PATENT SPECIFICATION

680,545

Date of filing Complete Specification: July 12, 1950.

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Index at Acceptance:—Class 55(i), B4(a : d : f), B(11 : 13).

COMPLETE SPECIFICATION.

An Improved Manufacture of Gases from Carbonaceous Materials.

I, John Conrad Arnold, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby

SPECIFICATION NO. 680545

By a direction given under Section 17(1) of the Patents Act 1949 this applica-
m proceeded in the name of Standard Oil Development Company, a Corporation duly
;anised and existing under the Laws of the State of Delaware, United States of
'rica, of Elizabeth, New Jersey, United States of America.

: PATENT OFFICE,
3rd September, 1952

DB 33299/1(56)/3289 150 8/52 R

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 alternatively in a make and blow fashion.

[*Price 2s. 8d.*]

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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 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.

When the heat is generated by burning carbonaceous solids within a gas generator employing the fluid solids technique for a continuous production of water gas, highly concentrated oxygen rather than air must be used as the oxidizing gas to avoid dilution of the product gas with large proportions of

THE PATENT OFFICE
LONDON

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COMPLETE SPECIFICATION.

An Improved Manufacture of Gases from Carbonaceous Materials.

I, JOHN CONRAD ARNOLD, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the invention, (a communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America), for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

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 alternatively in a make and blow fashion.

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The water gas process permits the production of gas mixtures of widely varying compositions and B.Th.U. content. The process as such, therefore, is extremely well suited not only for the production of fuel gases of varied B.Th.U. content but also for the production of gases for hydrogenation process and particularly for the catalytic synthesis of hydrocarbons and/or oxygenated organic compounds from carbon monoxide and hydrogen, which depending on the products desired, require $H_2 : CO$ 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 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.

When the heat is generated by burning carbonaceous solids within a gas generator employing the fluid solids technique for a continuous production of water gas, highly concentrated oxygen rather than air must be used as the oxidizing gas to avoid dilution of the product gas with large proportions of nitrogen. When the heat is generated by combustion in a separate heater as outlined above, considerable difficulties result from the limitations necessarily imposed on the practical temperature difference between the heater and gas generator. In order to maintain solids circulation within reasonable limits, this difference should be as large as possible. The conversion of steam in the water gas reaction increases under otherwise equal conditions with increasing temperatures in the range of about 1600° to 2100° F., it may amount to about 25 to 50% at temperatures up to about 1700° F., to about 85% at about 2000° F. and to about 98 to 99% at temperatures of 2100° F. and above. The gas generator temperature should, therefore, be as high as the heat resistance of economical construction materials available for fluid equipment and the fusion or softening point of the ash permit. However, the same factors limit the heater temperature. It follows that, even if the heater is operated at highest temperatures attainable in technically practical equipment and commensurate with the ash fusion or softening point which lies in the neighbourhood of about 2000° F. for such materials as high chrome-nickel steel and reasonably priced ceramic-lined steel, and for most coal ashes, the gas generator will have to operate at a temperature below about 2000° F.

For example, operation of the heater at about 1900° F. and of the generator at about 1800° F. requires a solids circulation rate between heater and generator of, say, about 20 lb. of solids per lb. of fresh coke supplied to the system. If it is desired to reduce solids circulation by an increase of the temperature differential between heater and generator, this may only be accomplished by reducing the generator temperature because any increase of the heater temperature increases the danger of ash fusion and sticking of the charge. A reduction of the generator temperature, however, is conducive to a corresponding decrease in the conversion rate and must be compensated for by a suitable increase of solids hold-up and steam-solids contact time. Thus, if the generator temperature is dropped to 1700° F. to obtain a temperature differential of about 200° F. and a reduction in the solids circulation rate of about 50%, the solids hold-up in the generator must be increased about three-fold. Since the generator diameter is fixed by gas velocity and fluidization considerations, the depth of the solids bed in the generator must be about three times that required in the case of the smaller temperature differential and may require prohibitive generator heights.

These difficulties are even more pronounced when the generator is maintained under elevated pressures of more than, say, 20 lb. per sq. in. gauge, because the conversion rate decreases as the pressure is increased, requiring a corresponding increase in temperature and/or contact time to avoid output losses.

In accordance with this invention, improvements are secured in the "separate heater" type of process mentioned above by carrying out a substantial proportion of the gasification reaction within a so-called "transfer line reactor" through which hot solids from the separate heater are passed in the form of a suspension. Briefly a transfer line reactor is an elongated solids transfer line having a relative small cross-section. A typical form of such reactor is described in prior Specification No. 625,523.

Accordingly the present invention provides a process of producing a gas mixture rich in CO by the gasification of solid carbonaceous materials which comprises subjecting subdivided carbonaceous solids to a combustion reaction with an oxygen-containing gas in the form of a dense turbulent mass of solids fluidized by an upwardly flowing gas to form a well defined upper level in a heating zone, heating said solids by combustion to a temperature above minimum gasification temperature, suspending solids so heated substantially at said first-named temperature in a gaseous medium adapted to react with carbon to produce carbon monoxide in an endothermic reaction at said temperature, passing the suspension thus formed, with substantially concurrent flow of gases and solids, through a transfer line reactor along the length of which a negative temperature gradient is maintained, and recovering the gas mixture so formed, the length of the transfer line reactor and the velocity of the suspension passing therethrough being so correlated that at least a major proportion of said gaseous medium is converted to said gas mixture in the transfer line reactor.

In one embodiment of the invention, finely divided carbonaceous solids of the type already specified above are continuously heated to a temperature of about 1800° to 2200° F. by a combustion reaction with oxygen in a heating zone wherein the solids are maintained in the form of a dense highly turbulent mass fluidized by the upwardly flowing combustion supporting gases and gaseous combustion products. The heated solids are continuously withdrawn from the fluidized mass in the heating zone and contacted with an excess of a gasifying agent adapted to react with carbon to produce CO, e.g. a gasifying agent such as superheated steam and/or CO_2, substantially in concurrent flow over an extended path in a transfer line-type of reactor for a time sufficient to permit the conversion of a major portion of the gasifying agent to CO essentially at equilibrium conditions. Unconverted solids and product gas are passed from the transfer-line reactor to the lower portion of a second reaction zone of enlarged diameter wherein a turbulent, dense, fluidized solids mass similar to the mass in the heating zone is formed. This second reaction zone is so dimensioned and operated that the conversion of the gasifying medium is substantially completed on its path upwardly through the second reaction zone under essentially equilibrium conditions and that an overall upward movement of the fluidized solids is accomplished. Excess carbonaceous solids are removed continuously from an upper portion of the second reaction zone and returned to the heating zone, preferably to a middle section thereof. The fresh carbonaceous solids feed may be charged either to the heating zone or to either one of the gasification zones.

As a result of the substantially concurrent flow of heated solids and gasifying medium in the gasification zones, there is an appreciable temperature differential along the path of the reactants through the gasification zones. The gas generating reaction is initiated substantially at the relatively high temperature of the heating zone and completed at a substantially lower temperature at which solids and gases are withdrawn from the top of the second gasification zone. However, most of the reaction will take place at temperatures substantially above this lowest temperature to establish an average reaction temperature for the complete gasification reaction sufficiently high to afford satisfactory reaction rates. In conventional fluid operation of the gas generation zone on the other hand, the entire reaction zone will be substantially at the relatively low temperature at which gases and solids are withdrawn therefrom. For example, at a heating zone temperature of, say, about 1900° F., the gasification reaction may take place over a temperature range of about 1900° to 1700° F. in accordance with the invention as compared with a substantially constant temperature of, say, about 1800° F. in conventional fluid operation. In this manner, the required solids circulation will be about one-half that of conventional fluid-type gasification at about 1800° F. and the contact time required will be about 30% less than that for conventional operation at about 1700° F. Of course in conventional operations such as have just been discussed, some gasification may take place in the conduit provided for the supply of hot solids from the heater to the reaction zone proper but, in contrast to the present invention, the amount of gasification taking place in such conduit will be insignificant as compared with that occurring in the fluidized reaction zone.

As previously indicated the process of the invention is so operated that a major portion of the gasifying medium fed is converted in the transfer line reactor at the relatively highest temperatures and this permits the second fluidized reaction zone wherein the temperature and with it the conversion rate are substantially reduced, to serve partly as a clean-up zone, preferably employing a relatively longer contact time and moderate solids hold-up even at the prevailing relatively low temperatures. Quite generally, contact times in the transfer line reactor of about 2—4 seconds and in the fluidized reaction zone of about 4—10 seconds are suitable for this purpose.

The temperatures in the system of the invention should be as high as the ash fusion point of the carbonaceous solids feed permits. The higher the temperature range the more compact may be the equipment. In addition, high gasification temperatures are conducive to the decomposition of undesirable constituents evolved by the carbonaceous feed, including thiophene, and thus to the production of a more valuable gas for most purposes, particularly the catalytic synthesis of hydrocarbons. Depending on the type of solids charged, the temperature may vary within the system from a maximum of about 1900°—2200° F. in the heater to a minimum of about 1600—1800° F. or less at the point of solids and gas withdrawal from the fluidized gasification zone.

The solids circulation rate through the system depends on the rate and magnitude of the temperature drop through the system, or the character of the solids charge and on the temperature of the steam used. Assuming a total temperature drop of about 200° F. within about 10 seconds of solids-steam contact time and a low temperature coke as the solids charge, circulation rates of about 25 to 50 lb. of hot coke per lb. of fresh coke charged will be adequate for the purposes of the invention. When using a high-volatile coal and feeding it to the reactor, the lower rate applies whereas with anthracite coal the higher rate applies.

Having set forth its object and general nature, the invention will be best understood from the subsequent more detailed description in which reference will be made to the drawing accompanying the Provisional Specification, which demonstrates a system suitable for carrying out a preferred embodiment of the invention.

Referring now in detail to the drawing, the system illustrated therein essentially comprises a solids heater 10, a transfer line reactor 15, and a fluid-type reactor 20 whose functions and co-operation will be forthwith described using as an example the gasification of a low temperature coke with steam to produce water gas. It should be noted, however, that the system of the drawing may be used in an essentially analogous manner for the gasification of other carbonaceous solids and the use of CO_2 in place of, or supplementing, steam as the gasifying medium.

In operation, heater 10 contains a dense highly turbulent fluidized mass of coke having a particle size of about 100 mesh to ¼ inch size, preferably initially about 4—50 mesh. The coke may have a composition about as follows :—

Moisture	3.0%
Volatile	10.0%
Fixed Carbon	80.0%
Ash	7.0%
	100.0%

A combustion-supporting gas, preferably air, is admitted through line 1 and a perforated distributing means, such as grid 3, to the bottom of heater 10. The superficial linear velocity of the air entering heater 10 is maintained within the approximate range of 0.1—3 ft. per second, preferably 0.3—2.5 ft. per second, so as to establish an apparent density of the coke mass in zone B of heater 10 of about 5—50 lb. per cu. ft., preferably about 10—30 lb. per cubic ft. To start up the process, the air may be preheated to or above the ignition temperature of the coke, say to about 800—1000° F. When the process is in equilibrium, lower air preheat, of, say, about 300°—500° F. is sufficient and may be readily provided by heat exchange with hot product or heater flue gases in a conventional manner. Combustion takes place in heater 10 and the air supply is so controlled that the coke in zone B of heater 10 is maintained at a temperature of about 1800—2200° F., preferably about 1900°—2100° F. A supply of about 45—100 standard cu. ft. of air per lb. of coke supplied to heater 10 is normally sufficient for this purpose ; it varies according to the temperatures of the air used and calorific value of the coke.

In order to accomplish combustion of carbon all the way to CO_2 and to prevent reduction of CO_2 formed, by its reaction with carbon to form CO and accompanying heat losses, secondary air is preferably supplied to an upper portion of heater 10 through tuyere means 5. In this manner, complete combustion of any combustible gasiform matter present in heater 10 is assured. The introduction of secondary air at the level indicated results in an increase of the superficial linear gas velocity and in a reduction of the bed density above this level in heater 10. This is usually a desirable condition because carbon concentration and, with it, reduction or CO_2 to CO are reduced. Undesirably high gas velocities leading to excessive solids entrainment may be avoided by enlarging the diameter of heater 10 in zone A above the level of tuyeres 5 as indicated in the drawing, in such a manner that the superficial linear gas velocity is kept below about 3 ft. per second and the fluidized mass in zone A will still assume a more or less defined upper level L_{10}. An amount of about 20—60% of the total air to the heater is supplied through tuyeres 5 normally for the purposes of the invention.

Flue gases containing some entrained coke pass overhead from level L_{10}, preferably through a gas-solids separator, such as cyclone separator 7, which may also be located outside heater 10 to prevent damage by the excessive heater temperatures. Solids separated in cyclone 7 may be returned to heater 10 or discarded as desired. The hot flue gases leaving cyclone 7 are passed through a steam superheater 9 wherein they give off most of their heat to steam which may be superheated thereby to about 800°—1200° F. or higher. Flue gases are withdrawn from the system through line 11. The flexibility of heat generation in heater 10 as a function of fluctuations in product gas making rates in reactors 15 and 20 and/or in solids circulation rates through the system may be increased and over-heating of coke in heater 10 may be avoided by recycling suitable proportions of the flue gas from line 11 through line 12 to the bottom of heater 10, preferably via air line 1.

Fluidized coke, partly burned but containing considerable fixed carbon and substantially at the temperature of zone B of heater 10, is withdrawn from heater 10 through a withdrawal well 13 preferably under the pseudohydrostatic pressure of at least a major portion of the bed height in heater 10, i.e., from a lower portion of heater 10. Superheated steam is passed from superheater 9 through line 14 into line 13 to establish a relatively dilute suspension of hot coke in superheated steam having an apparent density of about 5—15 lb. per cu. ft. This dilute suspension is passed under the pseudohydrostatic pressure of the fluidized mass in heater 10, preferably upwardly through transfer line reactor 15. The amount of steam supplied through line 14 depends on the desired composition of the final product gas but it is sufficient to carry the necessary amount of hot coke from heater 10 to reactor 20. A gasifying agent, such as superheated steam, preheated CO_2 or air, or mixture of these gases is supplied through line 16 to reactor 20. For an $H_2 : CO$ ratio of about 2 : 1 in the product gas, sufficient steam must contact the hot coke in line 15 and in reactor 20 to maintain a relatively low temperature of about 1600°—1700° F. in the solids in the upper zone of reactor 20. If the desired $H_2 : CO$ ratio is about 1 : 2, a lesser amount of total steam is supplied through conduit 14 and line 16 so that the mean temperature of the hot solids in reactor 20 is about 1700°—1800° F. The dimensions of reactor 15 should be such as will permit a chosen time of contact of the gas making fluid with the hot coke within reactor 15 of about, say, 2—6 seconds with substantially concurrent flow of solids and gases. Flow velocities of about 5—20 ft. per second are adequate for this purpose in reactor 15.

Reaction between coke and steam takes place very rapidly in reactor 15 as a result of the relatively high temperatures at which the reactants are supplied. At the high temperature conditions specified above about 60—85% of the steam supplied to reactor 15 may be converted by the coke to form H_2, CO, and CO_2 by the time the suspension has passed through reactor 15. As a result of the endothermic character of this reaction, the circulating solids leave reactor 15 at a reduced temperature of about 1750°—1850° F at which temperature they enter the bottom of enlarged reactor 20 either through a distributing grid 17 or by way of a conical distributing means 19.

Reactor 20 is so designed that a highly turbulent, dense, fluidized mass of residual coke suspended in product gas and unconverted steam is formed therein having a level L_{20} similar to the fluidized mass in heater 10. However, in accordance with the preferred embodiment of the invention the superficial linear gas velocity in reactor 20 is so controlled that an overall upward motion of the turbulent solids is accomplished. Superficial linear gas velocities of about 1—5 ft. per second and apparent bed densities of about 5—20 lb. per cu. ft. in reactor 20 are generally suitable for this purpose. The solids hold-up in reactor 20 is preferably such as will provide a steam-solids contact time therein of about 4—10 seconds, preferably about 5—7 seconds. Product gas is withdrawn overhead from level L_{20} and recovered through line 22, if desired, after separation of entrained solids in any manner known *per se*. The hot product gas may be passed through a waste heat boiler (not shown) to generate the steam required by the process and superheated in superheater 9 as described above. Highly heated solids at temperatures of 1800°—2100° F. tend to stick together and agglomerate unless they are kept in rapid motion until their surfaces are cooled to about 1750° F. After the partly gasified hot coke in reactor 15 enters reactor 20 at the reduced temperature, better intimacy of contact with steam is required hence a dense bed and lower linear velocities are employed in reactor 20.

At the conditions specified above, the temperature of the solids in the upper portion of reactor 20 is about 1700° F. Solids of this temperature are withdrawn from the upper portion of reactor 20 at a point below level L_{20} and returned through line 24 to zone B of heater 10. Line 24 preferably discharges into a middle section rather than into a lower portion of heater 10 in order not to affect the desired high temperature level at the point of solids withdrawal from heater 10. Excess solids may be discarded through line 26 from the system, although it is preferred that at least a major proportion of the solids which have undergone gasification should be returned to heater 10.

Fresh make-up coke may be supplied from storage line 28 either through line 30 to an upper portion of heater 10, or through line 32 to an upper portion of reactor 20, or through lines 34 and 14 to reactor 15, depending on certain effects desired. For example, coke feed to heater 10 affords a product gas of greatest purity because combustible impurities are burned in heater 10 before the charge reaches reactors 15 and 20. Coke feed to reactors 15 and/or 20 permits utilization of the volatile matter of the fresh charge in the water gas made and thus affords better yields at otherwise equal conditions. Any suitable combination of these ways of supplying the fresh coke may be used. At the conditions of this example the fresh coke feed rate is that required to maintain the levels L_{10} and L_{20}.

The system illustrated in the drawing permits of various modifications. Transfer line reactor 15 may be arranged substantially horizontally or at any desired angle, rather than vertically as shown in the drawing, as long as a substantially concurrent flow of solids and gases in maintained. The steam feed in line 14 may be partially or completely replaced by CO_2, if a product gas of relatively high CO concentration is desired and hydrocarbons may be added to reactor 20 to undergo a reforming reaction therein or to increase the heating value of the product gas. The system may be operated at subatmospheric, atmospheric or superatmospheric pressures which may range as high as 500 lb. per sq. inch or higher. If the product gas is to be used in the catalytic synthesis of hydrocarbons, the pressure in the system of the invention is preferably about the same as or slightly higher than the synthesis pressure which may range from about atmospheric to about 700 lb. per sq. in. A particularly advantageous modification involves the arrangement of non-fluidizable packings in either or both heater 10 and reactor 20, preferably in the upper portions thereof. Packings of this type which may consist of refractory Raschig rings, Berl saddles, or the like, and which may have interstices adequate to permit the fluidized solids to pass therethrough, assist in reducing vertical back mixing of solids and in establishing desirable temperature gradients over the height of the fluid beds involved.

Other modifications may appear to those skilled in the art without deviation from the spirit of the invention.

The invention will be further illustrated by the following specific example.

EXAMPLE.

Conditions suitable for making water gas in a system at 25 lb. gauge pressure, with the diameter of reactor 20 being substantially $^6/_{10}$ the diameter of heater 10, using coke and feeding the coke to the heater 10, may be as follows:

Coke size	Through 4 mesh on 8 mesh
Coke, B.Th.U. per lb.	13,000
Coke, consumed per 1,000 cu. ft. of gas made	36 lb.
AIR	
Air supplied to heater 10 per sq. ft. sectional area per minute (measured at 60° F. and atmospheric pressure but supplied at 500° F. and 27 lb. gauge pressure)	95 cu. ft.
Coke consumed per minute per sq. ft. sectional area of heater 10	0.66 lb.
Coke consumed per minute per sq. ft. sectional rear of reactor 20 on steam-fuel reaction (steam used in both reactors 20 and 15	1.8 lb.
Total steam consumed, supplied to reactors 15 and 20 per M.C.F. of water gas	30 lb.
Total steam to reactors 15 and 20 per minute/sq. ft. area of reactor 20 supplied at 1200° F. about	3.0 lb.
YIELDS	
Water gas made per minute/sq. ft. area of reactor 20	103 cu.ft.
Make of water gas per hr./sq. ft. area, about	6,000 cu. ft.

The foregoing description and exemplary operations have served to illustrate preferred embodiments of the invention but are not intended to be limiting in scope.

What I claim is :—

1. A process of producing a gas mixture rich in CO by the gasification of solid carbonaceous materials which comprises subjecting sub-divided carbonaceous solids to a combustion reaction with an oxygen-containing gas in the form of a dense turbulent mass of solids fluidized by an upwardly flowing gas to form a well defined upper level in a heating zone, heating said solids by combustion to a temperature above minimum gasification temperature, suspending solids so heated substantially at said first-named temperature in a gaseous medium adapted to react with carbon to produce carbon monoxide in an endothermic reaction at said temperature, passing the suspension thus formed, with substantially concurrent flow of gases and solids, through a transfer line reactor along the length of which a negative temperature gradient is maintained, and recovering the gas mixture so formed, the length of the transfer line reactor and the velocity of the suspension passing therethrough being so correlated that at least a major proportion of said gaseous medium is converted to said gas mixture in the transfer line reactor.

2. The process of Claim 1, in which said gaseous medium comprises superheated steam.

3. The process of Claim 1, in which solids and gases leaving said transfer line reactor are contacted in a secondary reaction zone to produce additional quantities of said gas mixture.

4. The process of Claim 3, in which the contact time of said solids with said gaseous medium in the transfer line reactor is about 2—6 seconds and about 4—10 seconds in said secondary reaction zone.

5. The process of Claim 3, in which said solids and gases in said secondary reaction zone form a dense turbulent mass of solids fluidized to have a well defined upper level.

6. The process of any one of the preceding claims, wherein at least a major portion of the solids which have been subjected to the gasification reaction to produce said gas mixture are returned to said heating zone.

7. The process of Claim 6, in which said solids returned to said heating zone have a temperature substantially lower than said first-named temperature.

8. The process of Claim 7, in which said last-mentioned temperature is lower than said first-named temperature by an amount of the order of 200° F.

9. The process of any one of the preceding claims, in which flue gases are withdrawn upwardly from said heating zone and at least a portion of said withdrawn flue gases is supplied to a lower portion of said heating zone so as to control the temperature of said heating zone.

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PROVISIONAL SPECIFICATION.

An Improved Manufacture of Gases from Carbonaceous Materials.

I, John Conrad Arnold, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention (a communication from Standard Oil Development Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America) to be as follows:—

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.Th.U. content. The process as such, therefore, is extremely well suited not only for the production of fuel gases of varied B.Th.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, required $H_2:CO$ 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 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.

When the heat is generated by burning carbonaceous solids within a gas-generator employing the fluid solids technique for a continuous production of water gas, highly concentrated oxygen rather than air must be used as the oxidizing gas to avoid dilution of the product gas with large proportions of nitrogen. When the heat is generated by combustion in a separate heater as outlined above, considerable difficulties result from the limitations necessarily imposed on the practical temperature difference between the heater and gas generator. In order to maintain solids circulation within reasonable limits, this difference should be as large as possible. The conversion of steam in the water gas reaction increases under otherwise equal conditions with increasing temperatures in the range of about 1600° to 2100° F.; it may amount to about 25 to 50% at temperatures up to about 1700° F., to about 85% at about 2000° F. and to about 98 to 99% at temperatures of 2100° F. and above. The gas generator temperature should, therefore, be as high as the heat resistance of economical construction materials available for fluid equipment and the fusion or softening point of the ash permit. However, the same factors limit the heater temperature. It follows that, even if the heater is operated at highest temperatures attainable in technically practical equipment and commensurate with the ash fusion or softening point which lies in the neighborhood of about

2000° F. for such materials as high chrome-nickel steel and reasonably priced ceramic-lined steel, and for most coal ashes, the gas generator will have to operate at a temperature below about 2000° F.

For example, operation of the heater at about 1900° F. and of the generator at about 1800° F. requires a solids circulation rate between heater and generator of, say, about 20 lb. of solid per lb. of fresh coke supplied to the system. If it is desired to reduce solids circulation by an increase of the temperature differential between heater and generator, this may only be accomplished by reducing the generator temperature because any increase of the heater temperature increases the danger of ash fusion and sticking of the charge. A reduction of the generator temperature, however, is conductive to a corresponding decrease in the conversion rate and must be compensated for by a suitable increase of solids hold-up and steam-solids contact time. Thus, if the generator temperature is dropped to 1700° F. to obtain a temperature differential of about 200° F. and a reduction in the solids circulation rate of about 50%, the solids hold-up in the generator must be increased about three-fold. Since the generator diameter is fixed by gas velocity and fluidization considerations, the depth of the solids bed in the generator must be about three times that required in the case of the smaller temperature differential and may require prohibitive generator heights.

These difficulties are even more pronounced when the generator is maintained under elevated pressures of more than, say, 20 lb. per sq. in. gauge, because the conversion rate decreases as the pressure is increased, requiring a corresponding increase in temperature and/or contact time to avoid output losses.

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 drawings.

It is, therefore, the principal object of the present invention to provide an improved process for the production of gas mixtures containing carbon monoxide and hydrogen.

A more specific object of the invention is to provide an improved process employing the fluid solids technique for the production of water gas by reacting solid carbonaceous materials with steam and supplying heat of reaction as sensible heat of solids heated by the combustion of carbonaceous materials.

Other objects and advantages of the invention will appear hereinafter.

In accordance with the present invention, finely divided carbonaceous solids of the type specified above are continuously heated to a temperature of about 1800° to 2200° F. by a combustion reaction with free oxygen in a heating zone wherein the solids are maintained in the form of a dense highly turbulent mass fluidized by the upwardly flowing combustion supporting gases and gaseous combustion products. The heated solids are continuously withdrawn from the fluidized mass in the heating zone and contacted with an excess of a suitable gasifying agent such as superheated steam and/or CO_2 substantially in concurrent flow over an extended path in a transfer line-type of reaction zone for a time sufficient to permit substantial gasification of the solids essentially at equilibrium conditions. Unconverted solids and product gas are passed from the transfer-line reaction zone to the lower portion of a second reaction zone of enlarged diameter wherein a turbulent, dense, fluidized solids mass similar to the mass in the heating zone is formed. This second reaction zone is so dimensioned and operated that the conversion of the gasifying medium is substantially completed on its path upwardly through the second reaction zone under essentially equilibrium conditions and that an overall upward movement of the fluidized solids is accomplished. Excess carbonaceous solids are removed continuously from an upper portion of the second reaction zone and returned to the heating zone, preferably to a middle section thereof. The fresh carbonaceous solids feed may be charged either to the heating zone or to either one of the gasification zones.

As a result of the substantially concurrent flow of heated solids and gasifying medium in the gasification zones, there is an appreciable temperature differential along the path of the reactants through the gasification zones. The gas generating reaction is initiated substantially at the relatively high temperature of the heating zone and completed at a substantially lower temperature at which solids and gases are withdrawn from the top of the second gasification zone. However, most of the reaction will take place at temperatures substantially above this lowest temperature to establish an average reaction temperature for the complete gasification reaction sufficiently high to afford satisfactory reaction rates. In conventional fluid operation of the gas generation zone on the other hand, the entire reaction zone will be substantially at the relatively low temperature at which gases and solids are withdrawn therefrom. For example, at a heating zone temperature of, say, about 1900° F., the gasification reaction may take place over a temperature range of about 1900° to 1700° F. in accordance with the invention as compared with a substantially constant temperature of, say, about 1800° F. in conventional fluid operation. In this manner, the required solids circulation will be about one-half that of conventional fluid-type gasification at about 1800° F. and the contact time required will be about 30% less than that for conventional operation at about 1700° F.

In accordance with the preferred embodiment of the invention, the process is so operated that a major portion of the gasifying medium fed is converted in the transfer line reaction zone at the relatively highest temperatures and that the second fluidized reaction zone wherein the temperature and with it the conversion rate are substantially reduced, serves partly as a clean-up zone, preferably employing a relatively longer contact time and moderate solids hold-up even at the prevailing relatively low temperatures. Quite generally, contact times in the transfer line reaction zone of about 2—4 seconds and in the fluidized reaction zone of about 4—10 seconds are suitable for this purpose.

The temperatures in the system of the invention should be as high as the ash fusion point of the carbonaceous solids feed permits. The higher the temperature range the more compact may be the equipment. In addition, high gasification temperatures are conducive to the decomposition of undesirable constituents evolved by the carbonaceous feed, including thiophene, and thus to the production of a more valuable gas for most purposes, particularly the catalytic synthesis of hydrocarbons. Depending on the type of solids charged, the temperature may vary within the system from a maximum of about 1900°—2200° F. in the heater to a minimum of about 1600°—1800° F. or less at the point of solids and gas withdrawal from the fluidized gasification zone.

The solids circulation rate through the system depends on the rate and magnitude of the temperature drop through the system, or the character of the solids charge and on the temperature of the steam used. Assuming a total temperature drop of about 200° F. within about 10 seconds of solids-steam contact time and a low temperature coke as the solids charge, circulation rates of about 25 to 50 lb. of hot coke per lb. of fresh coke charged will be adequate for the purposes of the invention. When using a high-volatile coal and feeding it to the reactor, as through line 32, the lower rate applies whereas with anthracite coal the higher rate applies.

Having set forth its object and general nature, the invention will be best understood from the subsequent more detailed description in which reference will be made to the accompanying drawing which demonstrates a system suitable for carrying out a preferred embodiment of the invention.

Referring now in detail to the drawing, the system illustrated therein essentially comprises a solids heater 10, a transfer line reactor 15, and a fluid-type reactor 20 whose functions and co-operation will be forthwith described using as an example the gasification of a low temperature coke with steam to produce water gas. It should be noted, however, that the system of the drawing may be used in an essentially analogous manner for the gasification of other carbonaceous solids and the use of CO_2 in place of, or supplementing, steam as the gasifying medium.

In operation, heater 10 contains a dense highly turbulent fluidized mass of coke having a particle size of about 100 mesh to ¼ inch size, preferably initially about 4—50 mesh. The coke may have a composition about as follows:

Moisture	3.0%
Volatile	10.0%
Fixed Carbon	80.0%
Ash	7.0%
	100.0%

A combustion-supporting gas, preferably air, is admitted through line 1 and a perforated distributing means, such as grid 3, to the bottom of heater 10. The superficial linear velocity of the air entering heater 10 is maintained within the approximate range of 0.1—3 ft. per second, preferably 0.3—2.5 ft. per second, so as to establish an apparent density of the coke mass in zone B of heater 10 of about 5—50 lb. per cu. ft., preferably about 10—30 lb. per cubic ft. To start up the process, the air may be preheated to or above the ignition temperature of the coke, say to about 800°—1000° F. When the process is in equilibrium, lower air preheat of, say, about 300°—500° F. is sufficient and may be readily provided by heat exchange with hot product or heater flue gases in a conventional manner. Combustion takes place in heater 10 and the air supply is so controlled that the coke in zone B of heater 10 is maintained at a temperature of about 1800°—2200° F., preferably about 1900°—2100° F. A supply of about 45—100 standard cu. ft. of air per lb. of coke supplied to heater 10 is normally sufficient for this purpose; it varies according to the temperatures of the air and steam used and calorific value of the coke.

In order to accomplish combustion of carbon all the way to CO_2 and to prevent reduction of CO_2 formed, by its reaction with carbon to form CO and accompanying heat losses, secondary air is preferably supplied to an upper portion of heater 10 through tuyere means 5. In this manner, complete combustion of any combustible gasiform matter present in heater 10 is assured. The introduction of secondary air at the level indicated results in an increase of the superficial linear gas velocity and in a reduction of the bed density above this level in heater 10. This is usually a desirable condition because carbon concentration and, with it, reduction of CO_2 to CO are reduced. Undesirably high gas velocities leading to excessive solids entrainment may be avoided by enlarging the diameter of heater 10 in zone A above the level of tuyeres 5 as indicated in the drawing, in such a manner that the superficial linear gas velocity is kept below about 3 ft. per second and the fluidized mass in zone A will still assume a more or less well defined upper level L_{10}. An amount of about 20—60% of the total air to the heater is supplied through tuyeres 5 normally for the purposes of the invention.

Flue gases containing some entrained coke pass overhead from level L_{10}, preferably through a gas-solids separator, such as cyclone separator 7, which may also be located outside heater 10 to prevent damage by the excessive heater temperatures. Solids separated in cyclone 7 may be returned to heater 10 or discarded as desired. The hot flue gases leaving cyclone 7 are passed through a steam superheater 9 wherein they give off most of their heat to steam which may be superheated thereby to about 800°—1200° F. or higher. Flue gases are withdrawn from the system through line 11. The flexibility of heat generation in heater 10 as a function of fluctuations in product gas making rates in reactors 15 and 20 and /or in solids circulation rates through the system may be increased and over-heating of coke in heater 10 may be avoided by recycling suitable proportions of the flue gas from line 11 through line 12 to the bottom of heater 10, preferably via air line 1.

Fluidized coke, partly burned but containing considerable fixed carbon and substantially at the temperature of zone B of heater 10, is withdrawn from heater 10 through a withdrawal well 13 preferably under the pseudo-hydrostatic pressure of at least a major portion of the bed height in heater 10, i.e., from a lower portion of heater 10. Superheated steam is passed from superheater 9 through line 14 into line 13 to establish a relatively dilute suspension of hot coke in superheated steam having an apparent density of about 5—15 lb. per cu. ft. This dilute suspension is passed under the pseudo-hydrostatic pressure of the fluidized mass in heater 10, preferably upwardly through transfer line reactor 15. The amount of steam supplied through line 14 depends on the desired composition of the final product gas but it is sufficient to carry the necessary amount of hot coke from heater 10 to reactor 20. Oxidizing gas, such as superheated steam, preheated CO_2 or air, or mixtures of these gases may be supplied through line 16 to reactor 20. For an $H_2 : CO$ ratio of about 2 : 1 in the product gas, sufficient steam must contact the hot coke in line 15 and in reactor 20 to maintain a relatively low temperature of about 1600°—1700° F. in the solids in the upper zone of reactor 20. If the desired $H_2 : CO$ ratio is about 1 : 2, a lesser amount of total steam is supplied through conduit 14 and line 16 so that the mean temperature of the hot solids in reactor 20 is about 1700—1800° F. The dimensions of reactor 15 should be such as will permit a chosen time of contact of the gas making fluid with the hot coke within reactor 15 of about, say, 2—6 seconds with substantially concurrent flow of solids and gases. Flow velocities of about 5—20 ft. per second are adequate for this purpose in reactor 15.

Reaction between coke and steam takes place very rapidly in reactor 15 as a result of the relatively high temperatures at which the reactants are supplied. At the high temperature conditions specified above about 60—85% of the steam supplied to reactor 15 may be converted by the coke to form H_2, CO, and CO_2 by the time the suspension has passed through reactor 15. As a result of the endothermic character of this reaction, the circulating solids leave reactor 15 at a reduced temperature of about 1750°—1850 F. at which temperature they enter the bottom of enlarged reactor 20 either through a distributing grid 17 or by way of a conical distributing means 19.

Reactor 20 is so designed that a highly turbulent, dense, fluidized mass of residual coke suspended in product gas and unconverted steam is formed therein having a level L_{20} similar to the fluidized mass in heater 10. However, in accordance with the preferred embodiment of the invention the superficial linear gas velocity in reactor 20 is so controlled that an overall upward motion of the turbulent solids is accomplished. Superficial linear gas velocities of about 1—5 ft. per second and apparent bed densities of about 5—20 lb. per cu. ft. in reactor 20 are generally suitable for this purpose. The solids hold-up in reactor 20 is preferably such as will provide a steam-solids contact time therein of about 4—10 seconds, preferably about 5—7 seconds. Product gas is withdrawn overhead from L_{20} and recovered through line 22, if desired, after separation of entrained solids in any manner known *per se*. The hot product gas may be passed through a waste heat boiler (not shown) to generate the steam required by the process and superheated in superheater 9 as described above. Highly heated solids at temperatures of 1800°—2100° F. tend to stick together and agglomerate unless they are kept in rapid motion until their surfaces are cooled to about 1750° F. After the partly burned hot coke in reactor 15 enters reactor 20 at the reduced temperature, better intimacy of contact with steam is required hence a dense bed and lower linear velocities are employed in reactor 20.

At the conditions specified above, the

temperature of the solids in the upper portion of reactor 20 is about 1700° F. Solids of this temperature are withdrawn from the upper portion of reactor 20 at a point below level L_{20} and returned through line 24 to zone B of heater 10. Line 24 preferably discharges into a middle section rather than into a lower portion of heater 10 in order not to affect the desired high temperature level at the point of solids withdrawal from heater 10. Excess solids may be discarded through line 26 from the system.

Fresh make-up coke may be supplied from storage line 28 either through line 30 to an upper portion of heater 10, or through line 32 to an upper portion of reactor 20, or through lines 34 and 14 to reactor 15, depending on certain effects desired. For example, coke feed to heater 10 affords a product gas of greatest purity because combustible impurities are burned in heater 10 before the charge reaches reactors 15 and 20. Coke feed to reactors 15 and/or 20 permits utilization of the volatile matter of the fresh charge in the water gas made and thus affords better yields at otherwise equal conditions. Any suitable combination of these ways of supplying the fresh coke charge may be used. At the conditions of this example the fresh coke feed rate is that required to maintain the levels L_{10} and L_{20}.

The system illustrated in the drawing permits of various modifications. Transfer line reactor 15 may be arranged substantially horizontally or at any desired angle, rather than vertically as shown in the drawing, as long as a substantially concurrent flow of solids and gases is maintained. The steam feed in line 14 may be partially or completely replaced by CO_2, if a product gas of relatively high CO concentration is desired and hydrocarbons may be added to reactor 20 to be reformed therein by reaction with an oxidant or to increase the heating value of the product gas. The system may be operated at subatmospheric, atmospheric or superatmospheric pressures which may range as high as 500 lb. per sq. inch or higher. If the product gas is to be used in the catalytic synthesis of hydrocarbons, the pressure in the system of the invention is preferably about the same as or slightly higher than the synthesis pressure which may range from about atmospheric to about 700 lb. per sq. in. A particularly advantageous modification involves the arrangement of non-fluidizable packings in either or both heater 10 and reactor 20, preferably in the upper portions thereof. Packings of this type which may consist of refractory Raschig rings, Berl saddles, or the like, and which may have interstices adequate to permit the fluidized solids to pass therethrough, assist in reducing vertical back mixing of solids and in establishing desirable temperature gradients over the height of the fluid beds involved.

Other modifications may appear to those skilled in the art without deviation from the spirit of the invention.

The invention will be further illustrated by the following specific example.

EXAMPLE.

Conditions suitable for making water gas in a system at 25 lb. gauge pressure, with the diameter of reactor 20 being substantially $^{5}/_{10}$ the diameter of heater 10, using coke and feeding the coke to the heater 10, may be as follows:—

Coke size	Through 4 mesh on 8 mesh
Coke, B.Th.U. per lb.	13,000
Coke, consumed per 1,000 cu. ft. of gas made	36 lb.
AIR	
Air supplied to heater 10 per sq. ft. sectional area per minute (measured at 60° F. and atmospheric pressure but supplied at 500° F. and 27 lb. gauge pressure)	95 cu. ft.
Coke consumed per minute per sq. ft. sectional area of heater 10	0.66 lb.
Coke consumed per minute per sq. ft. sectional area of reactor 20 on steam-fuel reaction (steam used in both reactors 20 and 15	1.8 lb.
Total steam consumed, supplied to reactors 15 and 20 per M.C.F. of water gas	30 lb.
Total steam to reactors 15 and 20 per minute/sq. ft. area of reactor 20 supplied at 1200° F. about	3.0 lb.
YIELDS	
Water gas made per minute/sq. ft. area of reactor 20	103 cu. ft.
Make of water gas per hr./sq. ft. area, about	6,000 cu. ft.

The foregoing description and exemplary operations have served to illustrate preferred embodiments of the invention but are not intended to be limiting in scope.

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680,545 PROVISIONAL SPECIFICATION

1 SHEET

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