon is oxidized or converted from the pebbles within chamber 19 by means of the gaseous material being superheated in that chamber, considerable heat being generated by the reaction. The resulting water gas together with superheated steam or steam and air is removed from the upper portion of chamber 19 through conduit 42 and passes through chamber 33 where the water gas is quenched as are the products resulting from the reaction within chamber 33. An inert gas, such as steam, is introduced into conduit 24 through conduit 46, forming a choke means which substantially prevents the passage of gas from chamber 11 to chamber 19 or from chamber 19 to chamber 11.

This form of the invention is particularly advantageous when the hydrocarbon feed is a relatively expensive liquefied petroleum gas. When liquefied petroleum gas is to be utilized to augment commercial gas systems, great care must be taken to convert that material to a heating gas having the desired B. t. u. content as efficiently as possible. Examination of the process described above will disclose the fact that very little heat loss is encountered in the operation of the device of Figure 1 of the drawings. Sensible heat is recovered from the reaction products in chamber 33 and is utilized in the conversion of the hydrocarbon material. Any carbon material which is not converted within the reaction chamber is converted to water gas in chamber 19, thereby increasing the volume of the desired product considerably more than in conventional systems in which the carbon is utilized in the heating step rather than as one of the reactant materials. Another ad-

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vantage is that the required capacity of the pebble heater apparatus is decreased by converting a normally high B. t. u., high gravity hydrocarbon material to a large volume of low B. t. u., low gravity material which may then be blended with another portion of the higher B. t. u. to produce a fuel of desired B. t. u. and specific gravity. It is well known that as the volume of a material being cracked is increased, the greater is the amount of carbon formation. Considerable saving of expensive material is obtained by operation in the method of this invention.

In the device shown in Figure 2 of the drawings, parts which are identical to those described in Figure 1 are identified by identical reference numerals. The device shown in Figure 2 of the drawings differs in the provision of chamber 48 which comprises upright shell 49 closed at its upper and lower ends by closure members 51 and 52. Chamber 48 is disposed between chambers 11 and 19 and is connected to the lower portion of chamber 11 by means of conduit 53 which is connected to closure member 51 of chamber 48. Conduit 54 extends between closure member 52 in the bottom portion of chamber 48 and closure member 22 in the upper end of chamber 19. Gaseous material inlet conduit 55 preferably extends about at least a portion of closure member 52 and communicates with the interior of chamber 48 through that closure member. Flow control valve 56 is provided in conduit 55 to control the flow of fluid therethrough. Inert gas inlet conduits 57 and 58 are provided in conduits 53 and 54, respectively. Effluent outlet conduit 59 extends between the upper end of chamber 48 and a point above the level of conduit 44 and intermediate the ends of chamber 33.

The operation of the device shown in Figure 2 of the drawings is very similar to that described in connection with Figure 1 of the drawings. Pebbles are introduced into chamber 11 and are heated therein by direct heat exchange with a hot fluid and the heated pebbles are gravitated into the upper portion of chamber 48 in which they form a flowing contiguous pebble mass. Steam is introduced into the lower portion of chamber 48 through inlet conduit 55 and flow control valve 56. Pebbles from reaction chamber 33 are introduced into the upper portion of chamber 48 together with the heated pebbles from chamber 11. The steam flows upwardly through chamber 48 countercurrent to the flow of pebbles within that chamber. A large part of the carbon material deposited on the pebbles within reaction chamber 33 is converted by the water gas reaction within chamber 48. The resulting reaction products are removed from the upper portion of chamber 48 through effluent outlet conduit 59 and are passed to chamber 33 in which they are combined with the reaction products resulting from the reaction within chamber 33. The reaction within chamber 48 removes a considerable amount of heat from the heated pebbles. That heat is transferred to the pebbles in chamber 33 by the products stream flowing through conduit 59. Pebbles which are still at a high temperature are gravitated through conduit 54 into the upper portion of chamber 19 in which they form a flowing contiguous pebble mass. A steam and air stream is introduced into the lower portion of chamber 19 through inlet conduit 25 and flow control valve 26 and passes upwardly through that chamber in direct heat exchange relation with the hot pebbles, cooling the pebbles thereby and superheating the gaseous materials. Any carbon remaining on the pebbles is removed by the water gas reaction. The superheated gaseous materials are removed from chamber 19 through conduit 42 and are introduced into the lower portion of chamber 33, furnishing an additional amount of heat which is required for the reaction of the hydrocarbon materials introduced into the lower portion of chamber 33 through conduit 44. The cooled pebbles are gravitated from chamber 19 through conduit 27 and peb-

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ble feeder 29 to elevator 28 which raises the pebbles to pebble conduit 31 in which the pebble stream is divided into two portions, which pebble portions are supplied to chambers 11 and 33. The cooled pebbles supplied to chamber 33 form a very effective quench for the hot reaction products passed through that chamber.

The apparatus shown in Figure 2 of the drawings and the method of operation of that apparatus is advantageously used in order to save a portion of the products resulting from the oxidation and conversion of the carbon after the carbon has been carried from the reaction chamber. The reaction products resulting from the water gas reaction within chamber 48 bypass a portion of reaction chamber 33 and excess air reacts with the hydrocarbon material rather than the water gas product from chamber 48.

The device shown in Figure 3 of the drawings is similar to that disclosed in Figure 1 of the drawings and identical parts are identified by identical reference numerals. The device of Figure 3 of the drawings differs from that of Figure 1 only with respect to the pebble conduit 61 which extends between closure member 36 in chamber 33 and a point intermediate the ends of chamber 11 rather than extending between closure member 36 and conduit 24.

The device of Figure 3 may be utilized when the saving of each possible portion of reaction product from the converted material is not of prime importance. The operation of the device of Figure 3 is the same as that of the device of Figure 1 of the drawings with the exception that pebbles from chamber 33 are passed into chamber 11 at a point intermediate the ends of that chamber and any carbon material which is deposited upon those pebbles is burned off in chamber 11. The carbon material does provide a source of heat for heating the pebbles within chamber 11.

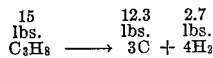
In each of the devices shown in the drawings, the very novel feature is provided by which the hydrocarbon material to be converted is introduced into the reaction chamber at a point adjacent the introduction point of another reactant material, which other reactant material has first been superheated to such a point that it provides the heat required to raise the hydrocarbon material to its reaction temperature. In this manner carbon is formed only in chamber 33 and is made available for further reaction by deposit on the pebbles which in turn flow to chambers 48 or 19. The carbon is then converted to water gas or in the device of Figure 3 is utilized as fuel. A maximum of reaction products is therefore recovered from any given feed of hydrocarbon materials. This invention also has the advantage that sensible heat of the reaction products is recovered by the cooled pebbles in the upper or quench portion of the reaction chamber and that heat is utilized in the conversion of the hydrocarbon material to carbon and/or water gas.

The system which is provided for conducting the reaction makes possible the blending of the necessary gases and of diluent materials, which diluent materials are ordinarily added to the cooled effluent or reaction products from the water gas reaction. The diluent materials are utilized as heat carriers to carry heat required for the reaction into the reaction chamber. Their residual heat is salvaged to a considerable extent and a very small net heat loss occurs. The amount of air which is preheated may be limited to substantially that which is required for the reaction and additional air may then be added together with other blending and dilution materials after the reaction has taken place. An additional advantage of this invention is the fact that carbon and tars are trapped by means of the cool pebbles in the upper part of the reaction chamber and are utilized as reactant materials. If the carbon and tars are not removed, they tend to foul up the effluent piping system and result in maintenance difficulties.

The equilibrium reached in the conversion of propane

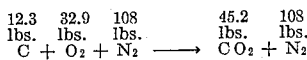
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to water gas is such that higher temperature not only favors the production of carbon monoxide and hydrogen when the propane is reformed with steam, but also the velocity of the reaction increases with the temperature. When propane is to be converted to water gas, approximately 15 per cent by weight of the feed is cracked to carbon and hydrogen and the resulting carbon which is formed on the pebbles within reaction chamber 33 is transported from that chamber by the pebbles before the steam can convert it to carbon monoxide. Conversion of 100 pounds of propane results in cracking of 15 pounds of the propane in a reaction which proceeds in the following manner at temperatures between 2000° F. and 2200° F.

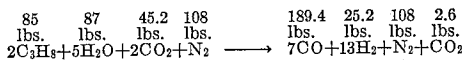


EXAMPLE I

One extreme in the conversion of propane is the total oxidation of the carbon formed thereby with air. The carbon-bearing pebbles are gravitated into chamber 19 and the carbon is converted to carbon dioxide by a controlled amount of air, steam being concomitantly superheated. The oxidation of the carbon with air proceeds as shown in the following equation.



This reaction releases about 179,000 B. t. u. which is 0.283 of the heat required for the total reforming reaction in chamber 33. The mixture of carbon dioxide, nitrogen, and superheated steam passes through conduit 42 to chamber 33. Propane is introduced into the lower portion of chamber 33 through conduit 44. The steam, propane, and carbon dioxide react in the following manner to form carbon monoxide and hydrogen, the nitrogen remaining as a heat carrier and diluent.



The residual carbon dioxide results from the fact that of the 45.2 pounds of carbon dioxide added to conversion chamber 33, only 42.6 pounds react with the propane. The remaining 2.6 pounds of carbon dioxide serve as a heat carrier and diluent. The gaseous materials removed through conduit 45 as compared to the feed introduced through conduits 25 and 44 may be compared in the following Table I.

Table I

Reactants, lbs.		Products		
		lbs.		Cu. ft., 60 F.
C ₃ H ₈ -----	100	CO-----	189.4	2,565
Steam-----	87	CO ₂ -----	2.6	22
Air-----	141	H ₂ -----	28.0	5,310
		N ₂ -----	108.0	1,462
	328		328.0	9,359

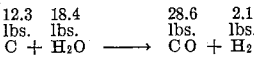
The gas removed through conduit 45 has a gravity of 0.462 compared with air and a heating value of about 263 B. t. u. per cubic foot. This gas must necessarily be blended with an additional amount of propane in order to raise its heating value to that required for fuel gas.

EXAMPLE II

On the other extreme, the total amount of carbon is converted to carbon monoxide by the water gas reaction. In this type of operation air is not required and steam is

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the only feed introduced through conduit 25 into chamber 19. The carbon and steam react as follows:



The gases removed from chamber 19 through conduit 42 and introduced into chamber 33 for reaction with the propane will be carbon monoxide, hydrogen, and steam. Since the products of the reaction of the propane with steam will be carbon monoxide and hydrogen, only the steam for chamber 33 will react with the propane as follows:



The gaseous materials removed through conduit 45 as compared with the feed material introduced through conduits 45 and 44 are set forth in Table II below.

Reactants, lbs.		Products	
		lbs.	Cu. ft., 60 F.
C ₃ H ₈ -----	100.0	CO-----	191.1
Steam-----	122.7	H ₂ -----	31.6
	222.7		222.7
			8,500

The gas removed through conduit 45 in this instance has a gravity of about 0.342 compared with air and a heating value of about 313 B. t. u. per cubic foot. A fuel gas of the required heating value can be obtained by blending this gas with propane.

The heating value and the gravity of the gaseous material removed from chamber 33 through conduit 45 may be varied by varying the quantity of air introduced into the system through conduit 25 and chamber 19. As the quantity of air added to chamber 19 is increased the heating value of the product gases removed through conduit 45 decreases and the gravity increases. An increase of air in excess of that considered in Example I would cause higher temperatures in reactor 33 because of resulting combustion of carbon monoxide or water. In each such case the final gas would be caused to increase further in gravity and its heating value would be concomitantly decreased.

From the above examples it will be apparent to those skilled in the art that the input of air into the system must be carefully controlled in order to obtain the most economic utilization of the hydrocarbon material which is being converted to a fuel gas.

Various other modifications and advantages will be apparent to those skilled in the art upon study of the accompanying disclosure. Although the apparatus of this invention has been shown for countercurrent flow of reactant material and steam with pebbles through chambers 19 and 48, the method of this invention also includes concurrent flow. It is believed that such modifications may be made, however, without departing from the spirit and the scope of the disclosure.

I claim:

1. The continuous method of forming fuel gas of a desired B. t. u. value from a hydrocarbon which comprises the steps of heating a flowing contiguous mass of pebbles in a pebble heating zone; passing said heated pebbles into a gas heating zone, said pebbles being heated in said pebble heating zone to a temperature so that said gas heating zone is maintained at a temperature within the range of between 1650° F. and 2500° F.; passing steam through said gas heating zone in direct heat exchange with said heated pebbles, whereby said steam is superheated; passing a mass of relatively cool pebbles through a conversion zone; passing said superheated steam into said conversion zone; introducing a hydrocar-

bon material into said conversion zone and reforming said hydrocarbon with said steam to form carbon monoxide and hydrogen; depositing carbon resulting from said reforming reaction on said pebbles in said conversion zone; passing said carbon-bearing pebbles from said conversion zone into said gas heating zone; converting said carbon to water gas by reaction with said steam in said gas heating zone; passing said resulting water gas from said gas heating zone through said conversion zone; removing gaseous materials from the upper portion of said conversion zone; removing pebbles from the lower portion of said gas heating zone; and passing said pebbles to the upper portion of said pebble heating and conversion zones.

2. The method of claim 1, wherein a controlled amount of air is introduced into said gas heating zone with said steam; oxidizing a portion of said carbon therein to form carbon dioxide and nitrogen; passing said carbon dioxide and nitrogen into said reaction zone with said steam and hydrocarbon; and reacting said carbon dioxide with said steam and hydrocarbon material to form carbon monoxide and hydrogen.

3. The method of claim 2, wherein the reaction products removed from the upper portion of said conversion zone are blended with a normally gaseous hydrocarbon to raise the B. t. u. value of the composite reaction product.

4. The method of claim 1, wherein the reaction products removed from the upper portion of said conversion zone are blended with a normally gaseous hydrocarbon to raise the B. t. u. value of the composite reaction product.

5. The continuous method of forming fuel gas of a desired B. t. u. value from a liquid hydrocarbon which comprises the steps of heating a downwardly flowing contiguous mass of pebbles to a temperature within the range of between 1850° F. and 2900° F. in a pebble heating zone; passing steam through a first gas heating zone in direct heat exchange with said heated pebbles, whereby said steam is superheated; gravitating a mass of relatively cool pebbles through a conversion zone; introducing a hydrocarbon material into the lower portion of said conversion zone; introducing said superheated steam from said first gas heating zone into said conversion zone at a point above the point of introduction of said hydrocarbon material; reforming said hydrocarbon material with said steam to form carbon monoxide and hydrogen; depositing carbon resulting from said reforming reaction on said pebbles in said conversion zone; gravitating said carbon-bearing pebbles from said conversion zone into said first gas heating zone; converting a portion of said carbon to water gas by reaction with said steam in said first gas heating zone; passing said resulting water gas from said first gas heating zone through said conversion zone; gravitating said carbon-bearing pebbles from said first gas heating zone into a second gas heating zone; passing steam and air through said second gas heating zone; converting carbon remaining on said pebbles in said second gas heating zone by reaction with said steam therein; introducing reaction products and air from said second gas heating zone into the lower portion of said conversion zone; reacting said hydrocarbon material with said heated air and further reacting resulting reaction products with said steam introduced above said hydrocarbon material inlet point; removing pebbles from the lower portion of said second gas heating zone; elevating said pebbles to the upper portion of said pebble heating and conversion zones; and removing gaseous materials from the upper portion of said conversion zone.

6. The method of claim 5, wherein reaction products removed from the upper portion of said conversion zone are blended with a normally gaseous hydrocarbon to raise the B. t. u. value of the composite reaction product.

7. The continuous method of forming a fuel gas of a

desired B. t. u. value from a normally gaseous hydrocarbon having at least three carbon atoms per molecule which comprises the steps of heating a downwardly flowing contiguous mass of pebbles to a temperature within the range of between 1850° F. and 2900° F. in a pebble heating zone; gravitating said heated pebbles into a gas heating zone; passing steam through said gas heating zone in direct heat exchange with said heated pebbles, whereby said steam is superheated; gravitating a mass of relatively cool pebbles through a conversion zone; passing said superheated steam into the lower portion of said conversion zone; introducing a normally gaseous hydrocarbon material having at least 3 carbon atoms per molecule into the lower portion of said conversion zone and reforming said hydrocarbon with said steam to form carbon monoxide and hydrogen; depositing carbon resulting from said conversion on said pebbles in said conversion zone; gravitating said carbon-bearing pebbles from said conversion zone into said gas heating zone; converting said carbon to water gas by reaction with said steam in said gas heating zone; passing said resulting water gas from said gas heating zone through said conversion zone; quenching gaseous materials in the upper portion of said conversion zone; removing quenched gaseous materials from the upper portion of said conversion zone; removing pebbles from the lower portion of said gas heating zone; elevating said pebbles to the upper portion of said heating and conversion zones; and blending gaseous materials from said conversion zone with additional normally gaseous hydrocarbons having at least three carbon atoms per molecule to raise the B. t. u. value of the composite gaseous material from said conversion zone.

8. Improved pebble heater apparatus comprising in combination a first upright closed chamber having a pebble inlet and an effluent outlet in its upper end portion; at least one additional upright closed chamber below said first chamber, said first and said additional chambers constituting a series of chambers; pebble conduit means serially connecting the lower end of each said chamber and the upper end of the next subjacent chamber; heating material inlet means in the lower portion of said first chamber; reactant material inlet means in the lower portion of each additional chamber of said series; a second upright closed chamber having a pebble inlet and an effluent outlet in its upper end portion; pebble transfer means extending from the lower end of said second chamber to one of the two uppermost chambers of said series; reactant material inlet means in the lower portion of said second chamber; effluent outlet means extending between the upper portion of all but the uppermost chamber of said series and said second chamber; and pebble transfer means extending between the lower end of said series of chambers and the pebble inlets in said first and second chambers.

9. The improved pebble heater apparatus of claim 8, wherein said pebble outlet from said second chamber extends to a point intermediate the ends of said first chamber.

10. The improved pebble heater apparatus of claim 8, wherein said pebble outlet from said second chamber extends to the upper end portion of the second chamber of said series.

11. The improved pebble heater apparatus of claim 8, wherein said series of chambers comprises two chambers.

12. The improved pebble heater apparatus of claim 8, wherein said series of chambers comprises three chambers.

13. The improved pebble heater apparatus of claim 12, wherein the effluent from the chamber positioned immediately below said first chamber communicates with the central portion of said second chamber; and the effluent from the lowermost chamber of said series of chambers communicates with the lower end portion of said second chamber.

14. The improved pebble heater apparatus of claim 8 in which a pebble feeder is positioned in the pebble outlet conduit extending from the lower end of said second chamber.

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