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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Water Gas from Solid Carbonaceous Materials

(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 Linden, New Jersey, United States of America).

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, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the production of gases from solid 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, 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 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., i.e. far below the optimum temperature range no matter how high the rate of circulation of heat carrying solids may be chosen. As a result, steam conversion remains incomplete and the process has a low degree of efficiency or required conversion space is excessive. Similar difficulties arise when the combustion is carried out within the gas generator itself because the temperature may not be raised above about 2000° F. in economically practical technical equipment and without troubles having arisen from ash fusion or softening.

These difficulties are particularly pronounced when the gasification reaction is to be carried out under elevated pressure above say 20 lbs. per sq. in. gauge because the rate of steam conversion drops rapidly when the pressure is increased and this drop in rate of conversion must be compensated for by a corresponding increase in temperature or increase in contact time.

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.

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

A more specific object of this 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 by the combustion of carbonaceous residue from the water gas reaction.

It has been found that these objects may be accomplished quite generally by employing in a fluid gas generator solid carbonaceous charging materials of relatively high chemical reactivity, i.e. materials which have an oxidation reactivity of T_{15} of 200°—250° C. and of T_{75} of 250°—300° C. where T_{15} and T_{75} are the temperatures at which the rate of heat release by oxidation of a sized sample becomes great enough to raise its temperature at rates of 15° C. per minute and 75° C. per minute respectively. In this manner, the steam conversion at a given temperature and under otherwise equal conditions may be considerably increased and the gas generator may be operated at temperatures considerably below the gas generation temperatures required for other feed material under similar conditions of pressure, steam concentration, contact time, carbon concentration, etc. without detrimentally affecting the steam conversion.

Accordingly the present invention comprises a process for producing gas mixtures containing carbon monoxide and hydrogen from solid carbonaceous materials and steam by passing steam into a gasification zone containing a mass of finely divided solid carbonaceous material having an oxidation reactivity as hereinbefore defined of $T_{15}=200—250°$ C., and $T_{75}=250—300°$ C., under such conditions to form a dense fluidized mass of finely divided solid, removing the residual solid from the said gasification zone, subjecting the same to treatment in the form of a fluidized ebullient mass with an oxidizing gas mixture to burn off the residual carbonaceous material and thereby heat the residual solid to a high temperature, and recycling the said heated solid to the gasification zone to use the sensible heat of the said heated solid to supply at least part of the heat required in the said gasification zone.

To determine whether any given solid carbonaceous material has the required oxidation reactivity, the method described by Sebastian and Mayes (Industrial and Engineering Chemistry, vol. 29, page 1118) may be used. However the preferred highly reactive carbonaceous starting material is low temperature coke obtained by carbonizing coal at temperatures not substantially higher than 1000° F., and preferably within the range of 600° to 950° F., to an oxidation reactivity of about $T_{15}=200°—210°$ C. and $T_{75}=250°—260°$ C. When low temperature coke of this type is charged to a fluid gas generator the gasification temperature may be lowered as much as about 100°—200° F. beneath the level required for conventional charging materials such as coal or high temperature coke, without affecting steam conversion under otherwise equal conditions. Substantially complete steam conversion of 98 to 99% may be achieved at temperatures in the neighborhood of about 1900° F., while at 1700° F. the steam conversion still amounts to about 80%. Gas generator plugging which may be a danger in fixed bed operation as a result of the use of a charge of low mechanical strength is avoided when the fluid solids technique is applied. Thus, the gas generation reaction may be efficiently conducted below the upper temperature limits drawn by the heat resistance of economic construction materials and the ash fusion or softening point.

Other suitable highly reactive charging materials include certain bituminous or sub-bituminous coal, lignites, brown coals, etc. uncoked or coked at temperatures not substantially above 100° F. preferably between about 600° and 1000° F., whose oxidation reactivity falls within the limits indicated above. Whenever a preparation such as carbonization, drying, oxidation, etc. of the charging material is required or advisable in order to attain the desired high degree of reactivity, it is preferred to employ the fluid solids technique for the purpose because this technique affords the greatest advantages with respect to temperature control and constancy as well as uniformity and constancy of product composition and reactivity.

The heat required for the gasification reaction and charge preparation is generated by combustion in a separate heater and circulation of highly heated solid combustion residue to the zones of heat consumption, although combustion within the latter zone by means of air and /or oxygen may be applied in addition to a separate heater, if desired. Thus employing the fluid solids technique, a system is used wherein carbonaceous residue from a fluidized gas generator bed is subjected in the form of a fluidized bed to combustion in a separate heater and the sensible heat of hot combustion residue is used to supply the heat required in the gas generator.

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

Referring now in detail to the drawing a solid carbonizable fuel is crushed or pulverized in crusher (1) to a finely divided form, for example, of the order of 50% having a size of less than 100 mesh per linear inch, though small lumps of up to $\frac{1}{4}$ or $\frac{1}{2}$ inch size may be used. For the purposes of the following description, the carbonaceous material will be referred to as a bituminous carbonization coal containing 30—35% volatile matter, but other materials can be used.

The properly sized carbonization coal is hoisted or conveyed in any manner known *per se* through line (3) to feed hopper (5). From here it is fed through line (10) provided with screw feeder (14) into pipe (18) provided with control valve (19) and then into a dispersing chamber (20). The finely divided coal is dispersed in dispersing chamber (20) in a stream of " fluidizing " gas, such as superheated steam, nitrogen, flue gases, carbonization gases or vapors, or the like, supplied through line (22) by compressor (24). The solids in the dispersion are now in the so-called fluidized state in which they are capable of flowing through pipes, valves, etc. similar to a liquid and exhibiting static and dynamic heads.

The fluidized coal enters the conical lower portion of the enlarged cylindrical carbonization chamber (26) and passes through a distributing grid (27) into the carbonization zone (28) where the carbonization coal is subjected in the form of a dense ebullient fluidized mass forming a well defined upper level (29) to coking temperatures of between about 600° and 950° F., preferably around 900° F. The heat required for the carbonization reaction is preferably supplied by highly heated solids recirculated from combustion chamber (60) through line (65) as will appear more clearly hereinafter. Volatile carbonization products containing small amounts of solids fines are passed through a gas-solids separator (30) which may be a centrifugal or electric type precipitator, and through line

(32) to any conventional system (34) for the recovery of such volatile carbonization products as coal gas, oil, tar, chemicals, etc. Undesired tar fractions may be returned through line (35) to chamber (26) to be converted into gas in the course of the carbonization treatment. Solids separated in (30) are recycled through pipe (31) to the dense phase in (28).

Fluidized low temperature carbonization coke is withdrawn from carbonization chamber (26) at a point above grid (27) through pipe (36), and passed through control valve (37) to dispersing pipe (38) where it is taken up by highly heated steam supplied from steam preheater (50) through line (40). From dispersing pipe (38) the fluidized coke is passed through line (39) into the lower conical portion of the cylindrical gas generator (42) provided with distributing grid (43) in an arrangement similar to that of carbonization chamber (26).

The gas generator is maintained at a temperature of between about 1600° and 1900° F., preferably about 1700°—1800° F. and a pressure of about 40—60 lbs. per sq. in. gauge to permit the water gas reaction to take place between the steam and the coke maintained in a dense, ebullient mass (44) forming a level (45) in generator (42). The heat required for the water gas reaction is supplied by highly heated solid residues recirculated from combustion zone (60) through line (69) at the desired temperature, as will appear more clearly hereinafter. At these conditions, the conversion of steam to carbon monoxide and hydrogen amounts to about 80 to 90% of the theoretical as compared with about 30 to 60% when a conventional gasification charge such as high temperature coke is used. The relative amounts and the contact time of coke and steam supplied to generator (42) are so controlled that about 80 to 90% of the steam is converted to H_2 and CO and about 80 to 90% of the coke is efficiently utilized in the combined heat and water gas generation.

A gas consisting mainly of carbon monoxide and hydrogen is taken overhead from generator (42) and freed in gas-solids separator (46) from entrained fines which may be returned through pipe (48) to the dense phase (44). The gas leaves separator (46) through line (49) and passes through steam preheater (50) in heat exchange with steam admitted through line (51), to a cooling system (52) from which it may be withdrawn for any desired use as a fuel gas, for hydrocarbon synthesis, and others. Tower (52) may also be a scrubber for removal of any traces of suspended solids not separated in (46). The steam preheated in (50) passes through line (40) to dispersing pipe (38), as outlined above.

Solid carbonaceous gasification residue is withdrawn through vertical pipe (53) from a point above grid (43) and passed through control valve (55) to dispersing pipe (56) where it taken up by hot air, oxygen, or other oxidizing gas supplied through line (57), as will appear more clearly blow. The mixture of solid gasification residue and oxidizing gas passes at about the temperature of the gasification zone through line (59) to the conical lower portion of the cylindrical combustion chamber (60) which has a construction similar to that of chambers (26) and (42) and serves as a heater for zones (26) and (42). The solids-gas mixture enters the cylindrical portion of heater (60) through a distributing grid (61) and forms thereabove a fluidized dense ebullient phase (62) having a well defined upper level (63). The temperature of zone (62) is maintained between 1700° and 2000° F. preferably at about 1800° to 1900° F. Solid combustion residue consisting essentially of coal ash is returned from a point above grid (61) at about the temperature of the combustion zone (62) through vertical pipe (65) provided with control valve (67) to the lower portion of carbonization chamber (26) in amounts sufficient to supply the heat required for carbonization. This amount may vary between about 100% and 200% by weight of the solids charged through line (20), depending on the temperature difference between combustion zone (62) and carbonization zone (28), good results being, in general, obtained at a solid recycle ratio of about 100% to 150%. A fluidizing gas may be supplied by compressor (24) through line (68) to facilitate the transport of the solid through line (65).

Another considerably larger amount of solid combustion residue is withdrawn from above grid (61) through vertical pipe (69) provided with control valve (71) to be returned through line (39) to gas generator (42) to supply the heat required in gasification zone (44). In accordance with the considerably higher temperature and the normally larger dimensions of gas generator (42), the amount of solids recycled to (42) is a high multiple of that recycled to carbonization chamber (26) and may vary between the approximate limits of 30 to 300 times the carbon content of the solids charged through line (36) or may be about 20 to 100 times the amounts of solids returned through line (65).

Flue gases are withdrawn overhead from heater (60) through gas-solids separator (72) where they are freed from solid fines. The fines may be returned through vertical pipe (73) to the dense phase (62) or withdrawn from the system. Hot flue gas substantially free of solids is passed through line (75) to air preheater (76) where it preheats the air supplied by compressor (78) through line (79). The preheated air passes through line (57) into dispersing pipe (56) as shown above. Flue gas, if desired after further dust removal in (80) may then be applied to any desired use, such as the operation of a flue gas turbine (82), for heat recovery, or discarded.

The superficial gas velocity in reactors (26), (42) and (60) are those commonly used for the fluidization of dense beds of solids of the particle size indicated and may range from about 0.3 to 10 ft. per second, preferably between about 0.5 to 3 ft. per second. The pressure of the system may be essentially atmospheric but is preferably kept within the approximate limits of 40 to 200 lbs. per sq. in gauge to save compression on the gas manufactured. Higher pressures may be used as feasibility and economy of construction techniques allow, particularly if water gas of high B.Th.U. value is desired. Our invention is particularly well adapted to high pressure operation since high steam conversion can be obtained at reasonable temperature even at the highest pressures desirable for gasification.

Means may be provided to withdraw ash from suitable points of the system in any manner known *per se*, for instance from pipes (65) and/or (69) in order to avoid a build up of ash in the system. If desired, an oxidizing gas such as air and/or oxygen may be supplied to chambers (26) and/or (42) to generate heat by combustion therein, in order to supplement the heat supplied from heater (60). Other modifications of the invention will appear to those skilled in the art.

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

EXAMPLE.

The superiority of the process of the invention over the gasification of a conventional gasification charge is illustrated by the data given below which summarize the essential conditions of water gas manufacture in a system of the type specifically described above and illustrated in the drawing, using conventional gasification feed on the one hand and gasification feed of the invention on the other hand.

RAW COAL INSPECTION.

Ash %	8.0
Volatile Matter %	37.5
Fixed Carbon %	54.5
B.Th.U.	13,710
Fusion Temperature °F.	2,150

	Conventional Gasification Feed	Present Gasification Feed
Carbonization Temperature °F.	1700	900
Coke Reactivity		
T_{15}, °C.	415	205
T_{75}, °C.	495	250
Gasification Temperature °F.	1800	1800
Gasification Pressure, lbs. per sq. in. gauge	45	45
Fluid Bed Height, Ft.	32	32
Fluid Bed Density, lbs./CF.	20	20
Inlet Steam Velocity. Ft./Sec.	0.5	0.5
Carbon Concentration, Wt. % of Solids	20	20
Steam Conversion, Wt. %	50	90

The above data demonstrate that steam conversion may be almost doubled when operating in accordance with the present invention under otherwise equal conditions.

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 the invention.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for producing gas mixtures containing carbon monoxide and hydrogen from solid carbonaceous materials and steam by passing steam into a gasification zone containing a mass of finely divided solid carbonaceous material having an oxidation reactivity as hereinbefore defined of $T_{15} = 200—250°$ C., and $T_{75} = 250—300°$ C., under such conditions to form a dense fluidized mass of finely divided solid, removing the residual solid from the said gasification zone, subjecting the same to treatment in the form of a fluidized ebullient mass with an oxidizing gas mixture to burn off the residual carbonaceous material and thereby heat the residual solid to a high temperature, and recycling

the said heated solid to the gasification zone to use the sensible heat of the said heated solid to supply at least part of the heat required in the said gasification zone.

2. A process as claimed in Claim 1, wherein the solid carbonaceous material is a low temperature carbonization coke, preferably carbonized at temperatures below 1000°F.

3. A process as claimed in Claims 1 and 2, wherein the gasification reaction is carried out at a pressure above 40 pounds per square inch.

Dated this 14th day of February, 1947.
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Agents for the Applicant.

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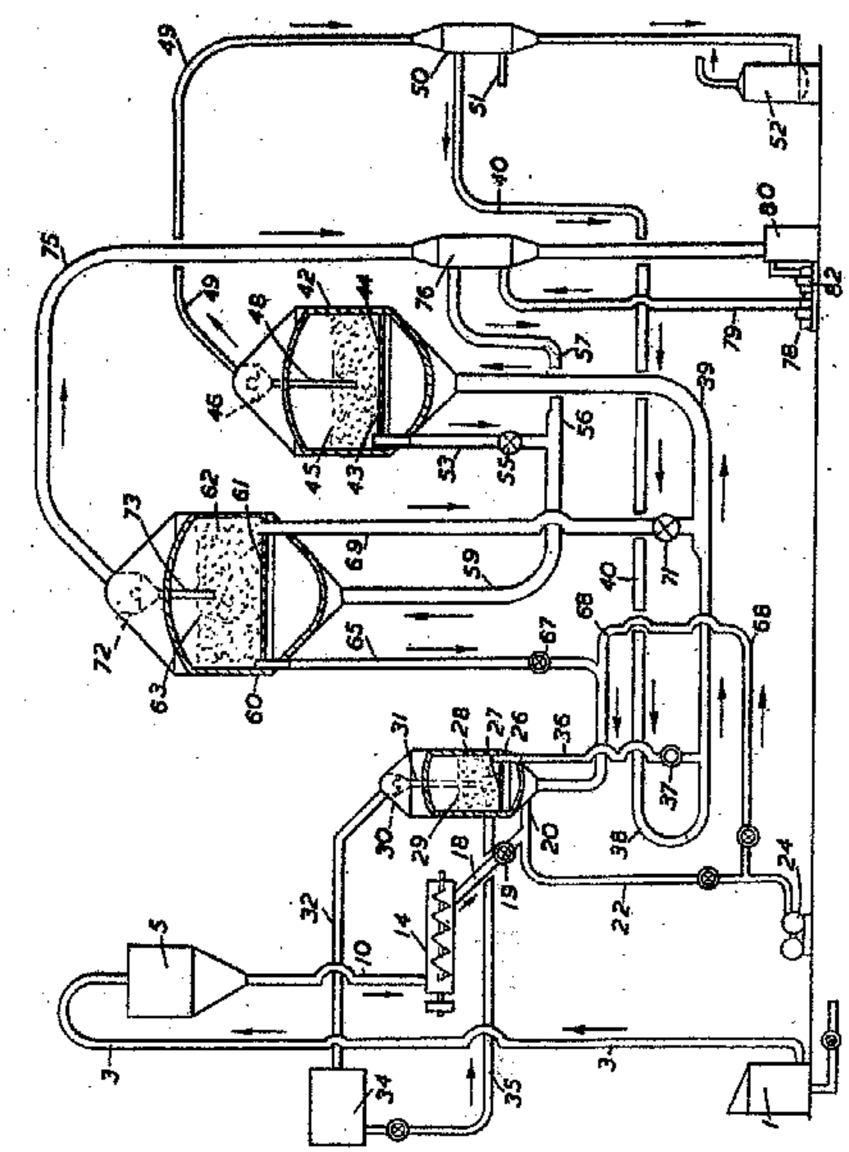

H.M.S.O. (Ty.P.)