

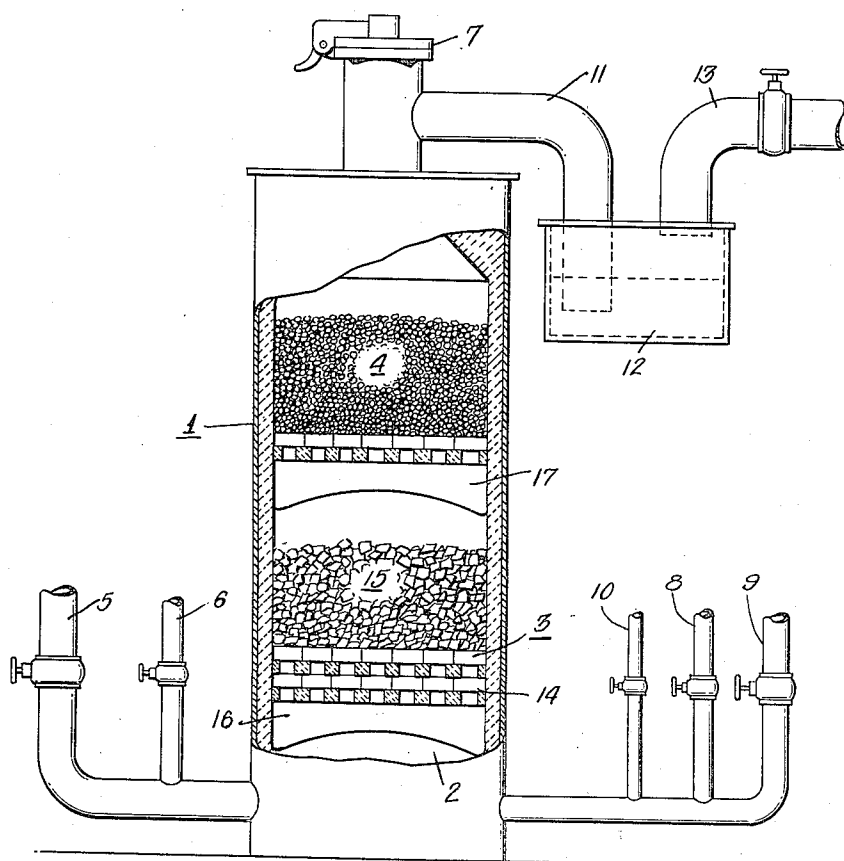
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METHOD OF REFORMING GASEOUS HYDROCARBONS

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METHOD OF REFORMING GASEOUS
HYDROCARBONS

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The present invention relates to the production of a gas suitable, upon enrichment, for distribution in city gas mains, from gaseous hydrocarbon material. More particularly, it relates to a cyclic process comprising a reaction between a gaseous hydrocarbon and steam, known as reforming, for the manufacture of a gas which is rich in free hydrogen and oxides of carbon, mainly carbon monoxide, and which, by the appropriate enrichment with a hydrocarbon gas, can be made interchangeable with any of the presently available manufactured gases distributed in city gas mains.

Natural gas, one of the most common gaseous hydrocarbons, is becoming of increasing availability and in locations relatively close to the natural gas fields where the gas is used in its original state as recovered, the various burning appliances are designed and adjusted for its use and there is therefore no necessity for treating or reforming the gas. In localities, however, where natural gas has not previously been available, various burning appliances such as the burners on gas ranges, refrigerators and heating services, have been designed and adjusted for the burning of some type of manufactured gas, for instance, water gas, or coke oven gas. If an attempt were to be made to introduce natural gas by itself to a system equipped with appliances and burners designed and adjusted for manufactured gas, its slower burning characteristics, if the flame did not go out entirely, would result in a lazy, smoky flame which would be hazardous because of incomplete combustion and the liberation of poisonous carbon monoxide. To change all of the appliances to adapt them for the burning of natural gas in its original state is an expensive process and would be impractical where winter peaks require augmentation of the supply by manufactured gas having faster burning characteristics because the construction of natural gas pipe line capacity for peak load service is prohibitively expensive. Therefore, the increasing availability of natural gas as a source of supply for the distribution systems of the public utility companies for domestic and industrial use, has presented the problem of reforming or converting natural gas into a product with suitable characteristics to enable its use as a component of mixed gas for distribution with manufactured gas in city gas mains. The desirability of reforming to develop suitable burning characteristics also applies to other gaseous hydrocarbons such as ethane, ethylene, propane, butane and the like, and hydrocarbon-rich gases such as refinery gas.

Heretofore, the reforming of a gaseous hydro-

carbon has been accomplished for the most part by passing it through a coke fire, preferably with process steam admixed. In this way, thermal cracking occurs with the formation of hydrogen and carbon. Little or none of the carbon content of the gaseous hydrocarbon, however, is converted directly to carbon monoxide in the vapor phase, although some of the deposited carbon may be converted to carbon monoxide and hydrogen by reaction of the steam with the hot coke fire bed. Generally, however, the carbon which is deposited in the fuel bed is consumed when blasting the fire. On the other hand, the carbon which passes out with the gas clogs the gas mains and condensing apparatus and must be scrubbed from the gas by water sprays or precipitated electrically, at considerable added expense. Furthermore, such carbon is obviously lost to the gas-making process.

It is known that gaseous hydrocarbons can be reacted with steam to liberate hydrogen and at the same time form carbon monoxide by union of the carbon of the hydrocarbon gas with the oxygen of the steam, and liberation of additional hydrogen from the steam, but the processes available have possessed certain disadvantages. For example, catalysts have been employed to permit the reaction to take place at a temperature below that at which thermal cracking occurs, in order to avoid production of carbon as an end product. The equipment hitherto used for catalytic conversion of the hydrocarbons with steam is very costly. It has mainly consisted of high alloy metal tubes or retorts filled with catalytic material heated externally in a furnace. The hydrocarbon gases and steam are passed through the catalytic material continuously with production of hydrogen, carbon monoxide, and small amounts of carbon dioxide. As stated, the process conducted in such equipment has certain disadvantages. Thus the temperature of the catalyst is maintained by conduction of the heat from the furnace, through the tubes, to supply the heat of formation of the product gas and its sensible heat. The conductivity of the catalytic material in discrete particle form is not high so that the metallic tubes or retorts, if the catalyst is held at a high temperature of, for example, from 1600° F.-1800° F., must operate at a temperature not very far below the maximum safe temperature of the most resistant metal alloy tubes and necessarily higher than the reaction temperature of the catalyst. Furthermore, since the conduction from particle to particle of the catalyst is poor, the temperature of the catalyst next to

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the tube or retort wall is higher than at the center, making a non-uniform temperature across the tube or retort. In addition, not only are the high alloy metal tubes expensive and subject to considerable maintenance costs but the multiplicity of tubes requires a multiplicity of valve connections and flow meters which in turn add to the expense of installation.

Because of these difficulties, inherent in a continuous, externally heated reforming system, various cyclic processes have been suggested from time to time. One such process involved the use of a catalyst bed which was alternately blasted with burning gases to store heat in the catalyst followed by passing the gaseous hydrocarbon and steam through the bed to effect conversion. However, by this method, in order to avoid destruction of the catalyst bed by excessive combustion temperatures, the quantity of heat stored in the catalyst bed was limited with the result that the incoming cooler steam and hydrocarbon gas, coupled with the high heat requirements of the reforming reaction itself rapidly cooled the catalyst to below reaction temperatures and caused wide and rapid fluctuations in temperature. Also since the heat required for raising the reactants to reaction temperature and for the resulting endothermic reaction, was supplied by the heat stored in the catalyst bed, excessively large amounts of catalyst, a very expensive item, were required. In addition, in many of these prior cyclic processes, relatively large amounts of carbon and other combustible materials were deposited on the catalyst which decreased its activity and clogged the gas passages through the catalyst bed.

One object of the present invention is to provide a process for the treatment of gaseous hydrocarbon material, particularly natural gas, and steam to produce a component of a combustible gas which can serve as a source of gas for distribution in city mains and where manufactured gas has previously been supplied, which process does not possess the disadvantages of either the thermal cracking process or the catalytic conversion processes presently known.

A further object of the invention is to provide a process by which natural gas can be economically and efficiently converted into a clean gas, rich in free hydrogen and in which the carbon content of the hydrocarbon reacted is present in gaseous form, mainly as carbon monoxide, and in which no significant amount of free carbon or other solid combustible matter is formed during the process.

Still another object of the invention is to furnish a method for the production of a combustible gas which is free from carbon particles and is available for admixture with other gas to provide a gaseous product which will be interchangeable with manufactured water gas or coke oven gas in the distribution systems of the public utility companies.

A further object of the invention is to provide a relatively inexpensive apparatus of high capacity for the process described and of a design to which existing gas-making equipment can be easily and economically converted.

Other objects will be apparent from a consideration of this specification and the claims.

In accordance with the process of the invention, hydrocarbon material which is normally gaseous, that is, exists in the gaseous state at atmospheric temperature and pressure conditions, is catalytically reacted with steam. In addition, air is preferably involved in the reac-

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tion also. As the result of the reformation or conversion reaction, a gas rich in free hydrogen and containing carbon in the form of gaseous oxides, mainly carbon monoxide, will be obtained.

The process involves the use of a cycle having a heat storage portion or stage in which hot combustion gases, formed by the combustion of a fluid fuel, are swept through a path of heat storage material and then through a bed of reforming catalyst, that is a catalyst for the endothermic reaction between gaseous hydrocarbons and steam, heating the heat storage material and catalyst by direct contact with combustion gases; and a reforming portion or stage in which the gaseous reactants, that is hydrocarbon gas and steam, or hydrocarbon gas, steam and air, are heated in the path of heat storage material and then reacted in the presence of the catalyst. Such a procedure may be designated as a cyclic process. Thus, in one part of the cycle fluid fuel is burned in a combustion chamber and the hot products of combustion are passed through a zone filled with heat storage material and then through a zone of catalyst to store heat therein and to supply the heat required for the process. In the other part of the cycle, the reacting hydrocarbon gas mixed with steam, and, in the preferred embodiment with air, is conducted first through the zone containing heat storage material, which serves as a preheating zone, to raise the temperature of the mixture to the reacting temperature, and then through the zone containing the catalyst in which the reaction takes place, producing a clean gas in which the hydrogen of the reacting hydrocarbon has been liberated and the carbon thereof has been combined with the oxygen in the steam (and of the air if air is used) to form carbon monoxide and carbon dioxide. It will be seen that before the reactants are brought in contact with the catalyst they are blended and uniformly preheated in a preheating zone containing the heat storage material which in turn is heated by the combustion gases in the heat storage portion of the cycle. As will be more fully discussed hereinafter, before distribution as city gas the gas produced during the reforming portion of the cycle will have mixed therewith a predetermined portion of normally gaseous hydrocarbon in order to provide the desired calorific value.

The process also comprises certain advantageous features whereby the hot products of combustion utilized for storing heat during the heat storage portion of the cycle are so controlled as to maintain the catalyst in a high state of activity, and wherein products of combustion, advantageously products of incomplete combustion, formed during the heat storage period, are mixed in controlled amount with the reformed gas produced during the reforming portion of the cycle, to provide a gas mixture possessing characteristics suitable for distribution in districts supplied with manufactured gas upon enrichment with hydrocarbon gas.

Since, in the process of the present invention, the heating step is internal as regards the heat storage and catalyst beds, no expensive externally heated tubes or retorts are needed to contain the catalyst, and one or two large vessels lined with refractory to contain the combustion chamber, the heat storage space, and the catalyst bed will suffice to provide a high capacity installation. Also, since the combustion gases and reacting gases follow the same paths in the same direction during their respective portions of the cycle, no

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expensive "hot-valves" are required which have given rise to numerous problems in certain past gas-producing systems. A few large pipes will replace the manifolds with the multiple connections necessary for the tube- or retort-style plant. The controls are likewise simplified and the cyclic changing of valves can be operated by the automatic control method established for many years in the water gas art. Furthermore, the cyclic system is more susceptible to thermal control because the temperatures can be regulated in a few minutes in contradistinction to the continuously fired tube or retort furnace, for instance, which requires considerable time to effect desired changes. Since the reactants are preheated to reaction temperatures prior to reaching the catalyst bed, wide and rapid fluctuations in catalyst temperature are eliminated, and much smaller amounts of catalyst are required than would be the case if the heat stored in the catalyst mass was relied upon to heat one or more of the reactant gases to reacting temperatures and also to supply the heat required in the endothermic reaction.

Another advantage of the process described resides in the ease with which existing carburetted water gas sets can be conveniently and readily converted for use in the process of the invention.

The accompanying drawing shows diagrammatically an apparatus in which the process of the present invention can be carried out.

In the drawing, 1 represents a refractory-lined chamber which may be the superheater of a conventional water gas set with appropriate modification as is obvious from the drawing. 2 represents the combustion chamber which may be nothing more than a space preceding the heat storage zone 3. Heat storage zone 3 consists of heat-accumulating refractory bodies such as fire brick arranged in familiar checkerwork pattern, 14, or randomly arranged pieces of refractory material, 15, or, as the drawing indicates, a combination of both. The heat storage material may be supported as by fire brick arch 16. The heat storage zone 3 advantageously consists of layers of different refractory pieces supported upon a checkerwork arch; the pieces nearer the checkerwork being relatively coarse pieces and supporting a deeper layer of smaller pieces advantageously of material of high heat conductivity, such as bonded silicon carbide, and the like. The catalyst bed is represented by 4, and may be supported as by fire brick arch 17. Numerals 5 and 6 represent respectively the air and fluid fuel supply means for combustion to heat the apparatus, and 7 the stack valve through which the waste heating gases may be discharged to the atmosphere, or to a waste heat boiler (not shown), before being vented to the atmosphere. The entrance for the gaseous hydrocarbon reactant and steam for introduction into the pre-heating zone at a position adjacent the combustion zone so that the reactants pass through the preheating bed and catalyst bed in the same direction as the hot products of combustion, are represented by 8 and 9, respectively, and the entrance for process air, if used, at 10. 11 represents the conduit through which gas leaves the reaction chamber, passing through wash box 12 to storage by conduit 13. In accordance with known gas practice, the gases leaving the reaction chamber or storage may pass through a waste heat boiler (not shown) before reaching the wash box.

The operation is, as stated, cyclic and the process comprises first a heating or blasting

period during which air and a fluid are admitted through connections 5 and 6, respectively, combustion taking place in the combustion chamber 2. The hot combustion gases are passed through the preheating or heat storage zone 3 which raises it to a temperature above the temperature required for the reformation reaction, are then passed through the catalyst bed at a somewhat reduced temperature, and may then be discharged through stack valve 7. After the set is heated to operating temperature, the stack valve 7 is closed and air and fuel connections 5 and 6 are also closed. At the same time, connections 8 and 9 are opened to admit respectively the gaseous hydrocarbon and the process steam to react with the hydrocarbon. If desired, and in accordance with the preferred embodiment, process air may be admitted by opening connection 10. The use of the air has the advantage of helping to maintain operating temperatures, maintaining the degree of temperature swing at a minimum and of augmenting the gaseous output of the apparatus. These reaction gases are preheated substantially to reaction temperature, which, as will be discussed more fully hereinafter, will be at a temperature below that at which thermal cracking takes place, by passing through the preheating or heat storage zone, absorbing heat therefrom. After leaving the preheating or heat storage zone, the reaction gases enter the catalyst bed where the following typical reactions take place (when natural gas is being reformed):

(1) with steam, $\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO} - 89021$
B. t. u. per lb. mol

(2) with air, $\text{CH}_4 + \frac{1}{2}\text{O}_2 + 1.9\text{N}_2 = 2\text{H}_2 + \text{CO} + 1.9\text{N}_2 + 13195$ B. t. u. per lb. mol

While the drawing illustrates one shell, it will be understood that a two or three shell set may be employed following the same general principles described above. For instance, the carburetter and superheater shells of a conventional carburetted water gas set may be employed. These shells are connected at their bases by an open conduit. In practicing the present process in this arrangement the fuel and air can be admitted to the top of the carburetter where combustion takes place, the hot products of combustion passing down through the carburetter, through the connecting conduit to the superheater and up through the preheating and catalyst zones as described. Similarly, in such an arrangement, the gaseous hydrocarbon reactant, steam, and process air if used, can be admitted to the carburetter top passing down through the carburetter, through the connecting conduit to the base of the superheater and up through the preheating and catalyst zones as described. Any checkerwork in the carburetter shell will function as part of the preheating zone. Similarly, in a three shell arrangement, employing also the generator of a conventional carburetted water gas set, the generator may serve as combustion chamber, and the various materials can be admitted to the generator, flowing to the carburetter top by way of the open conduit connecting the tops of the generator and carburetter, thence to the superheater as described.

In addition, it will be realized that in accordance with common gas-making practice steam purges may be, and preferably are, made between the heating and the gas-generating portions of the cycle, or between the gas-generating and heating portions of the cycle, or both. These purges, as known to those familiar with the gas-

making art, serve to clear the system of undesirable gases which may contaminate the generated gas or serve to force residual desirable gases to storage.

Catalysts for the endothermic reaction of gaseous hydrocarbons with steam to produce gas mixtures comprising free hydrogen and carbon monoxide, together with variable proportions of carbon dioxide, are well-known. The catalysts most frequently proposed for this purpose are metals of the iron group, with nickel and cobalt catalysts usually preferred, although other high melting metals such as vanadium, chromium, platinum and the like have been used. As between nickel and cobalt, the nickel catalysts have usually been used because the reaction is easier to control and the nickel catalysts are less expensive.

A suitable refractory carrier is frequently employed, on the surface of which the catalytic material is disposed or throughout which it is distributed. Difficultly reducible oxides such as alumina, silica, magnesia, calcium oxide, titanium oxide, chromium oxide, oxides of rare earth metals such as, for example, thoria, ceria and/or others may be present. Compounds such as chromates may be employed.

One method of catalyst preparation involves the precipitation of the catalyst in the form of a salt upon finely divided carrier material, calcination to produce the oxide of the catalyst metal, pelleting or the making of extruded shapes from a paste of the calcined material, and reduction of the oxide at elevated temperature to the metallic catalyst, either as a step in the preparation of the catalyst or after it has been placed in the gas-treating equipment. In the preparation of another type of catalyst, preformed refractory bodies, such as alundum balls, and the like are impregnated with a salt of the catalytic metal and thereafter the impregnated shapes are calcined to form the oxide of the metal which is subsequently reduced. The catalyst employed may be produced by any desired procedure which forms no part of this invention.

The gaseous hydrocarbon material reformed in the gas-generating portion of the cycle may comprise normally gaseous hydrocarbon material such, for example, as methane, ethane, propane and/or butane. Corresponding unsaturated hydrocarbons may be present in any desired concentration, such, for example, as ethylene, propylene, butylene, etc. Other conditions being the same, saturated hydrocarbon material is preferred, with paraffinic material most preferred. Natural gas, which is primarily methane and refinery oil gas, which is primarily methane and ethylene are among the hydrocarbon materials which may be employed. Natural gas, because of its availability is particularly preferred as the hydrocarbon reactant.

With respect to the fuel employed during the heat-storage period of the cycle, it may be any fluid—that is gaseous or liquid-combustible. Gaseous hydrocarbons, such as those mentioned above, and especially natural gas, are particularly satisfactory, although gaseous fuel not rich in hydrocarbons, such as water gas, producer gas, and the like may also be used. Liquid hydrocarbons, such as fuel oil, gas oil, gasoline, kerosene, tar, and the like may be employed if desired. In the event a liquid fuel is employed, conventional spraying or other vaporizing means may be utilized to facilitate combustion.

The proportions of gaseous hydrocarbon reactant to steam employed during the reforming

portion of the cycle generally run between about .8 mol and about 5 mols, and preferably between about 1.5 and about 2.5 mols, of steam for each mol of carbon in the hydrocarbon reactant.

When air is employed during the reforming portion of the cycle, the proportion of steam to hydrocarbon required may be decreased in which case as low as about .8 mol of steam per mol of carbon in the gaseous hydrocarbon reactant may be employed.

As stated, in accordance with the preferred embodiment of the process, some air is employed during the reforming portion of the cycle. The amount of air so employed will be less than about 2 mols thereof per mol of carbon in the gaseous hydrocarbon reactant and in most cases will be less than about 1 mol thereof per mol of carbon in the reactant. Preferably, the amount of air employed during the reforming portion of the cycle is between about .1 and about .6 mol thereof per mol of carbon in the hydrocarbon reactant.

Referring to the temperature conditions employed during the cycle, the reactants, as stated, must be heated substantially to reacting temperatures by their passage through the heat storage zone and before they pass through the catalyst zone. The main considerations, therefore, are that the gaseous hydrocarbon reactant, while being heated sufficiently to effect substantially complete reaction thereof in the catalyst zone, is not heated to a point where significant thermal cracking thereof takes place with formation of any significant quantity of carbon in the preheating zone. The exact temperature conditions governing these considerations will depend in part upon the particular gaseous hydrocarbon reactant employed. It has been found, for example, that, when reforming natural gas, the average temperature of the heat storage material in the preheating zone should not exceed about 2000° F., nor should it fall below about 1400° F. In other words, the heat storage material will have an average temperature at the beginning of the reforming portion of the cycle of not over about 2000° F., and, at the end of the reforming portion of the cycle, of not less than about 1400° F. To insure a reforming run of reasonable length, when reforming natural gas, the average temperature of the heat storage material, at the beginning of the reforming portion of the cycle will not be less than about 1500° F. Because of the direction of flow of the hot combustion gases during the heat storage portion of the cycle, first through heat storage material then through the catalyst zone, the temperature of the catalyst, at any one time, will normally be somewhat less than the average temperature of the preheat bed, and generally the temperatures in the catalyst bed, at the beginning of the reforming run, when reforming natural gas and referring to the above temperature ranges, will not exceed about 1800° F. and may be as low as about 1300° F. When reforming gaseous hydrocarbons heavier than methane it may be desirable to employ somewhat lower temperatures in the preheating zone in order to avoid thermal cracking and since the reformation of hydrocarbons heavier than methane, may not require temperatures as high as when methane is reformed. Thus, when reforming hydrocarbons heavier than methane, temperatures as low as about 1000° F. may be employed in the preheating zone.

Referring more particularly to the heat stor-

age portion of the cycle of the present process, it is conducted, as stated, by burning a fluid fuel, and passing the hot products of combustion serially through the heat storage zone and catalyst zone. The heat storage portion of the cycle may be conducted by burning the fuel with excess air, with insufficient air to support complete combustion, or with just the amount theoretically required for complete combustion, so long as the heat storage material and catalyst are raised to the required temperatures. In accordance with a preferred embodiment of the process, however, at least the latter part of the heating portion of the cycle is conducted by burning the fuel with insufficient air to support complete combustion, thereby producing combustion products substantially devoid of free oxygen and having a substantial content of hydrogen and carbon monoxide in addition to their content of carbon dioxide, water vapor and nitrogen. This insures the maintenance of the catalyst in a highly active state. The amount of air employed during this type of heat storage operation will usually be less than 95% of that theoretically required for complete combustion of the particular fuel and may be as low as about 70% of that required for complete combustion. The resulting combustion products supply heat to the heat storage material and to the catalyst by direct contact therewith without danger of oxidizing the metal catalyst. Preferably, the combustion during this type of heat storage operation is sufficiently incomplete so as to produce combustion products which are reducing with respect to the oxide of the metal catalyst, in order to favor the presence, at the start of the reforming portion of the cycle, of contact surfaces of highly active elemental metal catalyst rather than the oxide, while at the same time obtaining a practical efficiency in the use of the fuel. Thus the amount of air employed during this type of heat storage operation is preferably between about 85% and about 93% of that theoretically required for complete combustion of the particular fuel employed.

As indicated above, in accordance with a preferred form of operation of the present process at least the latter part of the heat storage portion of the cycle is conducted by burning the fuel with insufficient air for complete combustion. While the entire heat storage period may be conducted in such a manner, it is particularly preferred to conduct the first part of the heat storage period by burning the fuel with excess air so that the combustion gases contain free oxygen, and the latter part by burning the fuel with insufficient air for complete combustion as described. In this case, the amount of air employed during the first part of the heat storage period will usually be at least 2% in excess of that required for complete combustion of the fuel, and may in some cases be as high as about 50% in excess of that required for complete combustion. In most cases, excess air in an amount between about 5% and about 15% of that theoretically required for complete combustion of the fuel is satisfactory. The reasons for a heat storage stage in which excess air is employed are to obtain maximum efficiency of combustion, to shorten the flame and thus to obtain greater heat release in the combustion zone, and also to insure that any trace of combustible matter that may have been accidentally deposited on the refractory material and catalyst is removed. However, by the present process, as stated, very little,

if any, combustible matter is so deposited. Generally, the heat-storage stage, in this two-stage heat storage period, in which excess air is employed may make up between about 15% and about 50% of the total heat storage portion of the cycle. The remainder of the heat storage portion of the cycle, will, in this type of operation, be the stage during which insufficient air for complete combustion is employed as described.

Referring to the gas produced during the reforming portion of the cycle it will chiefly comprise hydrogen and carbon monoxide with small but varying amounts of gaseous hydrocarbons and carbon dioxide and with varying amounts of nitrogen depending upon the amount of air employed during the reforming portion of the cycle. While this gas is combustible it does not possess the characteristics which would make it usable per se as city gas. For instance, its calorific value will be lower than that required for utilization in city gas distribution systems. Thus before the gas produced during the reforming portion of the cycle is distributed as city gas it must be enriched with gas having a calorific value higher than that desired in the mixed gas. Such enriching gas may be any of the gaseous hydrocarbons mentioned above and particularly natural gas.

In many cases, however, the mere enrichment of the gas produced during the reforming portion of the present process with a gas of higher calorific value does not provide a mixed gas possessing all the characteristics required in a particular area. For instance, while a mixed gas possessing the desired calorific value may be obtained by mixing, for example, natural gas with the gas produced during the reforming portion of the present process, the specific gravity of the mixed gas may still be below, and/or the ratio of hydrogen to inerts above, the specifications in a particular area. Or, because of its availability in a particular area, it may be desirable to utilize coke oven gas as part of the distributed gas. Since coke oven gas is relatively rich in hydrogen, its admixture with the gas produced during the reforming portion of the present process, which is also rich in hydrogen, would result in a ratio of hydrogen to inerts well above that required.

For these reasons, it is often desirable to also mix with the gas produced during the reforming portion of the process a controlled quantity of a gas possessing a high specific gravity and a low ratio of hydrogen to inerts. Such a gas may be produced by the combustion of a hydrocarbon, preferably in the presence of insufficient air to support complete combustion. An especially advantageous gas in this regard is the product of incomplete combustion produced during the above-described heat storage stage in presence of insufficient air to support complete combustion which a fluid hydrocarbon fuel is burned in the combustion. Thus, in accordance with another embodiment of the present invention, at least a portion of the heating gases resulting from the combustion of the fluid hydrocarbon fuel in the presence of insufficient air to support complete combustion during the heat storage portion of the cycle is mixed with the gas produced during the reforming portion of the cycle to provide a mixed gas, which, when enriched as described, and blended with coke oven gas if desired, will meet the specifications required in the area where manufactured city gas is used, and which is, therefore, interchangeable with the manufac-

tured city gas. In accordance with this embodiment, while the products of incomplete combustion formed during the heat storage portion of the cycle may be led off to a storage vessel separate from that to which the gas produced during the reforming portion of the cycle is led, it is preferred to lead the desired quantity of products of incomplete combustion directly to a common storage vessel in the same manner as is the gas produced during the reforming portion of the cycle, that is, through conduit 13 by way of conduit 11 and wash box 12.

The exact proportions of enriching gas, and products of combustion if used, and coke oven gas if used, mixed with the gas produced during the reforming portion of the cycle to provide a finished gas suitable for distribution as city gas are subject to variation, depending not only upon the specifications to be met, but also upon the exact characteristics of the enriching gas, and of the gas produced during the reforming portion of the cycle, and also of the products of combustion and coke oven gas if used. Generally manufactured city gases have a calorific value of between about 520 and about 570 B. t. u., a specific gravity of between about .45 and about .75 and a ratio of hydrogen to inerts of from 1 to 1 up to about 6 to 1. On the other hand, the gas produced during the reforming portion of the cycle will have a calorific value lower than that recited above, for example, around 300 B. t. u., a specific gravity within or somewhat below (for example .35) the range recited above, and a ratio of hydrogen to inerts within or somewhat above (for example, 10 to 1) the range set forth above. The enriching gas will have a calorific value well above that required, natural gas having a heating value around 1050 B. t. u., a specific gravity around .61-.63, and a hydrogen to inerts ratio of zero, since it is usually free of hydrogen. The product of incomplete combustion will have a calorific value well below the above-recited range and may even be less than 100 B. t. u.; its specific gravity will be above the recited range often being around 1, and its hydrogen to inerts ratio will be well below the recited range.

It will be seen that although the proportions of the various gases that are to be mixed may vary widely, the determination of the exact proportions needed in any particular case will offer no difficulty to those familiar with the gas-making art, and can be arrived at by simple calculation. By varying the proportions of reactants, namely gaseous hydrocarbon and steam, or gaseous hydrocarbon, steam and air, used during the reforming portion of the cycle, the various characteristics of the resulting gas can be controlled as desired. In addition to these variables, by varying the amount of products of combustion, such as the products of incomplete combustion formed during the heat-storage portion of the cycle, which may be mixed with the gas produced during the reforming period, further control of the characteristics of resulting mixed gas is afforded. In any event, it will be seen that the present invention offers a process of wide flexibility to produce gas interchangeable with any manufactured city gas, or suitable for admixture with other gases, to meet changing situations encountered in the city gas industry.

The broader aspects of the invention as well as the above-described preferred embodiments will be better understood from a consideration of the following specific examples which are given for

purposes of illustration and are not intended to limit the scope of the invention in any way.

Example I

The reactor employed is the superheater shell of a conventional carburetted water gas set, the generator and carburetter being blanked off and the fuel, air, steam and hydrocarbon reactant being admitted to the base of the superheater as shown in the drawing. The reactor contains 144 cubic feet of randomly arranged silicon carbide pieces at a depth of 2 feet, 3 inches supported on a firebrick arch as shown in the drawing, and 305 cubic feet of nickel-impregnated refractory bodies supported on a firebrick arch as shown in the drawing.

A 1.5 minute cycle was employed, 44% of which was a heat storage period, 51% of which was a reforming period and 5% of which was a steam purge.

During the heat storage period air and natural gas were admitted to the combustion chamber at the rates of 8394 cubic feet per minute and 1000 cubic feet per minute respectively. At this rate the air was insufficient for complete combustion. The hot combustion products flowed serially through the heat storage zone and catalyst zone and out the stack to the atmosphere.

During the reforming period natural gas, steam and air were mixed and admitted to the space below the preheating zone at the following rates: natural gas, 2170 cubic feet per minute; steam, 143 pounds per minute; and air, 4197 cubic feet per minute. These gases passed through the heat storage zone becoming heated to reaction temperatures and thence through the catalytic zone where reformation took place. The reformed gases were led, by way of a wash box, to storage.

During the purge, steam was admitted to the combustion chamber at the rate of 266 pounds per minute forcing residual reformed gases to storage.

The cycles continued over a 24 hour period, the average temperatures during this period throughout various parts of the reactor being as follows:

	° F.
Bottom of heat-storage zone.....	1482
Top of heat-storage zone.....	1750
Bottom of catalytic zone.....	1780
Top of catalytic zone.....	1545

The gas produced during the reforming period had the following analysis and characteristics:

Illuminants	per cent..	0
CO	do.....	14
H ₂	do.....	41.6
CO ₂	do.....	4.4
CH ₄	do.....	5
C ₂ H ₆	do.....	2.7
O ₂	do.....	0.5
N ₂	do.....	31.8
B. t. u. per cubic foot		279
Specific gravity		.602
H ₂ /inerts ratio		1.16

With this gas was mixed sufficient natural gas having a heating value of 1039 B. t. u. per cubic foot to provide a mixed gas having a heating value of 530 B. t. u. per cubic foot. The mixture consisted of 67% of the above gas and 33% of natural gas and possessed, besides a heating value of 530 B. t. u. per cubic foot, a specific gravity of .607 and a hydrogen to inerts ratio of 1.11.

Example II

In this example, the same apparatus as that

used in Example I was employed. The cycle, however, was a three minute cycle, 34% of which was a heat storage period in which the combustion products passed out the stack to the atmosphere; 16% of which was a heat storage period in which natural gas was burned with insufficient air to support complete combustion and the resulting products of incomplete combustion were led off to storage by way of the wash box; 45% of which was a reforming period, and 5% of which was a steam purge.

During the heat storage period in which the combustion products were directed out the stack to the atmosphere, air and natural gas were admitted to the combustion chamber at the rate of 10,773 and 1000 cubic feet per minute, respectively, and burned. During the heat storage period in which products of incomplete combustion were led to storage, air and natural gas were admitted to the combustion chamber at the rate of 8563 and 980 cubic feet per minute, respectively, and burned.

During the reforming period natural gas, steam, and air were admitted to the space before the heat storage zone at the following rates: natural gas, 2500 cubic feet per minute; steam, 220 pounds per minute, and air, 1575 cubic feet per minute. During the purge 231 pounds of steam per minute were admitted to the combustion chamber forcing residual reformed gas to storage.

The cycles continued over a 24 hour period, the average temperatures during this period throughout various parts of the reactor being as follows:

	° F.
Bottom of heat-storage zone.....	1798
Top of heat-storage zone.....	1859
Bottom of catalytic zone.....	1755
Top of catalytic zone.....	1478

The mixed gas produced as the result of the reforming period and the heat storage period in which partial combustion products were led to storage had the following analysis and characteristics:

Illuminants	percent..	0
CO	do.....	12.0
H ₂	do.....	40.7
CO ₂	do.....	5.4
CH ₄	do.....	7.3
C ₂ H ₆	do.....	1.0
O ₂	do.....	.3
N ₂	do.....	32.4
B. t. u. per cubic foot.....		276
Specific gravity.....		.604
H ₂ /inerts ratio.....		1.08

With this gas was mixed sufficient natural gas having a heating value of 1034 B. t. u. per cubic foot to provide a mixed gas having a heating value of 530 B. t. u. per cubic foot. To provide this, a mixture consisting of 33.5% of natural gas and 66.5% of the above-described gas was necessary. This mixture possessed, besides a heating value of 530 B. t. u. per cubic foot, a specific gravity of .61 and a hydrogen to inerts ratio of 1.02.

Example III

Using the same apparatus as that employed in Examples I and II, a three minute cycle was employed, 59% of which was a heat storage period in which the fuel was burned in the presence of insufficient air to support complete combustion and the resulting products of combustion were

led off to storage by way of the wash box; 36% of which was reforming period, and 5% of which was a steam purge.

During the heat storage period, air and natural gas were admitted to the combustion chamber at the rates of 5865 and 662 cubic feet per minute, respectively, and burned. During the reforming period natural gas, steam and air were admitted to the space before the heat storage zone at the following rates; natural gas, 2400 cubic feet per minute; steam, 180 pounds per minute; and air, 1050 cubic feet per minute. During the purge, 200 pounds of steam per minute were admitted to the combustion chamber, forcing residual reformed gas to storage and eliminating any danger of having an explosive mixture present at the beginning of the following heat storage step.

The cycles continued over a 24 hour period, the average temperatures during this period throughout the various parts of the apparatus being as follows:

	° F.
Bottom of heat-storage zone.....	1762
Top of heat-storage zone.....	1822
Bottom of catalytic zone.....	1697
Top of catalytic zone.....	1452

The mixed gas produced as the result of the reforming period and the heat storage period were led to storage, and it will be noted that at no time is gas vented to the atmosphere. The resulting mixed gas had the following analysis and characteristics:

Illuminants	percent..	0
CO	do.....	9.1
H ₂	do.....	27.5
CO ₂	do.....	6.4
CH ₄	do.....	9.5
C ₂ H ₆	do.....	0.0
O ₂	do.....	0.4
N ₂	do.....	46.6
B. t. u. per cubic foot		224
Specific gravity		.72
H ₂ /inerts ratio		.52

In order to increase the heating value of this gas up to that required in the particular instance, natural gas having a heating value of 1034 B. t. u. per cubic foot was mixed with it such that the natural gas amounted to 37.8% of the resulting gas mixture. This enriched gas mixture possessed, besides a heating value of 530 B. t. u., a specific gravity of .68, and the ratio of hydrogen to inerts remained at .52.

This enriched gas was then mixed with coke oven gas having a heating value of 530 B. t. u. per cubic foot, a specific gravity of .48 and a ratio of hydrogen to inerts of 3.72, in an amount sufficient to raise its ratio of hydrogen to inerts to 1.1. This required 22 parts by volume of coke oven gas for each 100 parts by volume of the enriched gas.

The final gas mixture then possessed a heating value of 530 B. t. u. per cubic foot, a specific gravity of .662 and was distributed as city gas.

Considerable modification is possible in the selection of the gaseous hydrocarbon reactant, fuel gas, and blending gases, as well as in the proportions of reactants and blended gases, without departing from the scope of the invention.

I claim:

1. The cyclic process for the manufacture of a component of a combustible gas suitable for distribution in city gas systems which comprises, in one part of the cycle, burning a fluid fuel and

passing the hot products of combustion through a bed of heat storage material to store heat therein, then through a bed of catalyst for the endothermic reaction between gaseous hydrocarbons and steam to store heat therein, at least the latter portion of said burning being conducted in the presence of insufficient air to support complete combustion; and, during another part of the cycle, passing a normally gaseous hydrocarbon and steam through said bed of heat storage material to heat said gases; passing the hot gases through said catalyst bed at a temperature to effect conversion thereof to hydrogen and oxides of carbon, mainly carbon monoxide, and effecting in said catalyst bed conversion of said hot gases into a gas rich in hydrogen and carbon oxides, mainly carbon monoxide, and containing only a relatively small amount of hydrocarbons, and collecting the resulting gas.

2. The process of claim 1, wherein, during said conversion period, air is passed through said bed of heat storage material and catalyst bed with said gaseous hydrocarbon and steam, and wherein said catalyst comprises nickel.

3. The cyclic process for the manufacture of a component of a combustible gas suitable for distribution in city gas systems which comprises, in one part of the cycle, burning a fluid fuel in the presence of insufficient air to support complete combustion; passing the hot products of incomplete combustion through a bed of heat storage material to store heat therein, then through a bed of catalyst for the endothermic reaction between gaseous hydrocarbons and steam to store heat therein; and, in another part of the cycle, passing a normally gaseous hydrocarbon and steam through said bed of heat storage material to heat said gases; passing the hot gases through said catalyst bed at a temperature to effect conversion thereof into hydrogen and oxides of carbon, mainly carbon monoxide, and effecting in said catalyst bed conversion of said hot gases into a gas rich in hydrogen and carbon oxides, mainly carbon monoxide, and containing only a relatively small amount of hydrocarbons, and collecting the resulting gas.

4. The process of claim 3 wherein, during the said conversion period, air is passed through said bed of heat storage material and catalyst bed with said gaseous hydrocarbon and steam, and wherein the catalyst comprises nickel.

5. The cyclic process for the manufacture of a component of a combustible gas suitable for distribution in city gas systems which comprises, in one part of the cycle, first burning a fluid fuel in the presence of excess air and passing the hot products of combustion through a bed of heat storage material to store heat therein, and then through a bed of catalyst for the endothermic reaction between gaseous hydrocarbons and steam to store heat therein; then burning a fluid fuel in the presence of insufficient air for complete combustion, and passing the resulting hot products of incomplete combustion serially through said bed of heat storage material and said catalyst bed to store further heat therein; and, during another part of the cycle, passing a normally gaseous hydrocarbon and steam through said bed of heat storage material to heat said gases; passing said hot gases through said catalyst bed at a temperature to effect conversion thereof into hydrogen and oxides of carbon, mainly carbon monoxide, and effecting in said catalyst bed conversion of said hot gases into a gas rich in hydrogen and

carbon oxides, mainly carbon monoxide, and containing only a relatively small amount of hydrocarbons, and collecting the resulting gas.

6. The process of claim 5, wherein, during said conversion period, air is also passed through said bed of heat storage material and catalyst bed with said gaseous hydrocarbon and steam, and wherein said catalyst comprises nickel.

7. The process of claim 5 wherein that portion of the heat storage part of the cycle during which excess air is employed for the combustion of the fuel makes up between about 15% and about 50% of the total heat storage part of the cycle.

8. The process of claim 5 wherein the excess air employed to burn the fluid fuel is between about 2% and about 50% in excess of that required for complete combustion of the fuel.

9. The process of claim 5 wherein that portion of the heat storage part of the cycle during which excess air is employed for the combustion of the fuel makes up between about 15% and about 50% of the total heat storage part of the cycle; and wherein the excess air employed to burn the fuel is between about 2% and about 50% in excess of that required for complete combustion of the fuel.

10. The cyclic process for the manufacture of a component of a combustible gas suitable for distribution in city gas systems which comprises, in one part of the cycle, burning a fluid hydrocarbon fuel and passing the hot products of combustion through a bed of heat storage material to store heat therein then through a bed of catalyst for the endothermic reaction between gaseous hydrocarbons and steam to store heat therein, at least the latter portion of said burning being conducted in the presence of insufficient air to support complete combustion and leading at least a portion of the products of incomplete combustion leaving the catalyst bed to storage; and, during another part of the cycle, passing a normally gaseous hydrocarbon and steam through said bed of heat storage material to heat said gases; passing the hot gases through said catalyst bed at a temperature to effect conversion thereof to hydrogen and oxides of carbon, mainly carbon monoxide, and effecting in said catalyst bed conversion of said hot gases into a gas rich in hydrogen and carbon oxides, mainly carbon monoxide, and containing only a relatively small amount of hydrocarbons leading the resulting gas to storage; and admixing the latter with said products of incomplete combustion.

11. The process of claim 10 wherein, during said conversion period, air is passed through said bed of heat storage material and catalyst bed with gaseous hydrocarbon and steam, and wherein the catalyst comprises nickel.

12. The cyclic process for the manufacture of a component of a combustible gas suitable for distribution in city gas systems which comprises, in one part of the cycle, burning a fluid hydrocarbon fuel in the presence of insufficient air to support complete combustion; passing the hot products of incomplete combustion through a bed of heat storage material to store heat therein, then through a bed of catalyst for the endothermic reaction between gaseous hydrocarbons and steam to store heat therein, and then leading at least a portion of said products of incomplete combustion to storage; and, in another part of the cycle, passing a normally gaseous hydrocarbon and steam through said bed of heat storage material to heat said gases; passing the hot gases through said catalyst bed at a temperature to ef-

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fect conversion thereof into hydrogen and oxides of carbon, mainly carbon monoxide, and effecting in said catalyst bed conversion of said hot gases into a gas rich in hydrogen and carbon oxides, mainly carbon monoxide, and containing only a relatively small amount of hydrocarbons leading the resulting gas to storage; and admixing the latter with said products of incomplete combustion.

13. The process of claim 12 wherein, during said conversion period, air is passed through said bed of heat storage material and catalyst bed with said gaseous hydrocarbon and steam, and wherein the catalyst comprises nickel.

14. The cyclic process for the manufacture of a component of a combustible gas suitable for distribution in city gas systems which comprises, in one part of the cycle, first burning a fluid hydrocarbon fuel in the presence of excess air and passing the hot products of combustion through a bed of heat storage material to store heat therein, then through a bed of catalyst for the endothermic reaction between gaseous hydrocarbons and steam to store heat therein, and then to the atmosphere; then burning a fluid hydrocarbon fuel in the presence of insufficient air for complete combustion, passing the resulting hot products of incomplete combustion serially through said bed of heat storage material and said catalyst bed to store further heat therein, and then passing at least a portion of said products of incomplete combustion to storage; and, in another part of the cycle, passing a normally gaseous hydrocarbon and steam through said bed of heat storage material to heat said gases; passing said hot gases through said catalyst bed at a temperature to effect conversion thereof to hydrogen and oxides of carbon, mainly carbon monoxide, and effecting in said catalyst bed conversion of said hot gases into a gas rich in hydrogen and carbon oxides, mainly carbon monoxide, and containing only a relatively small amount of hydrocarbons; directing the resulting gas to storage and admixing the latter with said products of incomplete combustion.

15. The process of claim 14 wherein, during said conversion period, air is also passed through said bed of heat storage material and catalyst bed with said gaseous hydrocarbon and steam, and wherein said catalyst comprises nickel.

16. The process for the manufacture of a combustible gas suitable for distribution in a city gas

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distribution system serving appliances adjusted for the burning of manufactured gas of predetermined burning characteristics which comprises preparing gases in a cyclic process in which, in one part of the cycle, a fluid hydrocarbon fuel is burned and the hot products of combustion are passed through a bed of heat storage material to store heat therein and then through a bed of catalyst for the endothermic reaction between gaseous hydrocarbons and steam to store heat therein, at least the latter portion of said burning being conducted in the presence of insufficient air to support complete combustion and leading at least a portion of the products of incomplete combustion leaving the catalyst bed to storage, and, in another part of which cycle, a normally gaseous hydrocarbon and steam are passed through said bed of heat storage material to heat said gases and then through said catalyst bed at a temperature to effect conversion thereof into hydrogen and oxides of carbon, mainly carbon monoxide, and effecting in said catalyst bed conversion of said hot gases into a gas rich in hydrogen and carbon oxides, mainly carbon monoxide and containing only a relatively small amount of hydrocarbons; mixing the resulting gas with said products of incomplete combustion and with a gas having a calorific value higher than that desired in the resulting mixture in proportions to provide a mixed gas possessing burning characteristics comparable to the predetermined burning characteristics of said manufactured gas, whereby the resulting gas may be distributed in said city gas distribution system.

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