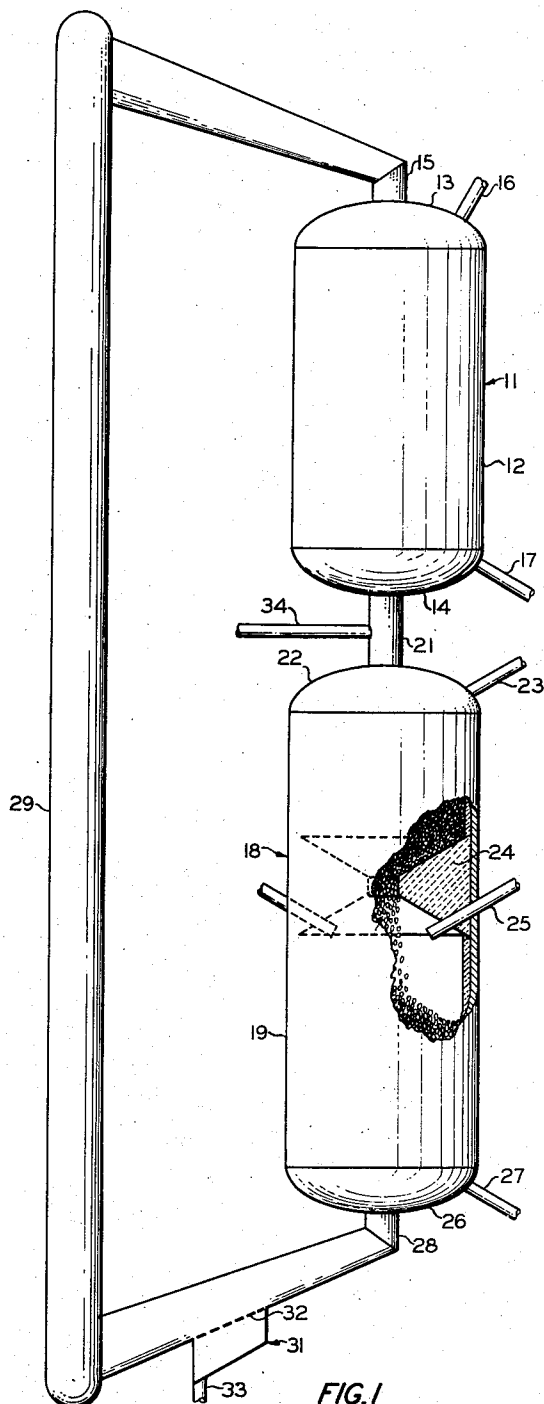
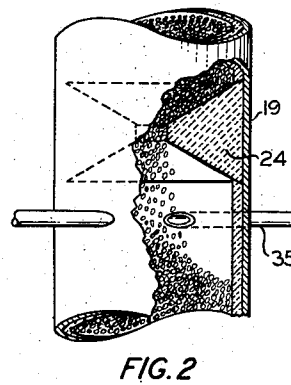


Nov. 3, 1953

B. J. MAYLAND
METHOD FOR GASIFYING COAL
Filed Sept. 12, 1949

2,657,501



INVENTOR.
B. J. MAYLAND

BY *Hudson and Young*

ATTORNEYS

UNITED STATES PATENT OFFICE

2,657,501

METHOD FOR GASIFYING COAL

Bertrand J. Mayland, Bartlesville, Okla., assignor
to Phillips Petroleum Company, a corporation
of Delaware

Application September 12, 1949, Serial No. 115,210

3 Claims. (Cl. 48—202)

1

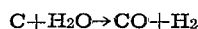
This invention relates to pebble heater apparatus. In one of its more specific aspects it relates to a method for the gasification of coking and low ash-fusion-temperature coals. In another of its more specific aspects it relates to an apparatus for the gasification of coking and low ash-fusion-temperature coals. In another of its more specific aspects it relates to a method and apparatus for removing sulfur impurities from water gas produced by the gasification of coal.

Thermal conversion processes which are carried out in so-called pebble heater apparatus utilize a flowing mass of solid heat exchange material, which mass is heated to a high temperature by passing hot gas therethrough in a first direct heat exchange step, and is then caused to contact a second fluid heat exchange material, furnishing heat thereto in a second direct heat exchange. The conventional pebble heater apparatus generally comprises two chambers which may be disposed in substantially vertical alignment. The solid heat exchange material is introduced into the upper portion of the first or upper chamber. That material forms a moving bed of solid heat exchange material which flows downwardly through the chamber in direct heat exchange with hot gaseous heat exchange material. The solid heat exchange material is heated to a high temperature in the heat exchange and is then passed to a second chamber in which the hot solid heat exchange material is caused to contact a second fluid heat exchange material in a second direct heat exchange relation, furnishing heat to the second fluid heat exchange material.

Conventional pebble heater chambers of pebble heater apparatus are generally formed as cylinders and a solid heat exchange material is passed thereinto in the form of a moving bed. Hot heat exchange gases are sometimes introduced into the upper cylindrical bed at its lower end and at the periphery of its enclosing chamber. A liquid fuel is sometimes used in place of the hot gas, the fuel being injected onto the surface of the downflowing solid heat exchange material and being burned thereon, heating the solid heat exchange material during the decomposition of the fuel and providing combustion gases which flow upwardly through the bed, providing additional heat to the downflowing pebbles. The solid heat exchange material is generally drawn from a substantially central point in the bottom of the bed and is passed downwardly into a gas heating chamber where a second moving bed of solid heat exchange material is formed.

2

Such pebble heater apparatus is readily adaptable to the gasification of coals. Conventional pebble heater apparatus, however, provides one rather serious difficulty when used for the purpose of converting coking and low ash-fusion-temperature coals to form water gas. The gasification of coal can be represented by the reaction between steam and carbon, i. e.,



This reaction takes place at temperatures in the neighborhood of approximately 1200° F., but in commercial operation it is ordinarily desirable to use higher temperatures so as to obtain a more rapid rate of reaction. Other reactions also occur in the gasification of coal, e. g.,



The resulting gas therefore is a mixture of hydrogen, carbon monoxide, steam, carbon dioxide, and hydrocarbons. At temperatures in the neighborhood of between 400° F. and 500° F., coal starts to lose its volatile material, the first released material being mainly loosely bound water. As the temperature is increased, more violent thermal decomposition of some coals occurs and hydrocarbon fragments are given off as volatile matter. Larger hydrocarbon fragments resulting either from cracking or polymerization of small hydrocarbon fragments remain in the coal and exert a solvent action thereon. When this occurs, the coals go through a plastic or semi-fluid state. The temperature at which the coals are converted to a plastic or semi-fluid state depends upon the particular coal which is being reacted. With a bituminous coal, a plastic or semi-fluid state is encountered at temperatures in the neighborhood of between 800° F. and 1000° F. Certain types of coals, such as lignitic and high rank anthracite coal, do not go through the plastic state.

Commercial gasification processes utilizing pebble heaters have heretofore used as feeds coke and coals which do not pass through a plastic or semi-fluid state. Since these materials do not go through a plastic stage, no difficulty is encountered in supplying the feed to the reaction chamber of the pebble heater apparatus. A good deal of the coal which is available for gasification in the United States is of a coking variety, such as bituminous and subbituminous coals. When these coals are supplied to pebble heater apparatus, considerable plugging of the feed inlet is encountered because of caking of coke in the inlet conduit. It has therefore been necessary,

heretofore, to convert such coal to coke before supplying the material to a gasification system or, if the coal has a low ash-fusion-temperature, to use a flux in combination with the coal or coke, which flux will liquefy the ash at reaction temperature so that it will drain off in a liquid state.

Some coals, especially the lower rank coals, have a fairly high sulfur content. As the coal is heated up to gasification temperature, much of this sulfur is released as organic sulfur compounds by thermal decomposition. These compounds are undesirable in synthesis operation because they poison Fischer-Tropsch catalysts and are equally undesirable in fuel gas application because they have unpleasant odors and are corrosive. Organic sulfur impurities are difficult to remove from gas by ordinary methods such as scrubbing.

The present invention is designed to overcome the obstacles and difficulties described above which beset conventional gasification processes when utilizing coking and low ash-fusion-temperature coals and coals which have a relatively high sulfur content. Broadly speaking, this invention comprises supplying powdered coal to a coking zone of a pebble heater apparatus as a suspension in a gas, such as steam. The coal is rapidly converted to coke and the coke so formed mixes with the pebbles and is converted to water gas by contact with steam which is introduced into the bottom portion of a reaction chamber. The resulting product gas is passed upwardly through the coking zone into a treating zone in the upper portion of the reaction chamber and is contacted with the hot solid heat exchange material in the absence of oxygen, during which time the organic sulfur impurities are converted to hydrogen sulfide. The resulting product gases are then removed from the reaction chamber, after which condensable materials are separated from the gas and the gas is subsequently scrubbed to remove the hydrogen sulfide therefrom.

An object of this invention is to provide improved means for gasifying coal. Another object of the invention is to provide an improved method for gasifying coal. Another object of the invention is to provide an improved method for gasifying low ash-fusion-temperature coals. Another object of the invention is to provide an improved method for removing organic sulfur impurities from product gases resulting in the gasification of coal. Other and further objects and advantages of this invention will be apparent to those skilled in the art upon study of the accompanying disclosure.

Solid heat exchange material which is conventionally used in pebble heater apparatus is generally called "pebbles." The term "pebbles" as used herein denotes any solid refractory material of flowable size and form which has considerable strength and which is suitable to carry large amounts of heat from the pebble heating chamber to the gas heating chamber without rapid deterioration or substantial breaking. Pebbles which may be satisfactorily used in this gasification system may be substantially spherical in shape and range from about $\frac{1}{8}$ inch to about 1 inch in diameter. When gasifying coal which is in a finely powdered state, I prefer to use pebbles which range within a size of from $\frac{1}{8}$ inch to $\frac{1}{2}$ inch in diameter. Silicon carbide, alumina, periclase, beryllia, stellite, zirconia, and mullite are a few of the materials which may be satisfactorily used to form such pebbles or may be

used in admixture with each other or with other materials.

More complete understanding of the invention will be obtained upon reference to Figure 1 of the drawing which is a schematic representation of the device of this invention. Figure 2 is a sectional view of a portion of the reaction chamber of this invention.

Referring particularly to the drawing, heater chamber 11 comprises an upright shell 12 which is closed at its upper and lower ends by closure members 13 and 14, respectively. Pebble inlet conduit 15 and gaseous effluent outlet conduit 16 are provided in closure member 13 and fluid heat exchange material inlet conduit 17 extends into the lower portion of shell 12. Although inlet conduit 17 is shown schematically as entering shell 12 at a single point, it is within the scope of this invention that the fluid heat exchange material inlet conduit may extend into shell 12 at a plurality of points distributed about the lower portion of that chamber. Reaction chamber 18 comprises upright shell 19 disposed below chamber 11 and pebble conduit 21 extends between the lower portion of chamber 11 and closure member 22 which closes the upper end of shell 19. Gaseous effluent outlet conduit 23 is provided in closure member 22. Pebble support member 24 is provided within shell 19 at a point intermediate its ends and is spaced downwardly from the upper end of shell 19 and upwardly from the bottom end thereof so as to divide chamber 19 into two sections. Pebble support member 24 is formed as a doughnut baffle which forms a pebble conduit in its central portion, which conduit extends between and provides communication between the upper and lower sections of chamber 18. The upper surface of support member 24 is preferably formed as an inverted cone, the included angle within said cone being between 60° and 100° . A support member which has such a slope on its upper surface will direct pebbles through its central inlet and substantially prevent the accumulation of stagnant pebbles on its upper surface. Coal inlet conduits 25 extend into chamber 19 to a point below pebble support member 24 as radii of an extended axis passing through the conduit formed in the center of a support member 24. The lower end of shell 19 is closed by closure member 26 and gasification medium inlet conduit 27 is provided in the lower portion of shell 19 and, like conduit 17 in chamber 12, may communicate with shell 19 at a plurality of points. Pebble outlet conduit 28 is provided in closure member 26 and provides outlet for pebbles from the lower portion of shell 19. Outlet conduit 28 is connected at its lower end to the lower portion of elevator 29. Elevator 29 is connected at its upper end portion with pebble inlet conduit 15. Separation means 31 is provided adjacent the bottom of a portion of pebble outlet conduit 28 and has a screen section 32 which forms a portion of the lower side of conduit 28 within the confines of a chamber also forming a part of separation means 31. Conduit 33 provides an outlet from separation means 31. It is preferred that conduit 21, which communicates between the lower end of chamber 12 and the upper end of shell 19, have a larger horizontal cross section than the conduit which is formed in the center of pebble support member 24. A conduit 34 is connected to pebble conduit 21 for transmitting an inert gas to conduit 21.

Figure 2 shows a portion of a reaction chamber which is similar to that shown in Figure 1

5

but is modified by the extension of the coal inlet conduits 35 tangentially into shell 19.

In the operation of the device shown as Figure 1 of the drawing, pebbles are supplied to the upper portion of chamber 11 through pebble inlet conduit 15 and form a flowing contiguous bed therein. A hot gas, such as the products of combustion, or a liquid or gaseous fuel is supplied to the lower portion of chamber 11. The hot gas is passed upwardly through chamber 11 countercurrent to the flow of the solid heat exchange material. If a liquid or gaseous fuel is supplied to the lower portion of chamber 11, the fuel is burned on the surface of the pebbles and resulting combustion products pass upwardly through the downflowing pebble mass, supplying heat thereto. Gaseous effluent materials are removed from the upper portion of chamber 11 through effluent outlet conduit 16. The heated pebble mass passes downwardly as a contiguous stream through pebble conduit 21 into the upper portion of chamber 18. The pebbles form a second flowing contiguous pebble mass in the upper portion of chamber 18 and flow downwardly through the conduit formed in the center of pebble support member 24. A third flowing contiguous pebble bed is formed in the lower portion of chamber 18, but the pebbles are removed from the lower end of that chamber at a sufficient rate to maintain a substantial void space between the lower side of pebble support member 24 and the upper surface of the pebble bed formed in the lower section of chamber 18.

Powdered coal is suspended in a gaseous medium, such as steam, and is injected into the void space formed between pebble support member 24 and the upper surface of the pebble bed formed in the lower portion of chamber 18. The powdered coal is rapidly diffused in the void space and is raised to its coking temperature, forming coke particles which settle on the surface of the pebble bed and flow downwardly through the lower portion of chamber 18 with the pebbles therein. Steam is injected into the lower portion of chamber 18 through inlet conduit 27 and flows upwardly countercurrent to the flow of hot pebbles and the coke. The pebbles preheat the steam as it passes upwardly there-through and the preheated steam reacts with the coke to form water gas as described above. The product gases pass upwardly through the void space, through the conduit formed by pebble support member 24 and into the upper portion of chamber 18 where a bed of hot pebbles is maintained. An inert gas, such as steam, is supplied to conduit 21 through conduit 34 so as to prevent product gas from passing into chamber 11.

The product gases are heat treated in the upper portion of chamber 18 in the heat exchange with the hot pebbles therein and a major portion of any organic sulfur impurities in the gases is converted to hydrogen sulfide. The heat treated product gases are removed from the upper portion of chamber 18 through gaseous effluent outlet conduit 23 and are passed to a condensation chamber, not shown, wherein the product gases are quenched and a portion of the condensable materials are removed therefrom. The cooled pebbles and solid ash are removed from the lower portion of chamber 18 through outlet conduit 28 and pass over screen 32 whereby the solid ash is separated from the pebbles. The solid ash is collected in separation means 31 and is removed therefrom through outlet conduit 33. The cooled pebbles are elevated by means of

6

elevator 29 to pebble inlet conduit 15 and thus to the upper portion of chamber 11.

The pebble heater apparatus shown in Figure 1 is if desired modified by changing the coal inlet conduits 35 so as to project tangentially into shell 19, as shown in Figure 2 of the drawing, when the coal to be gasified is of a type which passes less readily through the plastic or semi-fluid state. The ash-fusion-temperature is an important property of the coal which must be considered in coal gasification. Ash-fusion-temperatures vary from about 1200° F. to a temperature above 3000° F. The present invention is particularly adapted for gasifying coals at temperatures within the range of from 1200° F. to 2500° F. It is preferred to utilize reactor temperatures within the range of from 1500° F. to 2200° F. for the best commercial results.

Although the invention is described above as if the total amount of gasification was carried on within the pebble bed in the lower portion of chamber 18, it should be pointed out that a portion of the gasification takes place within the void space formed between the pebble support member 24 and the upper surface of the pebble bed in the lower portion of chamber 18. That void space, for all practical purposes, forms a coking zone and the pebble bed forms a gasification zone. It is obvious, however, that no definite line may be drawn between the two. By forming the conduit through pebble support member 24 with a smaller horizontal cross section than pebble conduit 21, a bed of pebbles is maintained in the upper portion of chamber 18 while allowing a void space to be formed between the lower side of pebble support member 24 and the upper surface of the pebble bed in the lower portion of chamber 18. The pebble stream which flows downwardly through pebble support member 24 forms the only portion of the pebble bed within the void space. Impingement of the coal particles upon the stream of pebbles flowing through the void space will result in temporary cakes of coke on the pebble surface, which cakes are removed in the lower portion of the reactor. In order to prevent a buildup of coke on the lower surface of the pebble support member or on the walls of shell 19 adjacent the void space, steam may be jetted against those surfaces at one or more points.

The description of the method of this invention has been restricted to substantially the operation of the apparatus which is shown in the drawings. The scope of the method of gasifying the coking variety of coal and of removing sulfur impurities from the product gases which is disclosed herein is broader than the specific apparatus herein disclosed. The device of this invention could be modified by providing a different type of pebble support member in chamber 19 which would allow the gases to filter therethrough at numerous points rather than causing all of the gases to pass through the central pebble conduit. It should be pointed out that such a device would not be as efficient as the device which I have disclosed, but nonetheless such a device would be adaptable for carrying on the method of this invention. By passing all of the reaction products upwardly through a single conduit countercurrent to the flow of pebbles any powdered coal which is entrained in the gases is removed from the gas stream by the pebbles.

Various other modifications of the invention

will be apparent to those skilled in the art upon study of the above disclosure. It is believed that such modifications are within the spirit and the scope of the disclosure.

I claim:

1. A method for gasifying coal which comprises in combination the steps of gravitating pebbles through a pebble heating zone as a contiguous mass; heating said pebbles in said heating zone to a temperature above the desired pebble inlet temperature to a gas treating zone; gravitating said hot pebbles through said gas treating zone as a contiguous mass; gravitating said hot pebbles from said gas treating zone through a substantially void coking zone as a restricted free-falling stream; introducing powdered coal into said coking zone in gaseous suspension; subjecting said powdered coal to radiant heat from said free-falling pebbles in said coking zone, whereby said coal is converted to coke; gravitating said pebbles and said coke particles from said coking zone through a gasification zone as a collected mass; passing steam into the lower portion of said gasification zone and upwardly therethrough in direct heat exchange with the gravitating mass of hot pebbles and coke; reacting said steam with said coke; passing resulting product gases from said gasification zone through said coking zone and said gas treating zone; subjecting said product gases to high temperatures in direct heat exchange with said hot pebbles in said gas treating zone, whereby a large portion

of any organic sulphur in said product gases is converted to hydrogen sulfide; removing said heat-treated product gases from said gas treating zone; removing said pebbles from the lower end of said gasification zone; and elevating said pebbles to the upper end of said heating zone.

2. The method of claim 1, wherein said solid heat exchange material is introduced into said gas treating zone at a temperature of between 1200° F. and 2500° F.

3. The method of claim 1, wherein said solid heat exchange material is introduced into said gas treating zone at a temperature of between 1500° F. and 2200° F.

BERTRAND J. MAYLAND.

References Cited in the file of this patent

UNITED STATES PATENTS

	Number	Name	Date
20	911,494	Hall	Feb. 2, 1909
	1,654,942	Nielsen et al.	Jan. 3, 1928
	1,977,684	Lucke	Oct. 23, 1934
	2,443,337	Weber	June 15, 1948
	2,445,092	Utterback	July 13, 1948
25	2,447,306	Bailey	Aug. 17, 1948
	2,469,332	Evans	May 3, 1949
	2,482,138	Schutte	Sept. 20, 1949
	2,486,627	Arnold	Nov. 1, 1949
30	2,493,036	Savage et al.	Jan. 3, 1950
	2,520,096	Harter	Aug. 22, 1950
	2,530,274	Weber	Nov. 14, 1950