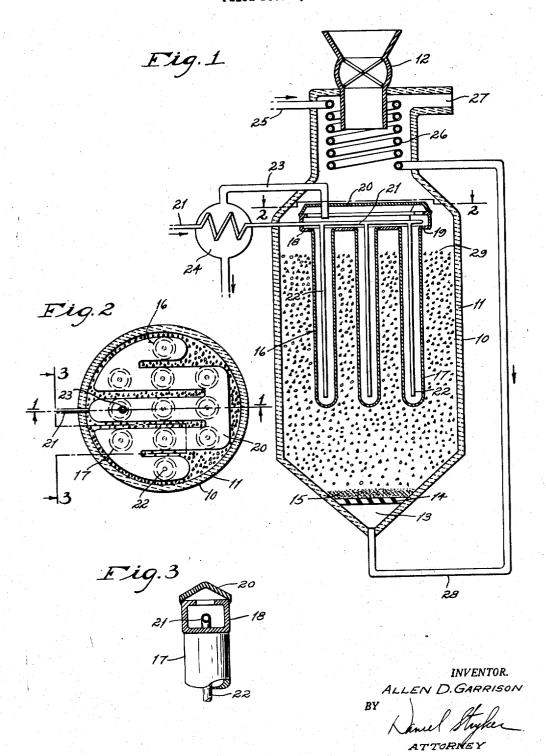Aug. 1, 1950

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METHOD AND APPARATUS FOR GASIFYING
CARBONACEOUS MATERIAL
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Fig.1

Fig.2

Fig.3

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METHOD AND APPARATUS FOR GASIFYING CARBONACEOUS MATERIAL

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The present invention relates to gasification of solid fuels and is more particularly concerned with the conversion of carbonaceous materials into a gaseous product of high heating value composed primarily of carbon monoxide and hydrogen, this application being a continuation-in-part of my copending application Serial No. 682,908, filed July 11, 1946.

In accordance with the present invention a stream of combustible gases, predominantly hydrogen and carbon monoxide, is produced by the reaction of water vapor with carbon or carbonaceous materials.

More specifically, the solid carbonaceous fuel is caused to react with the water vapor within the usual temperature range for this reaction, but in the presence of, at most, only a limited quantity of oxygen or other reactant conventionally supplied to furnish the requisite heat energy of the main reaction. In fact, the present invention may be carried out in the total absence of an oxygen feed to the reaction zone, or with a material reduction in the amount of oxygen hitherto considered necessary for feed to the reaction zone, a highly satisfactory fuel gas, low in inerts, being produced in either case. The thermal requirements of the process or a substantial portion thereof, at least, are met by means of the exothermic combustion of a stream of hydrogen diffused out of the reaction mass at a predetermined rate and caused to burn with oxygen, or an oxygen-containing gas such as air, adjacent a diffusion barrier disposed within the reaction mass in direct heat exchange relationship with the solid fuel. Accordingly, the diffusion barrier, raised to an elevated temperature by the combustion of the diffused product, supplies heat energy directly to the adjacent gasification zone.

Preferably the diffusion surfaces are disposed throughout the gasification zone in such area and arrangement as to present heat transfer surfaces adequate to maintain optimum fuel temperature. The opposite or effusion surfaces of the diffusion members are preferably physically separated from the fuel gasifying zone whereby the products of combustion of the diffused hydrogen may be withdrawn separately from the products of coal gasification and without dilution thereof.

As above indicated, the reaction of water vapor and carbon, being endothermic, requires the expenditure of heat energy to support the reaction as well as to maintain the desired elevated temperatures, for example, in the order of 1000° C. Heretofore, it has been proposed to accomplish

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this objective by alternately blasting an incandescent fuel bed with air to a high degree of incandescence and passing water vapor in the form of superheated steam through the hot incandescent bed. Obviously, this involves consumption of fuel during the air blast stages and has given way in many instances to the more recent proposal involving the continuous introduction of water vapor and oxygen to the fuel bed at a relative rate appropriate to maintain the required temperature of operation and support the reaction between the water vapor and incandescent carbon.

However, in the production of a gas of high heating value it is necessary to use high purity oxygen to avoid dilution of the product gases with nitrogen. The equipment for meeting the pure oxygen requirements, as, for example, a plant for the rectification and fractionation of air, may frequently impose an uneconomic burden upon the process.

Other proposals for the addition of extraneous heat energy to the reaction usually suffer from the fact that they require special equipment and involve economic burdens not encountered in self-contained operation.

The present invention, on the other hand, involves exothermic combustion of at least a portion of the hydrogen evolved as a reaction product of the water vapor-carbon reaction to supply heat energy requirements of the operation.

More specifically, the invention contemplates, for example, subjecting a carbonaceous solid fuel at elevated temperature to the action of water vapor with the production of hydrogen and carbon monoxide, diffusing product hydrogen preferentially through a permeable wall of the fuel gasification zone, subjecting the diffused hydrogen to combustion in the vicinity of the exterior or effusion surface so as to heat the wall or barrier to an elevated temperature, and the transmission of heat from the diffusion wall to the mass of reactants in the gasification zone so as to supply a portion, at least, of the heat required for the endothermic reaction.

The invention is of particular advantage, as indicated above, in reducing or obviating the requirement for high purity oxygen since the combustion of the hydrogen on the effusion surface of the diffusion member may be carried out with air or any similar oxygen-containing gas. This is particularly true where heat exchange between the incoming stream of oxygen-containing gas and the reaction products of the hydrogen combustion are exchanged efficiently as to heat con-

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tent so that there is no material loss of exothermic heat energy from the diffusion zone except that transmitted to the reactants in the gasification zone.

The invention is furthermore advantageous where it is desired to produce a heating gas relatively low in hydrogen, since the proportion of hydrogen which diffuses may be controlled within rather wide limits, the resulting product of gasification being largely carbon monoxide, if desired. On the other hand, it is to be noted that the invention is equally suitable for the production of a fuel gas containing relative proportions of carbon monoxide and hydrogen typical of those above mentioned processes wherein oxygen and water vapor are continuously supplied to an incandescent fuel bed. That is to say, where given amounts of oxygen, water-vapor and carbon are involved, the net thermal requirements are substantially the same whether the stream of oxygen is supplied to the incandescent fuel bed or reacted with diffused hydrogen and the resulting thermal energy supplied directly to the fuel bed. So also, where the net production of carbon monoxide and hydrogen approximates that of the aforementioned, earlier proposed process, the overall heat energy supplied, is substantially the same.

Preferably, the extent to which diffusion of hydrogen is carried out is such that its combustion with oxygen or air will just furnish the thermal requirements of the process. The extent of the diffusion may be controlled in any suitable manner, such as by selection of an appropriate diffusion barrier, by predetermining the thickness, area, disposition, size and surface area of the diffusion walls, by controlling contact time so that the reaction products are in the vicinity of the diffusion wall for only that time period required to diffuse the desired portion of hydrogen, and by other factors.

The present invention is particularly advantageous in connection with the use of fluidized fuel beds wherein the incandescent solids, usually in the form of fine particles or grains, are maintained in a turbulent condition by the upflowing gases. More specifically, under such conditions the solid fuel appears to form a mass similar to a boiling liquid, the particles of which continuously vibrate into and out of contact with the heated surfaces of the diffusion barrier with a resultant high efficiency of heat transfer.

Other objects and advantages of the invention will be apparent from the following description and claims wherein:

Figure 1 is a vertical section, diagrammatic in character, of a generator suitable for practicing the invention.

Figure 2 is a section taken on the line 2—2 of Figure 1.

Figure 3 is a section taken on the line 3—3 of Figure 2.

Referring to Figure 1, the numeral 10 represents a chamber lined with a suitable refractory 11 and continuously supplied with finely powdered coal, coke, or like carbonaceous material, from an upper feed hopper 12.

The particle size of the solid fuel is in the range of small particles and finer, capable of being fluidized by the upflow of reactant gas. In the embodiment disclosed, the reactant gas; namely, steam, is introduced at the bottom of the vessel 10 through inlet pipe 28, passing upwardly through a lower chamber 13 and a grate or screen 14 carrying a layer 15 of heavier refractory particles such as fire clay. The water vapor thus moves up-

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wardly into the mass of powdered fuel at any desired rate sufficient to maintain the required aeration and ebullition of the powdered fuel.

The numeral 16 represents overall a diffusion unit disposed within the reaction zone and formed of a plurality of diffusion tubes 17 supported from a header 18. In the embodiment shown, each of the diffusion tubes is formed of a suitable refractory such, for example, as magnesia or zirconia, closed at its bottom extremity and lined with a thin layer of palladium permeable to hydrogen. The upper extremity of each tube is provided with a flange 19 which seats in a suitable recess in the header 18, as shown. The header is provided with an upper, preferably removable, closure 20.

In plan, the header is preferably shaped as shown in Figure 2 or in some similar manner so that the solid fuel may fall freely thereby and the resultant gases rise without interference. Additionally, closure 20 may be sloped in section as shown in Figure 3 so that solid fuel will not collect thereon. Tubes 17 are provided in each branch of the header to contact all portions of the ebullient fuel.

Internally, header 18 is provided, as indicated, with a manifold 21, supporting a plurality of dependent tubes 22. The tubes 22, preferably formed of any suitable heat resisting material, extend coaxially into each of the diffusion tubes 17 to a point just short of the bottom thereof and are open at their lower extremities whereby gaseous reactants introduced therethrough reach each diffusion tube adjacent its base and pass upwardly along the interior or effusion walls thereof in close contact with the diffused gas, thereby acting to wipe, strip, purge, or sweep the diffused gas from the interior walls of the tubes. The combustion products are ultimately withdrawn from the header 18 through outlet pipe 23 which is connected to a heat exchanger 24 in heat exchange relation with manifold 21.

Alternatively, the direction of flow may be reversed with the gas introduced through pipe 23 and the products withdrawn through manifold 21. However, with manifold 21 as the inlet supplied with an oxygen-containing gas such as air from any suitable source, not shown, heat exchanger 24 serves to provide good countercurrent, indirect exchange with the hot gases in outlet pipe 23 so that the outlet gases are discharged at substantially the temperature of the fresh inlet gases, while the latter reach the interior of the diffusion unit at a temperature approximating normal operating temperature therein.

The supply of steam previously referred to is advantageously fed to pipe 28 by way of an inlet pipe 25 and a heat exchanger 26 disposed within the upper portion of the gasification chamber in the stream of fuel gas product emanating from the incandescent fuel bed and constructed to superheat the steam as high as possible. The ultimate fuel gas product is withdrawn through outlet conduit 27.

Obviously, the arrangement of heat exchangers should be designed to effect operation under good overall heat economy and may be rearranged widely as desired in furtherance of this ideal. For example, the steam may be at least in part heated by exchange with the hot effluent of the combustion of hydrogen in tubes 17 and the air preheated by the hot gaseous effluent of the gasification zone.

In operation, the chamber is provided with an ebullient bed of finely divided incandescent fuel

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to about the level shown at 29, superheated steam passing upwardly and maintaining the mass in fluidized condition. At an operating temperature of, for example, 700°–1000° C., the water vapor consumes carbon with the formation of carbon monoxide and hydrogen. A predetermined portion of the product hydrogen passing along the diffusion tubes 17 preferentially permeates therethrough. Meanwhile, a stream of air or other oxygen-containing gas introduced through manifold 21 and preheated, for example, to as high a temperature as possible by the reaction products of the diffusion chamber and by its passage through manifold 21 and tubes 22, passes upwardly in the annular space between pipes 22 and diffusion tubes 17, reacting with the hydrogen and transferring heat of reaction to tubes 17, thereby bringing them to a high degree of incandescence. The heated tubes thus transfer sensible heat to the fluidized fuel mass, maintaining the desired reaction temperature.

While reference has been made to a diffusion element or surface composed of a porous refractory tube lined with palladium, it is to be understood that the invention is not so limited but contemplates any suitable material refractory at the temperatures of reaction and adapted to promote preferential diffusion of hydrogen. Broadly, this member may comprise any suitable porous material having continuous capillary or other passages extending from side to side and of such cross-sectional dimensions as to permit the rapid permeation by hydrogen while relatively resisting diffusion of carbon monoxide or other gases of the reaction zone. Such diffusion barriers may be constructed of unglazed poreclain or porous Carborundum, for example, having a thickness of at least 0.010 inch and preferably from about 0.025 to 0.050 inch.

It is now known, however, that superior results are achieved and rapid and efficient diffusion of hydrogen may be carried out where the diffusion barrier is relatively thin and has apertures or pores of the order of 1 micron, for example. More specifically, the dimensions of the pores should tend to approximate the mean free path of hydrogen under the conditions existing in the gasification zone.

In view, however, of the difficulties of designing an efficient and serviceable refractory diffusion barrier and the superior efficiency of metallic diffusion barriers, I prefer to employ diffusion walls incorporating a suitable metal, such as palladium, iron, cobalt or nickel. While such barriers may be used without additional support, I prefer to employ them in thin layers mounted upon a suitable refractory support. Best illustrative of such an arrangement is, for example, a tube of porous Alundum, magnesia, zirconia, thoria, or other suitable refractory having an inner or outer layer of palladium of, for example, 1 to 10 one-thousandths inch in thickness. Such a tube is satisfactory for the present purposes where the porosity of the refractory is such that the reaction gases have substantially free access to the outer surface of the palladium layer. The metal may be applied to the refractory surface by any suitable method, such as metal spraying, electrodeposition, or the like, and may be etched or otherwise treated in any known manner to control its degree of permeability. Alternatively, a layer of metal foil 0.001 inch in thickness, for example, may be merely supported on the inner surfaces of the tubes. With this arrangement, the refractory provides mechanical support and more-

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over when disposed adjacent the diffusion membrane readily supports surface combustion.

It is to be borne in mind that the apparatus disclosed in the drawing is only diagrammatic in character and accordingly not necessarily exact as to disposition and proportioning of parts. In practice, the diffusion surfaces should be spaced uniformly throughout the fuel bed so as to present a sufficient area of diffusion and heat-exchange surface to maintain a temperature, as for example 700°–1000° C., proper for the reaction of water vapor with carbon. Moreover, the spacing between such surfaces should in no event be greater than that appropriate for maintaining good heat transfer throughout the mass of carbonaceous material. Such details, however, depend on numerous variables including the degree and character of fluidization, flow rates, etc., and must be determined for each case, in accordance with good engineering practice.

The relative rates of reactant flow can best be determined, as is usual in the art, by actual trial, until the fuel bed is properly fluidized while the oxygen supply is just sufficient to consume the diffused hydrogen with liberation of the desired thermal energy.

The invention is not limited, in its broadest aspect, to complete elimination of free oxygen from the fuel bed, but contemplates conservation of at least a portion of the feed normally required. In fact the operation may be supplemented by such addition of oxygen as may be required when operating with only partial diffusion of the hydrogen necessary to meet full thermal requirements. This not only limits the oxygen purification capacity required, but eliminates from the final fuel gas such amount of nitrogen as would otherwise find its way into the product by way of even high purity oxygen feed. In short, within commercially practical ranges of oxygen purification, nitrogen usually remains in the product and dilutes the fuel gas to some extent.

On the other hand, with no oxygen addition to the fuel bed, there is no appreciable dilution from this source, irrespective of the composition of the oxygen stream supplied to burn the diffused hydrogen. Moreover, even where high purity oxygen up to, for example, 95 per cent purity is used to burn the hydrogen, there is the advantage of a higher fuel value gaseous product free from such dilution.

In accordance with one illustrative example, a mass of coke having a particle size of one millimeter and finer is disposed about a tube of highly porous zirconia having a layer of palladium on its interior surface. The coke is heated to about 800° C. and a stream of superheated steam at a temperature of about 700° C. is passed upwardly therethrough at a rate sufficient to hold the particles in a good state of dense phase fluidization, immersing the tube to a depth of about two feet. Air is introduced into the interior of the tube at different trial rates until the tube ultimately reaches a temperature of about 900° C. and the combustion product withdrawn from the tube is essentially water vapor and nitrogen. Under these conditions, the fuel bed maintains its temperature continuously and its effluent products are essentially carbon monoxide with smaller proportions of hydrogen and carbon dioxide, substantially free of nitrogen. A small content of unreacted water vapor may be removed by condensation.

The process is best operative with those solid carbonaceous fuels such as coke, adapted to

fluidize at high temperatures without agglomeration and capable of ready reaction with water vapor. On the other hand, the invention is also applicable to coals, either hard or soft, and particularly so-called brown coal and lignite.

The invention may take advantage of any of the conventional expedients for ash or slag removal or other operating refinements, which per se, form no part thereof and are available to those skilled in the art.

The invention, moreover, is not necessarily limited to use of a fluidized fuel bed and may be operative in the absence of such a refinement where the diffusion elements are arranged to provide adequate transfer of sensible heat energy to the reactants.

Obviously, many other modifications and variations of the invention as set forth above may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the following claims interpreted in accordance with a fair and reasonable range of equivalents.

I claim:

1. In the method of gasifying solid carbonaceous fuel wherein water vapor is passed in contact with a mass of said solid fuel in a gasification zone at an elevated temperature at which reduction of the water vapor by the carbon proceeds with the formation of hydrogen and carbon monoxide, the improvement which comprises, separating hydrogen from the gaseous reaction products by diffusion through a diffusion member in the gasification zone, heating the diffusion member by burning the diffused hydrogen adjacent the effusion surface of said member by supplying a stream of oxygen to said last named surface, supplying at least a portion of the thermal requirements of said gasification zone by exchanging sensible heat energy directly from said diffusion member to the gasification zone, and separately recovering the products of gasification and the products of the said combustion of hydrogen.

2. In the method of gasifying a solid carbonaceous fuel which comprises passing gaseous reactants comprising water vapor into contact with said fuel in a fuel gasification zone at an elevated temperature at which the water vapor is reduced with the formation of hydrogen and carbon monoxide, preferentially separating hydrogen from the reaction products by diffusion through a diffusion barrier within the reaction zone, burning the diffused hydrogen with an oxygen-containing gas on the opposite side of said diffusion barrier whereby heat resulting from the combustion of hydrogen is transferred to the gasification zone through said barrier, and separately recovering the products of gasification and the products of combustion of hydrogen.

3. The method as defined in claim 2 wherein the solid carbonaceous fuel in the gasification zone comprises particles of fuel maintained in a state of dense phase fluidization by the incoming reactants.

4. The method as defined in claim 2 wherein a stream of oxygen is supplied to said gasification zone in a proportion substantially less than required per se for the maintenance of the thermal requirements of the gasification zone.

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