Oct. 6, 1953 E. GORIN 2,654,662

GASIFICATION OF CARBONACEOUS SOLID FUELS

Filed Nov. 19, 1949 2 Sheets-Sheet 1

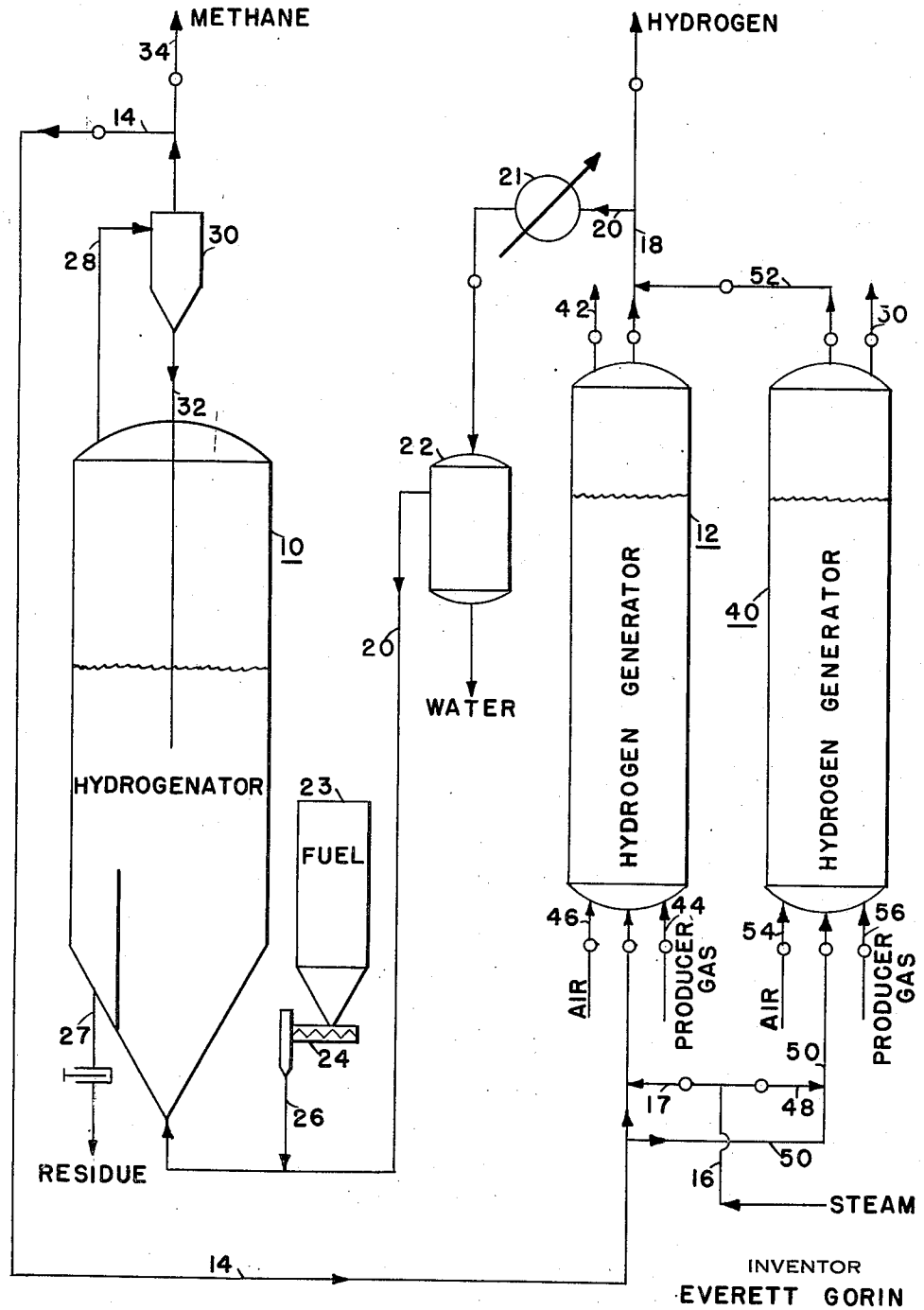


FIG. 1

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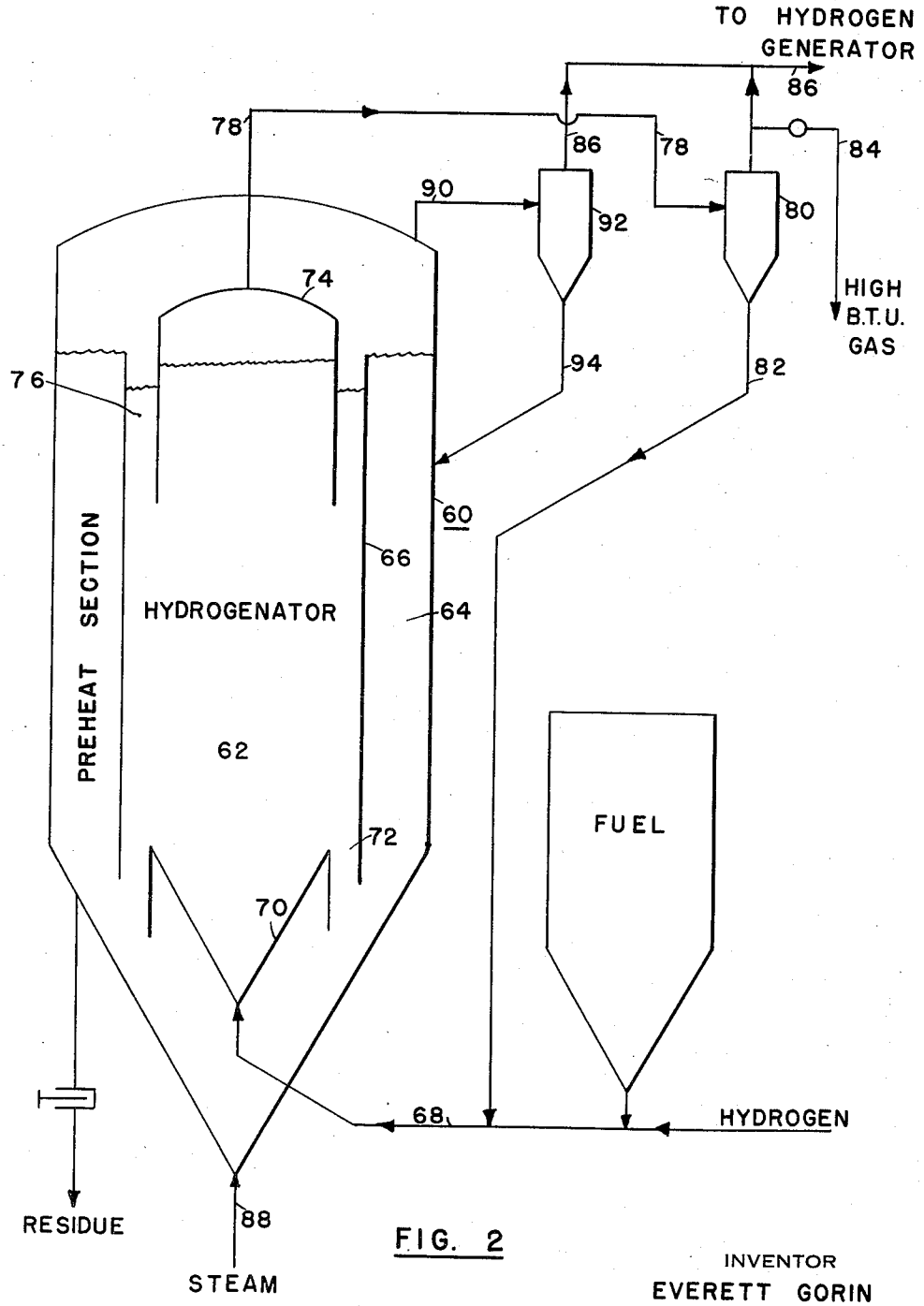


FIG. 2

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Patented Oct. 6, 1953

2,654,662

UNITED STATES PATENT OFFICE

2,654,662

GASIFICATION OF CARBONACEOUS SOLID FUELS

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Application November 19, 1949, Serial No. 128,436

1 Claim. (Cl. 48—197)

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This invention relates to the gasification of carbonaceous solid fuels, and particularly to the production of hydrogen or high B. t. u. gas from such fuels.

In application Serial No. 99,562, filed June 16, 1949, a process for the gasification of carbonaceous solid fuels by reaction between steam and solid fuels in the presence of barium oxide is described. In accordance with that process, barium oxide is mixed with carbonaceous solid fuels in certain critical proportions and under certain critical conditions of temperature and pressure and then subjected to reaction with steam. A gaseous product is obtained which contains methane and hydrogen in varying relative proportions depending upon the particular temperature and pressure conditions. As a result of the reaction between the steam and the carbonaceous solid fuels, an inert solid residue or ash is formed in admixture with the barium oxide. In order to reuse the barium oxide which is converted to barium carbonate during the reaction, it is necessary to separate the barium oxide from the ash and regenerate it at elevated temperatures. While various means are available for separating this ash from the barium oxide, it would be desirable to conduct the conversion of the carbonaceous solid fuels to gas in a system in which the oxide and solid fuels are not in admixture during the reaction, and yet in which substantially all the benefits of the use of the oxide in the process are secured, namely, high yields of hydrogen or methane as desired and under substantially thermoneutral conditions.

The primary object of this invention is to provide an improved two-vessel system for converting carbonaceous solid fuels into gas under substantially thermoneutral conditions. Another object of this invention is to provide a two-vessel system for making a high B. t. u. fuel gas which is rich in methane. A further object of the present invention is to provide a two-vessel system for converting carbonaceous solid fuels into a gas which is rich in hydrogen. Still another object of this invention is to provide a two-vessel system for gasifying carbonaceous solid fuels in which the gaseous products are substantially free of carbon dioxide.

For a better understanding of my invention, reference should be had to the following description and to the accompanying drawings, in which:

Figure 1 is a diagrammatic illustration of an apparatus comprising a two-vessel system adapted to carry out the preferred embodiment of my invention; and

Figure 2 is an illustration, partly diagrammatic and partly cross-sectional of a modified embodiment of a portion of the system shown in Figure 1.

In accordance with my invention, a two-vessel system is employed to convert carbonaceous

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solid fuels to a gas containing primarily methane and/or hydrogen as desired. In one of the two vessels, a bed of carbonaceous solid fuels in granular form is maintained, while in the other vessel a bed of granular barium oxide is confined. The temperature in the oxide vessel must be between 1700° and 2300° F., while that in the solids fuel vessel must be at least 1400° F. and preferably not above 1800° F. The pressures in the two vessels, while preferably, but not necessarily the same, must at least equal and preferably exceed one atmosphere when the temperature in the oxide vessel is in the range 1700° to 2050° F., and when the temperature in the oxide vessel is in the range 2050° to 2300° F., the pressure must exceed that given by the empirical relation

$$(1) \qquad p=1+4.9\times10^{-2}(t-2050)$$

where p is the minimum reaction pressure in atmospheres and t is the temperature in the oxide vessel in °F.

Steam and a gas containing methane are circulated through the vessel containing the barium oxide, and under the conditions of temperature and pressure recited, the methane is converted to a gas containing a high percentage of hydrogen. The amount of barium oxide maintained in the methane-steam reaction vessel must be sufficient to absorb substantially all of the carbon dioxide produced during the reaction in that vessel. Preferably, there are at least 800 parts by weight of barium oxide present for each 100 parts by weight of carbon contained in the gas circulating through the bed of barium oxide.

All or part of the hydrogen from the methane-steam reaction vessel (hereinafter sometimes referred to as the hydrogen generator) is circulated through the bed of carbonaceous solid fuels confined in the other vessel. Under the conditions of temperature and pressure existing in that vessel, the fuel is hydrogenated and a high B. t. u. gas containing methane in substantial quantities is produced. If it is desired to produce only a high B. t. u. gas from the system, in preference to substantially pure hydrogen, then part of the methane-containing gas is recycled to the hydrogen generator for manufacturing hydrogen, all of which is then returned to the solid fuel hydrogenerator vessel. If it is desired to produce hydrogen-rich gas, then only a part of the hydrogen produced in the hydrogen generator is circulated to the hydrogenerator and all of the methane produced in the latter is recycled to the hydrogen generator.

As stated above, the temperatures and pressures of the two reaction zones do not necessarily have to be the same. But for practical reasons, it is desirable to maintain the same pressure in both vessels. Preferably, the temperature in the solid fuel vessel is not higher than that in the steam-methane reaction zone. It may be less but

preferably not more than 200° F. lower. By operating under these preferred temperature conditions the amount of recycled gas can be kept at a minimum.

The barium oxide employed in the hydrogen generator is progressively converted to barium carbonate by the carbon dioxide produced. It therefore is necessary to regenerate the oxide from the carbonate from time to time. This may readily be done by separately heating the carbonate to its decomposition temperature in the same or different vessels. If the regeneration is effected in the same vessel, then it is necessary to operate a second vessel for carrying out the steam-methane reaction while the first vessel is on its regeneration cycle. Alternatively, the carbonate may be continuously withdrawn from the hydrogen generator and regenerated in a separate vessel from which it is continuously recycled to the generator.

The reactions in the two zones may be carried out using either fixed or fluidized beds. The use of fluidized beds is preferred when (1) the solid fuel used is a coking coal, and (2) it is desired to obtain precise temperature control in the oxide regeneration step.

The use of a fixed or moving bed is preferred when it is desired to obtain a maximum concentration of hydrogen leaving the methane-steam zone and a maximum concentration of methane leaving the coal or char hydrogenation zone. This is not only desirable in order to obtain a higher purity product but also to minimize the recycle of gas between the two zones. The purity of the hydrogen produced in the methane-steam reaction zone may be increased for example, by establishing a temperature gradient of at least 100° F. between the top and bottom of the barium oxide bed, the higher temperature being at the methane inlet end. Similarly, the concentration of methane leaving the hydrogenation zone may be increased by establishing a temperature gradient such that the temperatures of gases leaving are at least 100° F. less than they are at the hottest point in the bed. The desired temperature gradient may be established in a fixed bed by cooling the outlet portion of the bed; and in moving or fluidized beds, by maintaining a plurality of successive beds at progressively lower temperatures.

Finally a fluidized bed may be used in one of the operations and not in the other. For example, due to the relatively low temperature prevailing in the methane-steam reaction zone, moderately long residence times of the order of one-third to three minutes are required. Thus it is convenient to use relatively low velocities during the methane-steam reaction, i. e., 0.05 to 0.50 feet per second. These velocities using barium oxide in the size consist range of −20 to +325 mesh are either insufficient to fluidize the barium oxide or will effect only a "bubbling" type of fluidization. On the other hand, the oxide regeneration step is most suitably carried out at a higher velocity, i. e., at 0.5 to 3.0 feet per second, i. e., sufficient to maintain the barium oxide bed in the "streaming" fluidization range.

The methane-steam reaction may be carried out, therefore, using either a fixed or "bubbling" fluidized bed, while the oxide regeneration may be carried out using a "streaming" fluidized bed.

The rate of the methane-steam reaction may be increased substantially by the use of catalysts particularly the metals of the first transition group. The metals may be supported directly on the barium oxide or on an independent porous support, i. e., Ni, Co, or Fe on α-alumina, Cu on silica gel, etc. The barium oxide may be supported on a refractory basic oxide such as MgO to provide greater physical strength.

I have found that by operating the two vessels in the above manner, either hydrogen or a high B. t. u. gas containing methane in substantial quantities may be produced at will and under conditions such that the overall process is exothermic. In the barium oxide vessel heat is supplied for the endothermic steam-methane reaction by the exothermic reaction between the barium oxide and the carbon dioxide produced in the reaction. In the solid fuel vessel, the reaction between hydrogen and the fuel evolves heat. This desirable heat balance can readily be achieved by recycling either methane or hydrogen as the case may be.

In one of the embodiments of my new process, I utilize the heat evolved in the solid fuel hydrogenator to preheat the steam which is circulated to the hydrogen generator. Thus a more than adequate supply of heat is assured for the methane steam reaction.

In the following description of a specific embodiment of my invention, by way of example only, my new process is applied to the carbonaceous solid residue obtained by the low temperature distillation or carbonization of hydrocarbonaceous solid fuels, such as the high volatile bituminous coal found in the Pittsburgh Seam. This residue, for the purpose of convenience, I shall hereafter refer to as "char." It is to be understood, however, that the process is generally applicable to any carbonaceous solid fuels. Among such carbonaceous solids are included all ranks of coal, lignite, oil shale, tar sands, coke from coal or bituminous pitch, solid tar, etc. However, I prefer highly reactive solid fuels such as char, lignite and petroleum coke.

The apparatus shown in Figure 1 and its operation will now be described. A two-vessel system is employed comprising a solid fuels hydrogenation vessel 10 and a barium oxide-containing methane hydrolysis vessel 12. A fluidized bed of granular char is maintained in vessel 10 by means of gases circulating therethrough. The char feed should be ground so that substantially all passes through a 20 mesh screen and the velocity of the gases circulating therethrough to effect fluidization should be of the order of 0.2 to 1.2 feet per second. The bed of barium oxide may be maintained as a "bubbling" fluidized bed or as a fixed bed in vessel 12. The size consist of the barium oxide is preferably in the range of −20 to +325 mesh while the gas velocity is maintained at 0.05 to 0.50 feet per second.

A gas containing methane is introduced through a valved conduit 14 into vessel 12 along with steam fed to the conduit 14 from conduits 16 and 17. The bed of barium oxide through which the steam and methane are circulated is initially elevated to a temperature of 1700° to 2300° F. Once the reaction between the steam and hydrocarbon gas takes place, no heat need be added to maintain the reaction. The amount of barium oxide present in vessel 12 is sufficient to absorb substantially all of the carbon dioxide produced. There should be at least 800 parts by weight of oxide present for each 100 parts by weight of carbon contained in the methane passed through vessel 12. The pressure in this system is that previously recited, that is, it must equal or exceed one atmosphere in the temperature

range 1700° to 2050° F., and in the range 2050° to 2300° F. that given by the empirical relationship of Equation 1 but it is preferably maintained between 20 and 50 atmospheres. The gaseous product consisting essentially of hydrogen is withdrawn from vessel 12 through conduit 18. If it is desired to make a high B. t. u. gas rather than hydrogen, then all of the gas from the barium oxide vessel 12 is conducted through valved conduit 20 to the bottom of vessel 10. It is usually desirable to free the gas of water during its passage through conduit 20 by a condenser 21 and a collector 22.

Fresh char is introduced into the stream of gas in conduit 22 through conduit 26 from a hopper 23 provided with a motor-driven screw 24. Reacted char or ash is withdrawn through a draw-off tube 27 as necessary to maintain the level in the vessel. The gas circulates through the bed of solid fuels contained in vessel 10 and the hydrogen therein reacts with the fuel to produce a gas containing methane in substantial quantities. The latter is withdrawn from vessel 10 through a conduit 28 to a cyclone separator 30 where finely divided solids are returned to the vessel 10 through a dip leg 32. The solid-free methane gas is conveyed through a valved conduit 34 to suitable storage facilities. However, a part of the methane gas is recycled through the valved conduit 14 to vessel 12 to repeat the operation. The amount of methane recycled through conduit 14 is determined by the material balance in the system. In other words, sufficient methane must be recycled to produce in vessel 12 the hydrogen requirements in vessel 10. The temperature and pressure maintained in vessel 10 may be the same as those established in vessel 12, but in any case must lie within the limits previously recited.

If it is desired to produce only hydrogen from the system, then substantially all of the methane produced is recycled to vessel 12 from vessel 10 but only a portion of the hydrogen made in vessel 12 is recycled to vessel 10 for reaction with the solids. It is also possible by controlling the recycle from each of the vessels to porduce hydrogen and methane concurrently, which is one of the inherent advantages of the two-vessel system.

During the course of the reaction between the methane and steam in vessel 12 to make hydrogen, carbon dioxide is produced, and, as previously stated, is absorbed by the barium oxide with the formation of barium carbonate. It is necessary to regenerate the oxide periodically in order to maintain its effectiveness in the reaction. This regeneration is accomplished by raising the temperature of the carbonate to the decomposition point preferably 2300° to 2350° F. at atmospheric pressure. Since it is desirable not to suspend operation of the system during the regeneration, another vessel 40 corresponding to vessel 12 is provided for continuing the steam-carbon reaction while the vessel 12 is on regeneration.

When the barium oxide in vessel 12 is being regenerated, the flow of steam and methane through valved conduit 14 is stopped. The vessel 12 is reduced to atmospheric pressure by closing its communication with the remainder of the system and by opening the valve in an exhaust line 42. The necessary decomposition temperature is established in the bed of carbonate by burning producer gas introduced through a valved conduit 44 with air introduced through a valved conduit 46. Pulverized coal may be burned directly with air in vessel 12 in place of producer gas. A fine grind is employed, i. e., 80% through 200 mesh such that ash is not retained by the barium oxide but is carried off in the flue gases.

While vessel 12 is on a regeneration cycle, vessel 40 is operating as the steam-methane reaction zone in the same manner as previously described for vessel 12. Steam is conducted through a valved conduit 48 into a valved conduit 50 which carries methane from the recycling conduit 14 to vessel 40. The gaseous product from vessel 40 is conveyed to the main outlet conduit 18 by a valved conduit 52. When vessel 12 is operating on a hydrogen generation cycle, vessel 40 is placed on a regeneration of oxide cycle in the same manner as is vessel 12. Air and producer gas are introduced through valved conduits 54 and 56, respectively, and flue gases are discharged through a valved conduit 58 at atmospheric pressure.

The application of the above process to the production of a high B. t. u. gas from char may be illustrated specifically by the following example. Instead of BaO, the compound $BaO \cdot BaCO_3$ was used because of its smaller cost of regeneration. The reaction zones in the two vessels are maintained at 1750° F. and at 40 atmospheres pressure absolute. The recycle ratio of gas from the solid fuel hydrogenation vessel to net gas discharged through conduit 34 as product is 2.23. The molar ratio of steam to methane fed to the steam-methane reaction vessel is 1.67. A gas having a heating value on a dry basis of 515 B. t. u./cubic foot and the following composition is obtained: H_2—72 per cent by volume; CO—0.2 per cent by volume; CO_2—0.0 per cent by volume; and CH_4—27.8 per cent by volume. The overall steam conversion is 78 per cent and the net heat evolved over and above that required to maintain the system in operation is about 38,000 B. t. u./lb. mol. of carbon fed to the system.

The application of the above process to the production of a gas rich in hydrogen from char may be illustrated specifically by the following example. Again $BaO \cdot BaBO_3$ was employed instead of straight BaO. The reaction zones in the two vessels are maintained at 1750° F. and at 40 atmospheres pressure absolute. The recycle ratio of hydrogen gas from the steam-methane reaction vessel to the net hydrogen gas discharged through conduit 18 as product is 2.22. The molar ratio of steam to methane fed to the steam-methane reaction vessel is 2.44. A gas having a heating value on a dry basis of 338 B. t. u./cubic foot and the following composition is obtained: H_2—98 per cent by volume; CO—0.2 per cent by volume; CO_2—0.0 per cent by volume; and CH_4—1.8 per cent by volume. The overall steam conversion is 77.2 per cent and the net heat evolved over and above that required to maintain the system in operation is about 42,000 B. t. u./lb. mol. of carbon fed to the system.

In Figure 2 of the drawings there is shown a modification of the solid fuel hydrogenator which provides for utilizing the heat evolved by the reaction between hydrogen and the solid fuel to preheat the steam fed to the methane-steam reaction vessel. This is particularly desirable when the temperature prevailing in the latter vessel is in the upper end of the previously recited critical range since then the steam-methane reaction is at or about the thermoneutral point, rather than being highly exothermic,

At the same time, the per cent steam conversion is increased by virtue of partial reaction of the steam with the solid fuel in the hydrogenator vessel.

Referring specifically to Figure 2, numeral 60 designates a modified solid fuel hydrogenator vessel in which carbonaceous solid fuel is reacted with hydrogen from a hydrogen generator like that described above. The vessel is divided into an inner hydrogenation zone 62 and an outer annular-shaped steam preheating zone 64 by a cylindrically shaped chimney 66. The two zones communicate with one another at the bottom and the top of the chimney.

Finely divided solid fuel is carried into the inner hydrogenation zone 62 by the hydrogen gas produced in a hydrogen generator (not shown) which operates in the same manner as that described in connection with the system of Figure 1. The linear velocity of the hydrogen gas and the particle size of the solid fuel are regulated to produce a fluidized bed in the zone 62. A cone-shaped baffle element 70 is provided at the foot of the chimney to support the bed and is spaced from the walls of the chimney to form an annular passage 72 permitting communication with the outer zone 64.

The gases produced in the hydrogenation zone are collected in a bell-shaped member 74 which is supported within the top of the chimney 66 in a spaced position with respect to the chimney walls to form an annular pasasge 76 for communication between the two zones. The bed level in the vessel 60 is maintained sufficiently high to at least cover the top of the chimney and thereby assure free circulation of solids between the two zones at the bottom and the top of the chimney. Preferably, the solids overflow from the top of zone 64 into the top of zone 62 in order to provide an effective seal between the gas bell 74 and the chimney 66. This may be accomplished by circulating the fluidizing gas in zone 64 at a higher linear velocity than that circulating through zone 62. A conduit 78 serves to convey the high B. t. u. gas produced to a cyclone separator 80 which separates any entrained solids from the gas and returns them through a dip leg 82 to the feed line 68. The solid free gas is either discharged as product through conduit 84 or recycled through conduit 86 to the hydrogen generator.

Steam enters the outer zone 64 of vessel 60 through a conduit 88 and passes up through the hot solids at such linear velocity that the fluidized condition is maintained. Because the solids in vessel 60 are continuously circulating between the two zones, the temperature in the outer zone 64 is nearly as high as that in the inner zone 62. The steam circulating through the outer zone is consequently preheated to reaction temperature. At the same time a small amount of the steam, of the order of 20 per cent, is converted by reaction with the carbonaceous solids. The preheated steam and gaseous reaction products are conducted from vessel 60 through a conduit 90 to a cyclone separator 92 which separates the entrained solid fines and returns them to the outer zone 64 through a dip leg 94. The solid free steam and gases are discharged from the cyclone into conduit 86 where they become mixed with the methane rich gas from the hydrogenation zone and are then fed to the hydrogen generator.

Operating temperature and pressure ranges are the same as previously given for the system described in connection with Figure 1. The composition of the products of the modified system remains substantially unchanged.

According to the provisions of the patent statutes, I have explained the principle, preferred construction, and mode of operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claim, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

The method of making gas from carbonaceous solid fuels which comprises maintaining two separate reaction zones, the first of which contains barium oxide in granular form and the second of which contains carbonaceous solids in granular form, said second zone being divided into a hydrogenation section and a preheating section which intercommunicate and which are arranged in heat exchange relation with each other, maintaining said first reaction zone at a temperature between 1700° and 2300° F., maintaining said second reaction zone at a temperature between 1400° and 1800° F., maintaining pressures in both reaction zones which are at least one atmosphere when the temperature of said first reaction zone is in the range 1700° to 2050° F., and when the temperature is in the range 2050° to 2300° F., are at least those given by the empirical relationship

$$p=1+4.9\times10^{-2}(t-2050)$$

where p is the minimum reaction pressure in atmospheres and t is the temperature of the reaction zone in °F., circulating a methane containing gas and preheated steam through said first reaction zone in the absence of methane-steam converting catalysts, the amount of barium oxide present in said zone being at least 300 parts by weight for each 100 parts by weight of carbon contained in the methane containing gas, circulating at least a portion of the product hydrogen from said barium oxide reaction zone through the hydrogenation section of the second reaction zone under fluidizing conditions, passing steam through the preheating section of the second reaction zone under fluidizing conditions, circulating solids in the fluidized condition between said sections, recycling at least a portion of the gaseous reaction product from the hydrogenation section of said second zone together with the steam from the preheating section through said first reaction zone as the aforementioned methane containing gas and preheated steam, respectively, and recovering at least a portion of the gas produced in one of said zones.

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