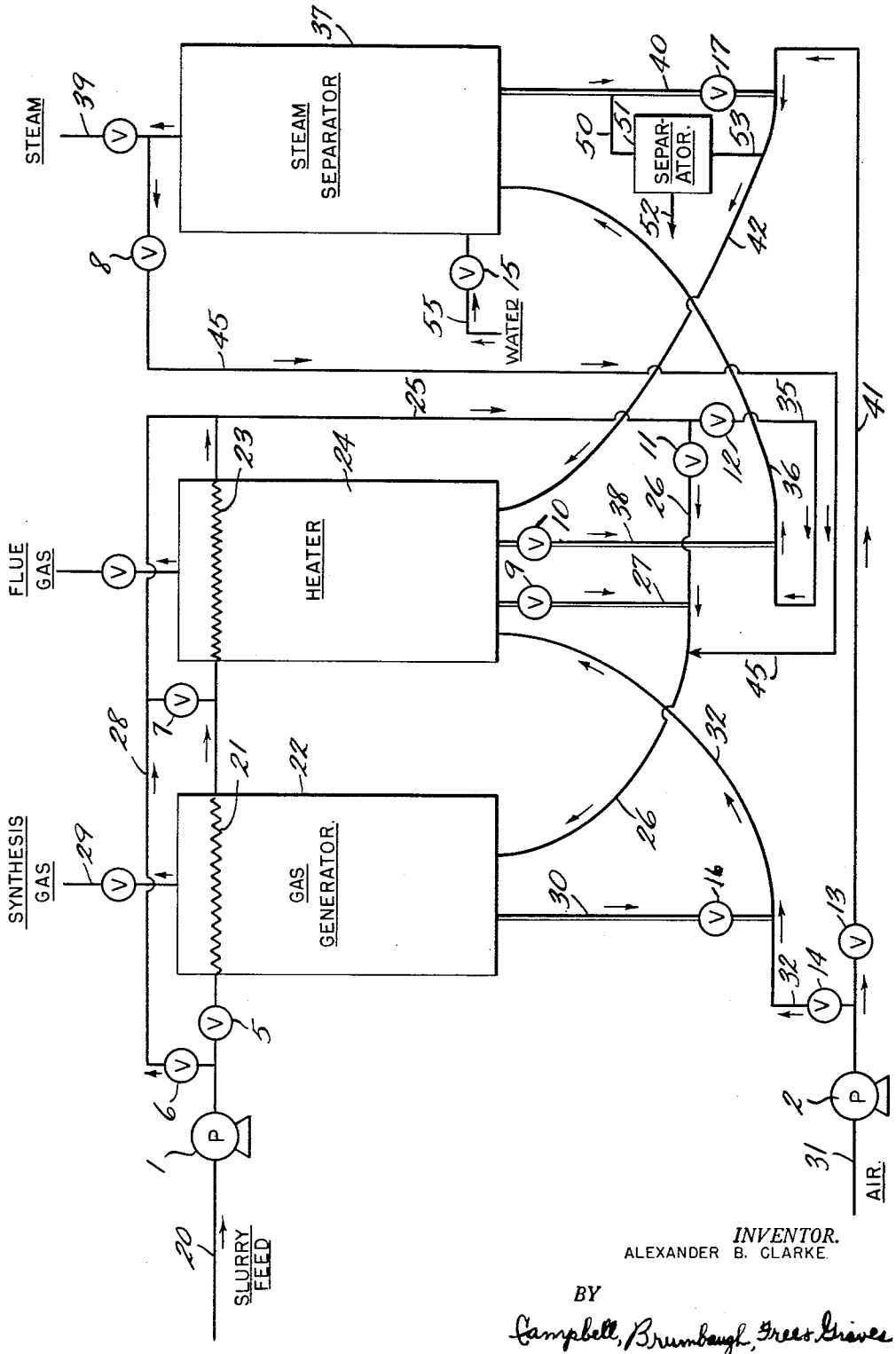
July 5, 1955 A. B. CLARKE 2,712,495

CONVERSION OF A CARBONACEOUS MATERIAL-WATER SLURRY

Filed Oct. 6, 1951



INVENTOR.
ALEXANDER B. CLARKE.

BY
Campbell, Brumbaugh, Frees & Graves
his ATTORNEYS.

United States Patent Office 2,712,495 Patented July 5, 1955

2,712,495

CONVERSION OF A CARBONACEOUS MATERIAL-WATER SLURRY

Alexander B. Clarke, Chagrin Falls, Ohio, assignor to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

Application October 6, 1951, Serial No. 250,126

12 Claims. (Cl. 48—206)

This invention relates to the treatment of suspensions of carbonaceous material in water by contacting them with hot fluidized heat transfer material in an improved process for the preparation of synthesis gas and/or for the preparation of process steam and the recovery of dry carbonaceous material from said mixtures.

The invention is particularly adaptable to a process of treating a mixture of water and carbonaceous material, such as coal, in a process wherein the major portion of the coal and water is converted into water-gas in the presence of heated material and the remainder of the mixture is treated whereby coal in the mixture is effectively recovered and utilized to reheat the heat transfer material which furnishes the heat necessary in the water-gas conversion process.

The conversion of coal, for example, to water-gas has been achieved by various methods in the art. Water-gas, or synthesis gas as it is called in these processes, is useful in the preparation of various organic products, such as the hydrocarbons, alcohols, ketones and the like, employing the well-known Fischer-Tropsch process, which is a method of treating synthesis gas consisting of essentially equal proportions of carbon monoxide and hydrogen, to obtain therefrom the above organic products. Synthesis gas may be obtained from the decomposition of lighter hydrocarbons, such as methane, etc., but the resulting proportions of carbon monoxide and hydrogen, as well as by-products, are less satisfactory than synthesis gas derived from coal and steam. The water-gas is also useful as a fuel in any operations in which flame from a gas source is required. Thus, improved processes for obtaining synthesis gas from coal and steam are desirable. The present invention provides an efficacious and improved process for the production of synthesis gas from conveniently available material.

The conversion of coal to gasoline and similar motor fuel is an example of the synthesis of water-gas to desirable organic products and has been achieved by various modifications of the basic Fischer-Tropsch process. However, the resulting gasoline has been too costly to make the prior processes commercially desirable, and the economical conversion of coal to gasoline via the water-gas synthesis is regarded as a major present-day technical problem.

There are extensive coal reserves available in this country, some of which are available at a rather low cost. However, the lower cost coal is so situated that rail transportation costs make its use in the synthesis of many compounds, such as gasoline and motor fuels, commercially unfavorable. Cheaper means of transportation of the coal to a location for processing in a form in which it may be readily utilized is, therefore, highly desirable in order that these synthesized products may be commercially competitive.

There is available at very low cost a method of transporting coal and this method is feasible for use in areas which are inaccessible to usual and cheaper rail transportation. This method is disclosed in U. S. Patent No. 2,128,913 to Burk, issued September 6, 1938, and involves

crushing the coal and suspending it in a carrier liquid, such as water, to make a pumpable mixture or slurry which may contain 5 to 50% coal by weight. The slurry may then be transported in a pipe line or other means. This process, however, requires the separation of the coal from the carrier liquid in order to condition the coal for burning and other usual uses to which the coal is applied.

In accordance with the present invention, it is found that the composition of the mixture of the crushed coal and water at which the coal is readily pumpable and easily transported is a desirable composition for use directly in the conversion of the coal and water into synthesis, or water, gas by the usual water-gas reaction. The coal may be of any size which will satisfy the conditions of being suspended and pumped as a water slurry and also of being handled as a fluidized solids stream. Accordingly, by the process to be described more fully below, a slurry as it is received from the pipe line is converted into synthesis gas which may be employed for any of the well-known uses to which water-gas is applied. Also by modifying the process slightly, the water of the mixture may all be converted to steam and substantially all of the coal recovered as a dry coal for use as a heating fuel or in any other application to which coal may be utilized, or, alternatively, all of the dried coal may be utilized to supply effectively the heat to convert the water of the slurry and also additional water to steam.

In the preparation of these products by the present invention, a fluidized heat transfer material is heated and circulated through the conversion zone, where it yields its heat to the promotion of the conversion process, and is recycled to a heating zone in which at least a portion of dried coal from the slurry is burned with air to reheat the heat transfer material for repeated use in the process. Thus the process is an integrated system requiring nothing but the coal and water slurry, other than circulating means, and a supply of ordinary air for the combustion of coal in a heating zone as below described.

Thus by the present invention, the cost of preparation of the synthesis gas from coal, for example, is much lower and makes the over-all process of converting coal into gasoline via this process and the usual Fischer-Tropsch synthesis more attractive economically. Similarly, this procedure provides a means by which the method of transporting coal in a slurry with water may be commercially feasible in those instances in which the coal is to be recovered for use in a dry and crushed form and/or where a large and readily available supply of steam is desired.

An object, therefore, of the invention is to provide a process for treating a mixture of carbonaceous material and water by contacting the mixture with hot fluidized heat transfer material to convert the water and carbonaceous material into synthesis gas and/or to convert the water into steam and to recover dry carbonaceous material.

An object of the invention is to provide a process for the conversion of a slurry of carbonaceous material and water in the presence of hot heat transfer material into synthesis gas by the water-gas reaction, recovering in a dry state a portion of the coal before it is converted, and utilizing the same to reheat the heat transfer materials for recycling to the process.

Still another object of the invention is the provision of a process for treating a mixture of carbonaceous material and water by contacting it with hot fluidized heat transfer material to convert the water into steam, separating the steam and coal, and burning at least a portion of the latter with air in the presence of the heat transfer material to supply the heat to the heat transfer material for utilization in the process.

These and other objects will be apparent to those skilled in the art from an explanation of the process described in connection with the accompanying drawing, which is a flow diagram of the process.

In the drawing, the numeral 1 indicates a pump for circulating a feed slurry of coal and water and pump 2 circulates air to the process. Valves for the various lines in the flow diagram are indicated by the numerals 5 through 17. In the over-all process for the preparation of synthesis gas from a coal-and-water slurry according to a preferred modification of the process, valves 5, 9, 10, 11, 12, 13, 14, 16 and 17 are open, and valves 6, 7, 8 and 15 are closed. The feed, which is preferably a slurry of equal proportions of water and coal, is introduced via the pump 1 in a line 20 and through a section 21 of a gas generator 22 and a section 23 of a heater 24 into a line 25 and via a line 26 into the gas generator 22. In this manner the feed is preheated in passing through the gas generator and the heater. The extent of preheating may be controlled by by-passing these zones with a portion of the slurry feed through a valve 6 in line 28 as required to adjust the temperature of the feed in line 25. The feed, which is preheated by passing through the gas generator and the heater, is admixed with highly heated heat transfer material from a standpipe 27 which collects heated heat transfer material from the bottom of the heater 24. The highly heated material from the standpipe raises the temperature of the feed and converts the water therein into superheated steam upon mixing with the feed. By reason of the increased volume and rate of flow due to the sudden volatization of the water into steam, the heat transfer and carbonaceous materials are suspended in the feed stream and flow therewith as a "fluidized" solids stream. The fluidized technique and the conditions for attaining it are well known. The admixture of feed and fluidized heat transfer material continues through line 26 into the gas generator 22. Conditions of temperature and pressure in the gas generator are such as to promote the conversion of the steam and coal into water gas. For instance, temperatures of the order of 1400° F. to 1800° F., preferably about 1600° F. and pressure of 0 p. s. i. to 500 p. s. i., preferably about 250 pounds per square inch, may be maintained in the gas generator. Synthesis gas is removed from the gas generator through a line 29 and passed to a purification system (not shown) and thence to a synthesis zone for the preparation of organic products, if desired. The gas generator may be any of the conventional chambers employed to handle fluidized solid material—for example a cylindrical chamber with a conical section at the bottom to direct the heat transfer material, after it has expended its heat to the conversion reaction, to the bottom of the chamber, where it is removed by a line 30. It may be expedient to employ a separator (not shown), such as a cyclone separator at the gas outlet on the generator to recover any of the heat transfer material entrained with the issuing gases.

Air under pressure is introduced by the pump 2 in a line 31 and pumped into line 32, where the air picks up the cooled heat transfer material from the line 30 from the bottom of the generator and carries the material into the heater 24, where it is again heated for recycling to the process.

A portion of the pre-heated feed in line 25 is diverted by means of a line 35 and flows past the base of a standpipe 38 where it picks up a portion of the heated heat transfer material from the bottom of the heater 24. The heat transfer material is carried with the diverted feed through a line 36 into a steam separator 37 where the water in the diverted feed is vaporized into steam. The steam thus formed is removed from the separator through a line 39. It may also be efficacious to employ a separator (not shown), such as a cyclone separator, on the steam outlet to separate the steam from the fluidized solids which will be returned to the steam separator chamber. Dry coal from the feed mixed with the heat transfer material is removed from the bottom of the steam separator through a line 40, where it is picked up by air under pressure in a line 41 and carried by means of line 42 into the heater 24. The coal is ignited and burned in the presence of the air in the heater to heat the heat transfer material for recycle to the gas generator and for circulation to the steam generator, as described above.

In the event that there is sufficient water in the slurry feed as supplied to provide the proper proportions of steam and coal in the gas generator for the desired conversion in the water-gas reaction the proportion may be adjusted before processing or a portion of the steam from the steam generator may be injected through a line 45 into riser 26 if desired.

In a preferred operation of the process, a portion, such as approximately 10%, of the coal in the feed slurry to the gas generator is recovered unconsumed together with the heat transfer material in the bottom of the gas generator and is recycled with the heat transfer material and air through the line 32 to the heater. By this provision of delivering to the heater a small portion of the coal out of the gas generator, the fly ash which is liberated by the coal in the process will be released substantially entirely in the heater and removed from the system with the flue-gas products, thus eliminating the fly ash from the synthesis gas where it would be an undesirable impurity which is difficult to remove in the purification thereof.

A distinct advantage of the present process is the absence of the necessity of providing an oxygen supply plant for furnishing the usual substantial quantities of high grade oxygen to the water-gas conversion step.

In the modification just described, excess steam is generated in a separate chamber by the vaporization of the water from that portion of the slurry which is diverted from the conversion stream as a source of dried coal for combustion and heating of the heat transfer material. The excess steam is removed and used for any desirable purpose.

In another modification of the process the steam separator 37 and the equipment related thereto is not employed and may even be eliminated. In this modification, valves 5, 9, 11, 14 and 16 will be open and valves 6, 7, 8, 10, 12, 13, 15 and 17 will be closed. The slurry feed will be introduced through lines 20, 25 and 26 into the gas generator 22, picking up heated heat transfer material from the standpipe 27, as described previously. However, in the gas generator the coal will not be completely consumed but a substantial portion of the coal, such as approximately one-third of the coal in the slurry feed, will be removed with the heat transfer material from the bottom of the gas generator through the line 30 and carried by the air with the heat transfer material through line 32 into the heater, where the coal will be ignited and burned to heat the material for recycle to the gas generator with additional slurry feed. In this operation all of the water in the slurry and any additional water which may be required to adjust the proportions of water and coal in the feed will be utilized in the water-gas conversion reaction in the gas chamber.

In the event that it is desired to operate the process purely for the preparation of steam and/or dried coal, the process may also be modified so as not to employ or to eliminate the gas generator 22. In this modification, valves 5, 10, 12, 13 and 17 will be opened and the valves 8, 9, 11, 14, 15 and 16 will be closed. Valves 6 and 7 may be opened or closed depending upon whether feed slurry is by-passed the gas generator unit and the heater. The slurry feed will again be introduced through lines 20 and 25 and passed through lines 35 and 36 into the steam generator 37. In passing from line 35 into line 36, the feed will pick up hot heat transfer material from the standpipe 38 and carry it in a fluidized stream into

the steam generator, where all of the water in the feed will be vaporized and removed through the line **39**. The dry coal will be removed with the cooled heat transfer material from the bottom of the steam generator through the line **40**, picked up by air under pressure through the line **41** and carried in a fluidized stream through line **42** into the heater **24**, where it is ignited and burned to reheat the heat transfer material for recycle to the steam generator.

If it is desired to recover dried coal from the process, a portion of the dried coal and heat transfer material may be diverted through a line **50** into a separator **51**, in which the coal can be separated by any suitable means, employing a separation process based on a difference in density or particle size or both, and removed through a line **52**. The heat transfer material will then be removed through a line **53** and returned to the mixture of coal and heat transfer material passing into the heater. If, however, it is desired to operate the process strictly for the conversion of water into steam, all of the coal may be passed to the heater and ignited therein to heat the heat transfer material which may now be circulated at a more rapid rate to provide the equivalent heat to the given amount of water being introduced with the slurry feed or, alternatively, the rate of circulation of the heat transfer material may be substantially the same and additional water to utilize the increased heat of the heat transfer material may be introduced to the steam generator through a line **55**; in the latter arrangement there will be an increased production of steam over that obtainable from the water of the feed alone. This modification of the process is especially desirable for use in plants producing or requiring large quantities of steam and provides an advantageous system for the utilization of a slurry of coal and water. In this modification conditions should be selected, especially a low enough temperature, to avoid undesirable contamination by volatiles from the coal.

Various other valves, pumps, gages, and minor equipment may be required and will be apparent to those skilled in the art. However, such equipment does not change the process described and these elements of equipment have been omitted from the drawing and description for sake of simplicity and clarity.

Any suitable heat transfer material may be selected, such as the usual refractory materials of silica, alumina or mixtures thereof, provided the material exhibits properties to withstand substantially the temperatures, handling and abrasive shock of circulation except where carbonaceous materials are employed as the heat transfer medium and possibly consumed in the process as more fully described below. The material should be of particle size sufficiently small to be fluidized, generally not greater than about ⅛". Examples of refractory materials are the well-known natural clays and the synthetic beads and refractory pebbles of discrete size. The refractory material may conveniently be a catalyst for the water-gas conversion if it also satisfies the above conditions. In some instances, the carbonaceous material or coal similar to that in the slurry feed of the process may be used as the heat transfer medium and will be recirculated and reheated in the process. All of the carbonaceous material will not be consumed in the heater since the supply of air for combustion will be limited only to that necessary to burn sufficient of the carbonaceous material to raise the temperature to the desired elevated temperature. Additional heat transfer material to make up for losses may be supplied through means not shown to the heat transfer circulating system at a suitable point, such as in the heater.

It may be that if the proportions of carbonaceous material and water in the feed slurry are not appropriate for the complete water-gas conversion, a portion of the carbonaceous material supplying additional heat may be utilized in furthering the conversion of more steam into water gas in to the gas generator. Similar adjustments of the various streams of the process may be made to accommodate carbonaceous material as the heat transfer medium in the modification in which only steam is produced from the process as described above.

The gas or vapor velocities are such that the heat transfer material is maintained suspended in the gas or vapor, such as in the range of 5 to 120 linear feet per second under the operating condition and to allow a desired rate of settling in the gas generator, the heater and the steam separator such that the most effective recovery of the heat may be realized from the heat transfer particles in these chambers.

In an example of a preferred modification of the process in the preparation of synthesis gas, a slurry of equal proportions by weight of coal and water is introduced to the system through line **20** at the rate of 370 tons per hour and is divided into two portions with 275 tons per hour passing through the line **26**, where it picks up 4150 tons per hour of refractory material at 2200° F. The slurry is heated to a temperature of about 1600° F. and the mixture passes into the gas generator where substantially all of the coal and the steam is converted into synthesis gas. A pressure of about 250 pounds per square inch is maintained in the gas generator. About 12 tons per hour of the coal from the feed is removed unconsumed with the refractory material from the bottom of the generator where the mixture is picked up by air introduced at a rate of approximately 304,000 cubic feet per minute and carried into the heater where the coal is burned and the refractory material is raised to a temperature of 2200° F.

About 95 tons of the feed slurry per hour, which constitutes the second portion of the feed, is diverted through the line **35** and picks up about 75 tons per hour of the hot refractory material at 2200° F. which raises the temperature of the slurry to about 500° F. This mixture of refractory material and slurry passes into the steam separator where the water of the slurry is converted into steam at a pressure of about 250 pounds per square inch. The steam is removed from the steam separator at 440° F. and the refractory material and coal is removed from the bottom of the separator where it is picked up with air introduced at the rate of 26,000 cubic feet per minute and is carried into the heater where the coal is burned under a pressure of about 250 pounds per square inch to heat the refractory material to a temperature of 2200° F. for recirculation to the gas generator and to the steam separator.

This system may be modified as described earlier and the particular conditions of operation modified to accommodate the material in the feed slurry in the operation of the process for the production of synthesis gas and for heating the heat transfer material for circulation in the process without the provision of the steam separator where a larger amount of the coal will be circulated unconsumed from the gas generator to the heater and burned therein to supply all the heat necessary to heat the heat transfer material for the process. Also the process may be operated for the production only of steam by adjusting the operating conditions to accommodate the slurry feed in the process eliminating the gas generator, as described above.

In the preceding consideration of the process, coal has been discussed as a preferred example of a carbonaceous material which may advantageously be utilized in the process. However, other carbonaceous substances, such as coke-like residues or wastes, wood, straw, coke, fermentation slops and the like, may also be used. Impurities in the carbonaceous substances, such as ash in coal as described in the above U. S. Patent No. 2,128,913, may be removed from the slurry and, where desirable, the slurry may be concentrated or diluted as required to provide a suitable concentration of the respective components thereof.

Various other modifications and variations of the process will occur to those familiar with the art and from the

description above, which is illustrative only. It will be understood that it is intended to claim all of the modifications inherent in the invention as described.

I claim:

1. An improved process for the treatment of a suspension of carbonaceous material in water to prepare steam and water gas by the water-gas reaction between said carbonaceous material and the water, which comprises dividing the suspension into two portions and heating a first portion of the suspension in a gas generator under pressure by the transfer of heat from hot fluidized heat transfer material to volatilize said water into steam at water-gas reaction temperatures and to convert carbonaceous material and steam into water gas, separately withdrawing the resulting water gas as a product of the conversion from the cooled heat transfer material, passing said cooled heat transfer material with air to a heating zone, passing the second portion of the suspension to a steam separator in the presence of heated heat transfer material, drying the carbonaceous material in said second portion by volatilizing the water therein to steam and separately removing the steam from the heat transfer material and the carbonaceous material in the separator as a product of the volatilization, passing at least a portion of the heat transfer material and dried carbonaceous material with air into said heating zone, burning said carbonaceous material in the heating zone in the presence of the air to reheat said heat transfer material, and recycling said reheated heat transfer material to said gas generator and to said steam separator.

2. The process of claim 1 in which said heat transfer material is a refractory material.

3. The process of claim 1 in which said heat transfer material is the carbonaceous material of the process.

4. The process of claim 1 in which said heat transfer material is a catalyst for the water-gas reaction.

5. An improved process for the treatment of a suspension of coal in water to prepare water gas by the water-gas reaction between said coal and the water, which comprises dividing the suspension into two portions and heating a first portion of the suspension in a gas generator under pressure by transfer of heat from hot fluidized heat transfer material to volatilize said water into steam at water-gas reaction temperatures and to convert coal and steam into water-gas, separately withdrawing the resulting water gas as a product of the conversion from the cooled heat transfer material, passing said cooled heat transfer material with air into a heating zone, passing the second portion of the suspension to a steam separator in the presence of heated heat transfer material, drying the carbonaceous material in said second portion by volatilizing the water therein to steam and separately removing the steam from the heat transfer material and the dried coal in the separator, passing the heat transfer material and dried coal with air into said heating zone, burning said coal in the heating zone in the presence of the air to reheat said heat transfer material, and recycling said reheated heat transfer material to said gas generator and to said steam separator.

6. The process of claim 5 in which said heat transfer material is a refractory material.

7. The process of claim 5 in which said heat transfer material is coal.

8. The process of claim 5 in which said heat transfer material is a catalyst for the water-gas reaction.

9. A process according to claim 5 in which the suspension is a mixture containing 5 to 50% by weight of coal suspended in water.

10. A process according to claim 5 in which the steam and coal is heated by said heat transfer material in said gas generator to a temperature of about 1600° F. at a pressure of about 200 pounds per square inch.

11. A process according to claim 10, in which the heat tranfer material at a temperature of about 2200° F. heats the steam and coal in the gas generator to a temperature of about 1600° F. at a pressure of about 250 pounds per square inch and a minor portion of said coal is unconsumed and is withdrawn with the heat transfer material into the heating zone.

12. A process according to claim 5 in which the temperature in the steam generator is about 500° F. at a pressure of about 250 pounds per square inch.

References Cited in the file of this patent

UNITED STATES PATENTS

2,094,946	Hubmann	Oct. 5, 1937
2,461,021	Atwell	Feb. 8, 1949
2,534,051	Nelson	Dec. 12, 1950
2,579,397	Roetheli	Dec. 18, 1951
2,595,234	Eastman	May 6, 1952
2,614,038	Barr	Oct. 14, 1952

FOREIGN PATENTS

155,553	Canada (Abstract)	May 12, 1914
948,501	France	Jan. 31, 1949
534,660	Germany	Sept. 30, 1931