

March 31, 1953

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Filed Dec. 3, 1947

2 SHEETS—SHEET 1

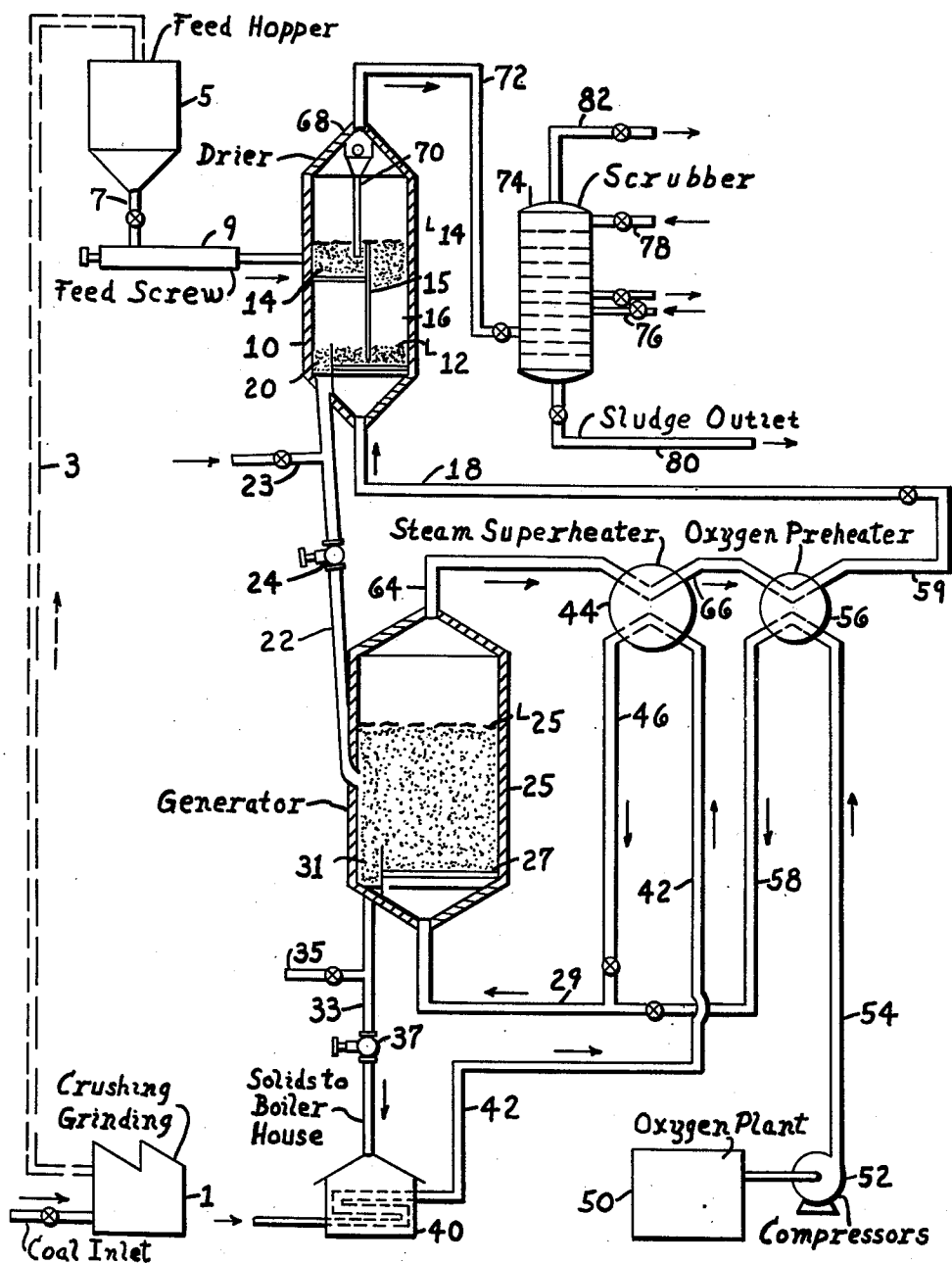


FIG.-1

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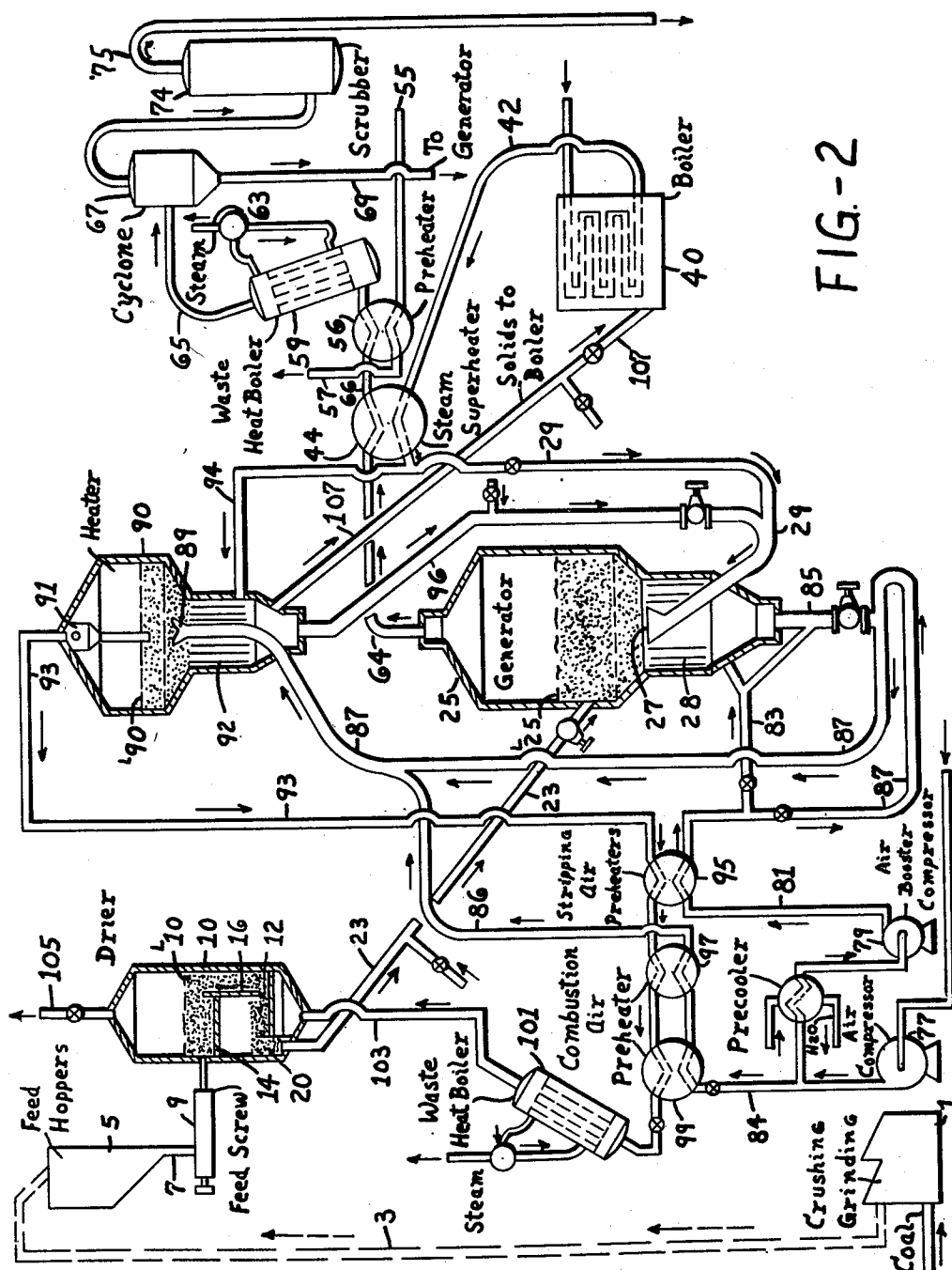
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2 SHEETS—SHEET 2



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UNITED STATES PATENT OFFICE

2,633,416

GASIFICATION OF CARBONACEOUS SOLIDS

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Application December 3, 1947, Serial No. 789,424

6 Claims. (Cl. 48—203)

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The present invention relates to the production of gases from non-gaseous carbonaceous materials and, more particularly, to the production of gas mixtures containing carbon monoxide and hydrogen, such as water gas, from such solid carbonaceous materials as coke, various coals, lignites, brown coals, peat, oil shale, oil coke, tar sands, cellulosic materials including lignin, and the like.

It has long been known that solid fuel materials, such as coal, coke and the like, may be converted into more valuable gases which can be more easily handled and more efficiently used for a greater variety of purposes. One of the most widely practiced gas generating conversions is the so-called water gas process in which solid fuels, such as coal or coke of any origin, are reacted with steam at temperatures of about 1400° to 3000° F., to produce water gas mixtures of carbon monoxide and hydrogen in varying proportions, depending mainly on the time of contact, conversion temperatures and the feed ratio of steam. The overall water gas reaction being endothermic, heat must be supplied which is usually accomplished by the combustion of a portion of the carbonaceous feed with an oxidizing gas, such as air and/or oxygen, at about 1600° to 3000° F. The combustion reaction may be carried out either simultaneously with the water gas reaction or alternately in a make and blow fashion.

The water gas process permits the production of gas mixtures of widely varying compositions and B. t. u. content. The process as such, therefore, is extremely well suited not only for the production of fuel gases of varied B. t. u. content but also for the production of gases for hydrogenation processes and particularly for the catalytic synthesis of hydrocarbons and/or oxygenated organic compounds from carbon monoxide and hydrogen, which, depending on the products desired, requires $H_2:CO$ ratios varying within the wide limits of 0.5 to 5 volumes of H_2 per volume of CO.

However, the technical utilization of the water gas process, particularly for hydrogenation processes and the production of synthesis gas, has been appreciably impeded by difficulties encountered particularly in heat supply, continuity of operation and limitations in temperature imposed by low ash fusion or softening points. The problem of continuity of operation has been satisfactorily solved heretofore by the application of the so-called fluid solids technique wherein the carbonaceous charge is reacted in the form

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of a dense turbulent mass of finely divided solids fluidized by the gaseous reactants and products. With respect to heat supply, such processes contemplate either generation of heat by combustion of carbonaceous materials within the gas generator or a continued circulation of solid carbonaceous material in a fluidized state to a separate heater in which heat is generated by combustion of the carbonaceous constituents of the residue, and recirculation of the highly heated solid fluidized combustion residue to the gas generation zone to supply the heat required therein.

In either case considerable difficulties arise in arriving at heat economies adequate for large scale economical operation. More particularly, it has been found that conventional methods of preheating the solids feed are too wasteful of heat to be practical in connection with the fluid processes here involved. In addition, there exists the difficult problem of reconciling the requirement of high gas yields per unit weight of coal and unit of reaction space with a complete conversion of available carbon into product gas and heat required in the process. This difficulty results from the fact that carbon gasification is directly proportional to the weight of carbon held up in the fluid generator. Most efficient heat generation by combustion, on the other hand, requires low carbon concentrations in the heater.

The present invention overcomes the aforementioned difficulties and affords various additional advantages. These advantages, the nature of the invention and the manner in which it is carried out will be fully understood from the following description thereof read with reference to the accompanying drawing.

In accordance with the present invention, the carbonaceous solids to be gasified are dried and preheated in direct heat exchange with hot gases produced in the gasification stage and flowing upwardly through two or more fluidized beds of solids to which the solids feed is supplied countercurrently to the gases which serve simultaneously as heating and fluidizing medium. The arrangement of a plurality of fluidized preheating beds or zones in combination with the countercurrent flow of solids and gases permits the utilization of the available waste heat of the product gases at different temperature levels in an order affording the greatest heat transfer efficiency and maximum heat recovery. For example, the temperature in the preheating bed first contacted by the product gases may be maintained just below the level of beginning car-

bonization, while the temperature in the preheating bed last contacted by the product gases should be kept substantially above the dew point of the product gases. By this arrangement, maximum heat is recovered from the product gases and maximum preheat is transferred to the solids entering the gas generator. Considerable savings of oxygen and process coal are thus secured in the gasification stage, which may amount to about 10-20%.

The carbonaceous solids thus efficiently preheated are then subjected to gasification at a relatively high carbon concentration of about 30-70% by weight of the solids held up in the gasification zone. Carbon losses are avoided by feeding the high carbon gasification residue directly to a combustion zone wherein their sensible and potential heat content is converted into steam. In this manner, it is possible to keep the generator size at a minimum without wasting carbon and to recover the sensible heat in the hot solids discharged from the generator. About 15,000-30,000 B.t.u. of sensible heat per 100 lbs. of coal fed to the generator may thus be utilized in the process.

Having set forth its general nature and objects, the invention will be best understood from the subsequent more detailed description wherein reference will be made to the accompanying drawing wherein

Figure 1 is a semi-digrammatic illustration of a system suitable for carrying out a preferred embodiment of the invention involving heat generation by combustion within the gas generation zone; and

Figure 2 is a similar illustration of a system involving heat generation in a separate heater.

Referring now to Figure 1 of the drawing, the system illustrated therein essentially comprises a drier and preheater 10, a gas generator 25 and a boiler 40, whose functions and cooperation will be forthwith explained using as an example the production of a synthesis gas having an $H_2:CO$ ratio of about 1:1 directly from coal. It should be understood, however, that water gas of the same or a different composition may be produced from other carbonaceous solids such as coke, shale, etc. in a generally analogous manner.

For purposes of illustration, it is assumed that the system of the drawing is designed to produce about 130 million standard cu. ft. of H_2+CO in the approximate ratio of 0.85:1 from a bituminous coal having a moisture content of about 7.0%, a heating value of about 8,900 B.t.u./lb. as received and about the following composition:

	Weight per cent
H_2O -----	7.0
C -----	53.1
H_2 -----	3.0
N_2 -----	1.2
O_2 -----	11.3
S -----	1.3
Ash -----	23.1

About 4,750 tons of this coal per day is crushed in crusher 1 to pass through a 30 mesh screen. The ground coal is hoisted or conveyed in any suitable manner through line 3 to feed hopper 5. From here it is fed through line 7 by a screw conveyor 9 at a pressure of about 30-500 lbs. per sq. in. abs. to an upper portion of drier 10. At least two horizontal perforated plates, such as grids 12 and 14, are arranged in drier 10 in spaced relationship to each other, the upper grid

14 being provided with an overflow downcomer 16 formed by the wall of drier 10 and a baffle 15 which terminates just above grid 12. The coal feed enters drier 10 at a point above grid 14. Simultaneously, hot product gas from generator 25 is supplied through line 18 to the bottom of heater 10 at a point below grid 12. This gas enters the main section of drier 10 at a superficial linear velocity of about 0.3-5 ft. per second, preferably about 0.3-1 ft. per second, to convert the coal feed into two dense, turbulent, fluidized beds forming above grids 12 and 14, respectively, and having well defined upper levels L_{12} and L_{14} .

The product gas may enter the lower coal bed above grid 12 at a temperature of about 800°-900° F. The solids hold-up of the lower fluidized bed is preferably so controlled as to permit the solids therein to reach a temperature of about 500°-700° F. Gas solids contact times of about 2 to 5 seconds are generally sufficient for this purpose though longer contact times may be used. The partially cooled product gas then enters the upper fluidized bed through grid 14 to dry and heat the solids therein to about 250°-300° F. at gas-solids contact times similar to those in the lower bed. Dried and preheated coal overflows over baffle 15 to enter the lower fluidized bed through downcomer 16, at the rate at which it is supplied to drier 10. Cooled product gas is withdrawn upwardly from level L_{14} and further treated as will appear hereinafter.

The preheated coal is withdrawn from the lower bed of drier 10 through a bottom drawoff well 20 and fed through a conventional standpipe 22 provided with one or more aeration taps 23 and a flow control means, such as slide valve 24, to generator 25. Standpipe 22 may be sufficiently high to feed the coal against the back pressure of the gas in generator 25 which may be operated at an elevated pressure of, say, about 50-400 lbs. per sq. in.

The coal feed enters generator 25 at a point above grid 27 arranged in the lower portion of generator 25. Simultaneously, generator 25 receives from line 29 through grid 27 a mixture of steam and oxygen produced and preheated to a temperature of about 1000°-1200° F. as will appear more clearly hereinafter. The gas mixture enters the main section of generator 25 at a superficial linear velocity of about 0.3-1 ft. per second adapted to maintain the solids above grid 27 in the form of a dense, turbulent, fluidized mass having a well defined upper level L_{25} .

The absolute and relative proportions of steam and oxygen are so chosen that about 70 to 95% of the carbon fed to the generator 25 is converted by steam and oxygen to CO and H_2 at a steam conversion of about 40-80% and about 10 to 20% of the carbon is burned by the oxygen to CO_2 to supply the heat required by the water gas reaction and to maintain a gasification temperature of about 1600°-2000° F., preferably about 1700° F. Amounts of about 0.3 to 0.4 lb. of steam and about 0.0070 to 0.0080 mol of oxygen per lb. of coal supplied to generator 25 are generally adequate for this purpose. For example, the gas mixture supplied through line 29 may be composed of about 2.8 MM. lbs./day of steam and 27.5 MM. standard cu. ft. of oxygen (95% pure) per day, for a generator bed height of about 30 ft. Depending on the carbon concentration in the generator, the reactivity of the carbonaceous material and the reaction temperature, the bed height may vary between about 5 and about 40 ft.

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An amount of about 1,930 tons of solid gasification residue per day containing about 30–50 wt. per cent of carbon is withdrawn through bottom drawoff well 31 and passed through standpipe 33 provided with aeration taps 35 and control valve 37, substantially at the temperature of generator 25 to boiler house 40 wherein the remainder of the carbon is burned to produce steam required in the process.

Steam produced in boiler 40 passes through line 42, heat exchanger 44 and line 46 to gas feed line 29 at a temperature of about 1500°–1600° F. Simultaneously, oxygen of about 95% purity is produced in oxygen plant 50 and pumped by compressor 52 through line 54, heat exchanger 56 and line 58, at a preheat temperature of about 700°–900° F. to gas feed line 29 to make up the steam-oxygen mixture described above.

Returning now to generator 25, product gases are withdrawn overhead from level L₂₅. The gases containing some entrained solids leave through line 64, enter heat exchanger 44 at about 1700° F. to preheat the process steam to about 1550° F. as described above. The partially cooled product gas then flows through line 66 to heat exchanger 56 which it leaves at about 1280° F. after having preheated the oxygen to about 800° F. The gas leaving heat exchanger 56 through line 59 is passed, if desired after further heat exchange with process materials, to line 18 and from there to drier 10 as described above.

The cooled product gas leaving level L₁₄ of drier 10 is passed through a conventional gas-solids separation system such as cyclone 68 from which separated solids may be returned through line 70 to drier 10. The gas then flows through line 72 to a water scrubber which may be supplied through lines 76 and 78 with a total of about 650 to 750 gal. of water per minute for scrubbing and further cooling to about 100° F. A suspension of scrubbed solids in water leaves through line 80 to be disposed of in any desired manner. Product gas is withdrawn through line 82 in an amount of about 200 million standard cu. ft. per day containing about 130 million cu. ft. per day of H₂+CO in the ratio of 0.85:1 and having the following approximate composition:

	Vol. per cent
CO ₂ -----	12.3
CO -----	40.8
H ₂ -----	34.8
CH ₄ -----	8.0
H ₂ S -----	0.9
N ₂ -----	1.7
H ₂ O -----	1.5
	100.0

The gas may be further purified by CO₂ and sulfur removal in any conventional manner (not shown) and is then ready for use in the hydrocarbon synthesis. If desired, the H₂/CO ratio may be increased to any desirable value in a regular shift converter.

For the size and type of operation illustrated in Figure 1, the heat supplied to the coal in drier 10 is equivalent to about 100,000,000 B. t. u. per hour. If the coal were fed directly to generator 25 without drying and preheating as hereabove described, an additional 5.4 million standard cu. ft. of oxygen and a corresponding amount of additional coal would have to be provided for the gas generation. The amount of heat recovered as sensible heat of gasification residue fed to the boiler house is about 69,600,000 B. t. u. per hour.

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Referring now to Figure 2, the system illustrated therein comprises, in addition to the essential elements of Figure 1, a separate heater 90 in which gasification residue is burned to generate the heat required in generator 25 and the preheat for drier 10 as will be explained below, like reference characters designating like system elements.

The crushed coal supplied to drier 10 as described before is dried, preheated and fluidized therein by hot flue gases from heater 90 supplied through line 103 at a temperature of about 600°–800° F. as will appear more clearly hereinafter. The coal preheated in the lower bed of drier 10 to a temperature of, say, about 500° F. is withdrawn through bottom drawoff well 20 and standpipe 23 and passed to generator 25 at a point above gas distributing cone 27 arranged in the lower portion of generator 25. Cone 27 is surrounded by a stripping section 28 containing a plurality of concentric vertical baffles as apparent from the drawing.

Simultaneously, generator 25 receives from line 29 an amount of about 0.3 to 0.4 lb. of steam per lb. of coal supplied to generator 25 at a pressure of about 70 lbs. per sq. in. abs. The steam may be preheated to about 1100° F. in heat exchange with product gas as will appear more clearly hereafter. Generator 25 is so designed that the steam enters the main generator section of generator 25 at a superficial linear velocity of about 0.5–1 ft. per second to maintain the solids therein in the form of a dense, turbulent, fluidizing mass about 30 ft. high having a well defined upper level L₂₅. The temperature of this mass is maintained at about 1800° F. by the supply of highly heated solids from heater 90 as will appear hereinafter.

The total product gas, which amounts to about 21.0 standard cu. ft. per lb. of coal fed and which may contain about 0.002–0.05 lb. per cu. ft. of entrained solids fines, is withdrawn overhead from level L₂₅ at a pressure of about 65 lbs. per sq. in. through line 64. The gas may have a composition about as follows:

	Mol per cent
H ₂ -----	45.7
CO -----	26.9
CO ₂ -----	5.8
CH ₄ -----	2.9
N ₂ -----	2.2
H ₂ O -----	16.1
S (as H ₂ S) -----	0.4

This gas is passed to heat exchanger 44 where it preheats process and stripping steam produced in boiler 40 and supplied through line 42 to exchanger 44. About 90% of the steam preheated to about 1100° F. in heat exchanger 44 flows through line 29 to generator 25 as described above.

The product gas now cooled to about 1480° F. may then flow through line 66 to a second heat exchanger 56, which may be used to reheat product gas after H₂S and CO₂ removal, to a temperature of about 600° F., suitable for the removal of organic sulfur by any known catalytic process. This synthesis gas to be reheated may enter heat exchanger 56 through line 55 at about 300° F. and leave through line 57 at about 600° F.

The product gas which may leave heat exchanger 56 at a temperature of about 1225° F. is then passed to a waste heat boiler 59 wherein further steam may be produced and withdrawn through line 63. The product gas, now cooled to about 500° F., passes through line 65 to a cyclone

67 wherein most of the entrained solids, say about 80 to 95% thereof, are separated to be returned to generator 25 through line 69. The remainder of the solids may be removed and the temperature of the product gas may be reduced to a temperature suitable by CO₂ and H₂S removal, by scrubbing with water in scrubber 74, substantially as described in connection with Figure 1. Product gas is withdrawn through line 75 at a temperature of about 100° F. This wet gas, which amounts, per lb. of coal charged, to about 17 to 19 standard cu. ft. and contains about 14 to 16 standard cu. ft. of H₂+CO in the ratio of 1.70:1, may be further purified by CO₂ and sulfur removal and is then ready for use in the hydro-carbon synthesis.

Returning now to generator 25, solid, fluidized gasification residue containing about 30-40% of carbon is withdrawn downwardly through the concentric spaces formed by the concentric baffles in stripping section 28. Simultaneously, air supplied from air compressor 77 and air booster 79 through lines 81 and 83 is blown upwardly into these concentric spaces in order to strip the carbonaceous residue of occluded product gas and steam. The amount of solids withdrawn through section 28 may be about 40 to 45 lb. per lb. of coal fed to the generator.

The fluidized residue together with entrained air and carbon oxides formed in section 28 is withdrawn from the bottom of generator 25 through a standpipe 85 and suspended in line 87 in air supplied by compressor 77 and booster 79 through line 81 after preheating in heat exchanger 95 to about 1200° F. in heat exchange with flue gases from heater 90 as will appear hereinafter. The air supplied through line 87 serves to support the desired combustion in heater 90 which generates substantially all the heat required in the system. About 20 to 25 standard cu. ft. of air per lb. of coal charged to generator 25 is sufficient for this purpose, at the conditions specified for the present example. Additional air may be supplied from compressor 77 via line 84, preheaters 99 and 97 through line 86.

The dilute suspension of gasification residue in air flows under the combined air pressure and pseudo-hydrostatic pressure of the fluidized solids in standpipe 85, upwardly through line 87 and distributing cone 89 into heater 90. The gas enters heater 90 at a superficial linear velocity of about 0.3-1 ft. per second at which the entrained solids form a dense, turbulent, fluidized mass having a well defined upper level L₉₀. The temperature in heater 90 is preferably maintained at about 1900° F. at a pressure of about 50 lbs. per sq. in.

An amount of about 40 to 45 lbs. of hot heater residue per lb. of coal charged to generator 25 passes downwardly through the concentric spaces formed by the concentric baffles of stripping section 92. Simultaneously, preheated steam is passed from heat exchanger 44 through line 94 at about 1100° F. upwardly through stripping section 92 to strip the heater residue of occluded flue gases and air. The stripped heater residue then flows through a conventional standpipe 96 substantially at the temperature of heater 90 to steam feed line 29 to be carried by the steam into generator 25 and to supply the heat required therein.

Returning now to heater 90, hot flue gases amounting to about 20 to 30 standard cu. ft. per lb. of coal charged to generator 25 leave level L₉₀ overhead and are freed of entrained solids in

a conventional gas solids separator 91. The flue gases then flow through line 93 to heat exchanger 95 wherein they preheat the stripping and part of the combustion air as described above. Partially cooled flue gases then pass through exchangers 97 and 99 in heat exchange with further combustion air and enter waste heat boiler 101 at a temperature of about 1100° F. to generate further process and stripping steam. Flue gases now cooled down to about 600°-800° F. enter the lower portion of drier 10 through line 103 to preheat the fresh coal charge to about 500° F. in the lower bed and to about 260° F. in the upper bed of drier 10. Cooled flue gases are vented through line 105 at about 100° F.

A second minor proportion of hot heater residue amounting to about 0.3 to 0.35 lb. per lb. of fresh coal charged is passed from the bottom of heater 90 through line 107 at the temperature of heater 90 to the boiler house 40 wherein the sensible heat of the residue, amounting to about 150 B. t. u. per lb. of coal charged to generator 25 and its carbon content of about 30-40%, by weight, are converted into process steam.

It will be understood by those skilled in the art that the system of Figure 2, as a result of the efficient heat utilization in drier 10 and the use of hot high-carbon heater residue in boiler house 40, affords heat economies similar to those outlined in connection with Figure 1.

While specific numerical values have been given in the above examples for the various process conditions including temperatures, pressures, flow rates of gases and solids etc. it should be understood that the invention is not limited to these values which are given for illustration purposes only and which may vary within fairly wide ranges, depending on the character of the solids charge, the product gas desired and the specific design of the system as will be understood by those skilled in the art. If it is desired to charge coke rather than coal to generator 25, a suitable fluid type coking vessel may be interposed between drier 10 and generator 25, substantially as described in the copending Roetheli applications, Serial Nos. 487,187 and 609,662 filed May 15, 1943, and August 8, 1945, respectively, and assigned to the same interests as the present application. These applications are here specifically referred to with respect to possible variations in operation and equipment design, such as the use of standpipes in place of mechanical feeders, variations in the order of reaction zones passed through by the circulating solids, variations in heat generation, etc. When product gas of the type of producer gas is desired, the steam supply to generator 25 may be at least in part replaced by corresponding amounts of CO₂. Other modifications of the systems illustrated may appear to those skilled in the art without deviating from the spirit of the invention.

The embodiment of the invention described above with reference to Figure 2 of the drawing is specifically claimed in the co-pending Gornowski-Nelson application Serial No. 273,986, filed February 28, 1952, which is a division of the present application.

While the foregoing description and exemplary operations have served to illustrate specific applications and results of the invention, other modifications obvious to those skilled in the art are within the scope of our invention. Only such limitations should be imposed on the invention as are indicated in the appended claims.

What is claimed is:

1. In the process of producing gas mixtures containing CO and H₂ from solid carbonaceous materials and an oxidizing gas containing steam, wherein the oxidizing gas is contacted in a gasification zone at gasification temperatures of about 1600°-2000° F. with a dense, ebullient, fluidized mass of finely divided carbonaceous solids, and the heat required by said gasification process is supplied by combustion of a portion of said carbonaceous solids and direct heat exchange of burned solids and solids undergoing said gasification, the improvement which comprises maintaining at least two dense, ebullient, fluidized beds of finely divided fresh carbonaceous solids in a preheating zone, passing hot gases produced in said gasification process by the oxidation of carbonaceous materials upwardly through said beds in series, passing finely divided solids from bed to bed countercurrently to said hot gases, heating the solids in a bed first contacted by said hot gases to a relatively high temperature of about 500°-700° F. but below the level of beginning carbonization of carbonizable solids in heat exchange with said hot gases, and the solids in a subsequent bed in heat exchange with gases leaving said first bed to a relatively low temperature but above the dew point of said hot gases, feeding preheated solids from said first bed directly to said gasification zone, maintaining the carbon concentration in said gasification residue of about 30-70%, supplying gasification residue of said carbon concentration substantially at said gasification temperature to a combustion zone and subjecting it to combustion therein, and converting the heat available in said combustion zone into steam.

2. The process of claim 1 in which a portion of the sensible heat of said hot gases produced in said gasification process is supplied to gasification process feed gases at a point outside said gasification zone prior to the contact of said hot gases with said fresh carbonaceous solids.

3. The process of claim 1 wherein said carbonaceous solids are carbonizable.

4. The process of claim 1 in which said oxidizing gas comprises free oxygen.

5. In the process of producing gas mixtures containing CO and H₂ from solid carbonaceous materials and steam, wherein steam is contacted in a gasification zone at gasification temperatures

of about 1600°-2000° F. with a dense, ebullient, fluidized mass of finely divided carbonaceous solids and the heat required by said gasification process is supplied by combustion of a portion of said carbonaceous solids and direct heat exchange of burned solids and solids undergoing said gasification, the improvement which comprises maintaining at least two dense, ebullient, fluidized beds of finely divided fresh carbonaceous solids in a preheating zone, passing hot gases produced in said gasification process by the oxidation of carbonaceous materials upwardly through said beds in series, passing finely divided solids from bed to bed countercurrently to said hot gases, heating the solids in a bed first contacted by said hot gases to a relatively high temperature of about 500°-700° F. but below the level of beginning carbonization of carbonizable solids in heat exchange with said hot gases, and solids in a subsequent bed to a relatively low temperature above the dew point of and in heat exchange with gases leaving said first bed, feeding preheated solids from said first bed to said gasification zone, maintaining the carbon content in said gasification residue of said high carbon concentration at a temperature not substantially lower than said gasification temperature to a combustion zone, subjecting said gasification residue to combustion therein, and converting the heat available in said combustion zone into steam.

6. The process of claim 5 in which said carbonaceous solid is coal, said gasification temperature is about 1600°-1800° F., and said relatively low temperature about 200°-300° F.

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