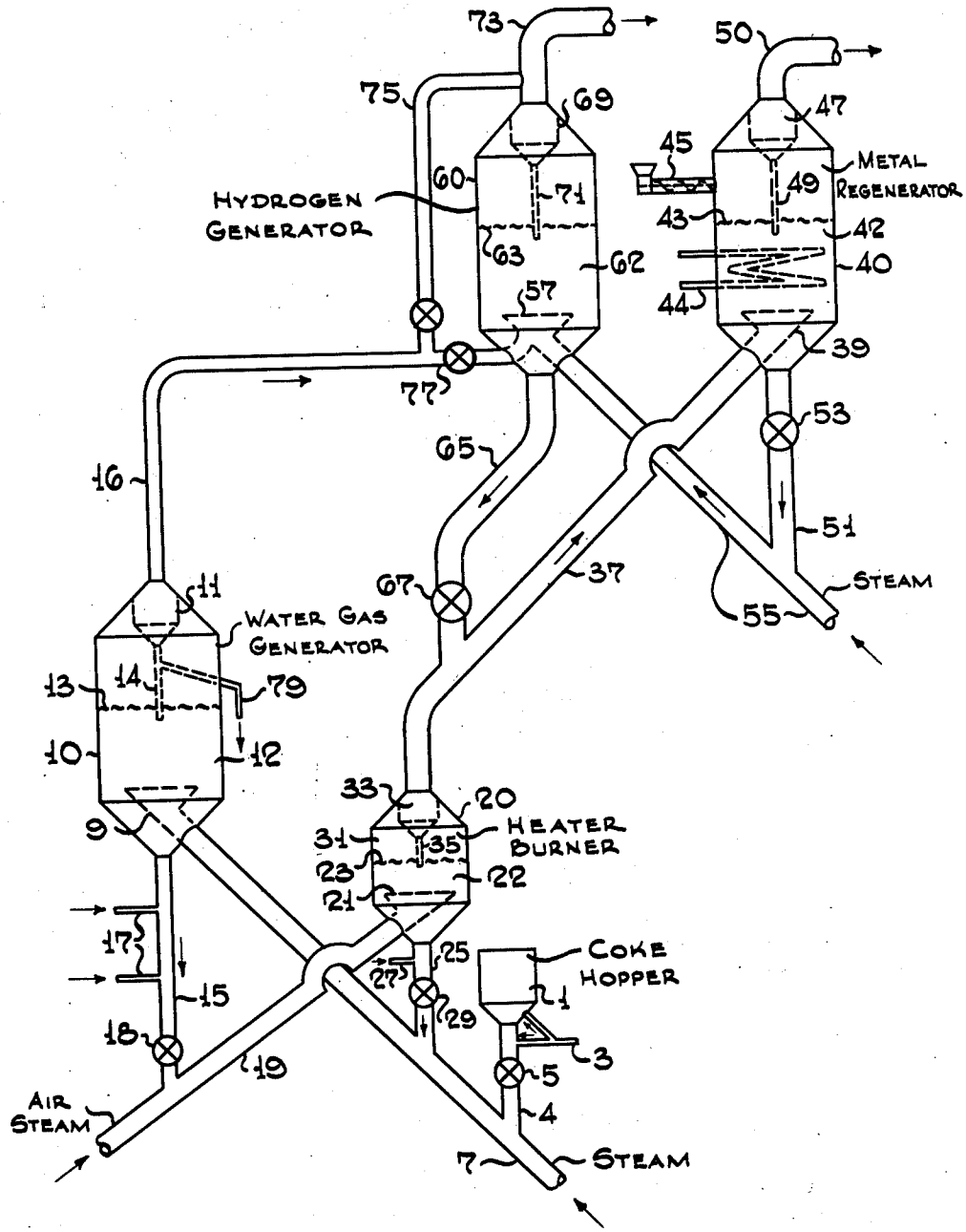
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PRODUCTION OF MIXTURES OF CARBON MONOXIDE AND HYDROGEN

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PRODUCTION OF MIXTURES OF CARBON MONOXIDE AND HYDROGEN

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The present invention relates to the production of combustible gases from solid carbonaceous materials. More particularly, the invention is concerned with the conversion of solid carbonaceous materials such as coal, coke from coal or petroleum, peat, tar sands, oil shale, cellulosic materials, etc., into gas mixtures useful in the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen.

The use of solid fuels such as coal, coke, oil shale, or the like as plentiful and inexpensive starting materials for the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen has been the object of extensive research work in recent years. The ultimate aim of these studies is a process which permits the continuous and substantially complete conversion of the carbon available in the solid starting material into suitable mixtures of carbon monoxide and hydrogen and heat required by this conversion. All prior art processes of which I am aware have fallen short of accomplishing this result. The conventional water-gas processes provide for a conversion of solid fuels with steam into so-called "blue water gas" by blowing steam and air and/or oxygen simultaneously or alternately through a fixed bed of the solid starting material. These processes require frequent cleaning periods resulting in discontinuous operation or they involve incomplete conversion of the available carbon into water gas and heat. The operation may be made fully continuous by employing the so-called fluid solids technique in which the reactions take place in a dense fluidized bed of finely divided solids maintained in a turbulent ebullient state by means of fluidizing gases. This technique has highly desirable additional advantages such as greatly improved heat distribution and ease of solids handling.

In accordance with a more recent development of the latter technique the heat required by the gasification reaction is supplied in the form of sensible heat of solid combustion residues circulated to the heat-consuming reaction from a zone wherein solid carbonaceous material such as solid carbonaceous gasification residue is subjected to combustion. In this manner, the gasification zone and product may be kept entirely free of combustion products and diluting gases such as nitrogen. However, aside from the fact that large quantities of heat are wasted as sensible heat of the volatile products of gasification and combustion this process yields hydrogen and carbon monoxide in the substantially fixed ratio of about 1 to 1.3 moles of hydrogen per 1 mole of carbon monoxide while the synthesis of hydrocarbons usually requires a feed gas having a considerably greater hydrogen content of about 2 or more moles of hydrogen per mole of carbon monoxide. Therefore, it has been necessary heretofore to enrich the water gas obtained from solid fuels with hydrogen produced in a separate and

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thermally independent process, either electrolytically or by the reduction of steam or by other means adding considerably to the investment and operating cost of synthesis gas manufacture.

The present invention overcomes the aforementioned drawbacks 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 drawing which gives a semi-diagrammatic view of a system particularly adapted to carry out the invention.

It is an important object of my invention to provide an improved process for the conversion of finely divided solid carbonaceous materials into combustible gases.

Another object of my invention is to provide a process for continuously converting finely divided solid carbonaceous materials into combustible gases comprising mixtures of carbon monoxide and hydrogen of suitable composition for the catalytic synthesis of hydrocarbons.

Other objects and advantages of my invention will appear hereinafter.

I have found that mixtures of hydrogen and carbon monoxide containing more than about one mole of hydrogen per mole of carbon monoxide may be produced from solid carbonaceous materials in an economical manner when heat and reducing gases generated in the manufacture of "blue water gas" are utilized for the production of make-up hydrogen by the reduction of steam. In accordance with my invention carbonaceous solids are reacted with steam to form "blue water gas," heat required for this endothermic reaction being generated by the combustion of carbonaceous solids in a separate heating zone operated to produce substantial amounts of carbon monoxide which is used in the reduction of steam to produce make-up hydrogen. For the latter purpose, I prefer to contact steam with a reducing metal such as iron or alloys thereof with activity-controlling metals such as manganese, tungsten, or the like to form hydrogen and metal oxide and to regenerate the metal by reducing the metal oxide with the carbon monoxide produced in the heating zone of the water gas manufacture.

By employing the fluid solids technique my process may be operated in a fully continuous manner and all the heat required for the endothermic water gas and hydrogen producing stages may be generated in and recovered from other stages of the process. More specifically, I prefer to use both the carbonaceous solids and the reducing metal in the form of dense fluidized beds of finely divided solids maintained in water gas and hydrogen generation zones, respectively, to supply the heat to the wate gas generation as sensible heat of solid combustion residue from a separate fluid solids burner producing carbon monoxide, and to supply at least a

portion of the heat required for the hydrogen generation as sensible heat of reducing metal withdrawn from a separate heat-generating fluidized regeneration zone wherein the metal oxide formed in the hydrogen generation zone is reduced by means of the carbon monoxide produced in the burner. Additional heat may be supplied to the hydrogen producing system as sensible heat of the carbon monoxide produced at high temperatures in the burner and as sensible heat of the water gas produced in the water gas generation zone. The rate of hydrogen production may be controlled by controlling the rate of addition of reducing metal and steam to the hydrogen generation zone. In this manner, all heat generated in the process and available in the various streams of gases and solids is fully utilized for the purposes of my process, the only materials to be rejected from the process being the products of complete combustion, that is, completely burned flue gas withdrawn from the metal regeneration zone and ash which may be withdrawn from any suitable portion of the water gas producing section of the system.

The conditions of temperature and pressure may vary within wide limits depending on the character of the carbonaceous solids used, the type of reducing metal employed and the composition of the product gas desired. In general, the water gas generation zone may be maintained at a temperature of about 1400°–2400° F., preferably about 1600°–1800° F. at burner temperatures of about 1600°–2500° F., preferably about 1800°–1900° F. for an air-fuel ratio appreciably less than that required for complete combustion of the available carbon. The temperature of the hydrogen generation and metal regeneration zones may fall within the approximate ranges of about 600°–1200° F., preferably 700°–1100° F., and about 1200°–1700° F., preferably about 1300°–1500° F. respectively. Pressures ranging from subatmospheric to about 200 lbs./sq. in. may be applied in any or all of the treating zones. However, the pressure is preferably so adjusted that the final product gas leaves the system at the pressure at which it is used in the hydrocarbon synthesis.

Having set forth the 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 a preferred embodiment of the invention.

The system shown in the drawing essentially comprises a water gas generator **10**, a heater burner **20**, a hydrogen generator **60** and a metal regenerator **40**. The function and manner of cooperation of these elements will be presently explained using coke as an example for a suitable initial carbonaceous solid and iron as an exmple for a reducing metal. It should be understood, however, that other carbonaceous starting materials and reducing metals may be used in an analogous manner.

Referring now in detail to the drawing, coke ground by any conventional means (not shown) to a fluidizable particle size, for example of the order of 50% having a size of less than 100 mesh, although small lumps of up to ¼ or ½ inch size may be used, is fed in any manner known per se to feed hopper **1**. An aerating gas, such as flue gas, steam or the like, may be supplied through line **3** to maintain the coke in hopper **1** in the form of a dense fluidized mass flowing like a liquid through ducts and valves. The fluidized coke flows through pipe **4** carrying control valve **5**, into pipe **7**. The flow of solids through pipe **4** may be further facilitated by the addition of aerating gas from line **3** as indicated. In line **7**, the coke is picked up by a stream of steam to form a suspension of lower density which is passed under the pseudo-hydrostatic pressure of column **4** to the lower portion of water gas generator **10** which it enters through a perforated distribution device **9**. The water gas generator is maintained at a temperature of about 1600°–1800° F. and a pressure of preferably about 30 lbs./sq. in. to permit the water gas reaction to take place between the steam and the coke. The superficial velocity of the steam is so controlled that the coke forms a dense turbulent mass **12** fluidized by the steam and the water gas formed and having a well defined upper level **13**. Superficial gas velocities of about 0.3–5 ft. per second are generally adequate for this purpose. The amount of steam supplied per pound of coke is preferably less than that required to convert the entire amount of carbon available into water gas and the contact time is preferably so controlled that about 5–30% of carbon remains unconverted. The heat required for the water gas reaction is supplied by highly heated solid combustion residue recirculated from heater-burner **20** as will appear more clearly hereinafter. "Blue water gas" consisting substantially of hydrogen and carbon monoxide in the approximate volumetric ratio of about 5:4 is withdrawn overhead from the dense phase **12**, through a conventional gas-solids separator **11** of the electrical and/or centrifugal type, provided with a solids return pipe **14** and from here through lines **16**, **75** and **73** to any desired further treatment.

Fluidized solid carbonaceous gasification residue is withdrawn downwardly from zone **12** through vertical pipe **15** aerated through lines **17**, and passed through control valve **18** into line **19** where it is picked up by an oxidizing gas such as air and/or oxygen to form a suspension of low density which is passed under the pseudo-hydrostatic pressure of standpipe **15** and substantially at the temperature of gasification zone **12** to the lower portion of heater-burner **20** which it enters through a distributing device **21**. The oxidizing gas supplied to line **19** may be preheated to temperatures of about 1200°–1500° F., particularly during the starting period. The air-fuel ratio is preferably so controlled that about 3 to 30 cu. ft. of oxygen is supplied per pound of carbon burned to yield by partial combustion a producer gas containing about 25–35% of carbon monoxide and about 3–10% of carbon dioxide at a heater temperature of about 1800°–1900° F. and a pressure of about 30 lbs./sq. in. If desired, steam, say up to about 20%, may be added to the oxidizing gas, in which case the producer gas will contain about 10–15% of hydrogen in addition to the carbon monoxide. The superficial velocity of the gas flowing upwardly through heater-burner **20** is maintained between about 0.3 and 10 ft. per second, preferably in the neighborhood of about 1.5 ft. per second to establish a dense fluidized solids phase **22** having an upper level **23**, similar to dense phase **12** in generator **10**. Fluidized solid combustion residue passes downwardly from zone **22** through pipe **25** aerated through line **27** and provided with control valve **29** to enter pipe **7** and to form therein a dilute suspension in steam, which is passed under the pseudo-hydrostatic pressure of standpipe **25** and substantially at the tem-

perature of zone 22 to water gas generator 10 to supply the heat required therein. The amount of solids circulating between heater-burner 20 and water-gas generator 10 in either direction may vary between the approximate limits of 30 to 300 times the carbon content of the fresh carbonaceous feed depending on the temperature difference between phases 22 and 12 and is preferably so controlled that levels 13 and 23 are maintained substantially constant.

Producer gas of the composition mentioned above passes upwardly from zone 22 through the free space 31 above level 23 wherein a substantial portion of entrained solids drops out, and then, if desired, through a conventional gas-solids separator 33 from which separated solids fines may be returned to dense phase 22 through line 35. Producer gas substantially free of solids passes through line 37 where it picks up finely divided oxidized iron of the approximate average composition of Fe_3O_4 withdrawn from hydrogen generator 60 through line 65 as will appear more clearly hereinafter, and the dilute suspension formed enters the lower section of metal regenerator 40 through a distributing device 39, to form in regenerator 40 a dense fluidized solids phase 42 having an upper level 43, similar to phases 12 and 22. The temperature of dense phase 42 is maintained at about 1300°–1600° F. to cause substantial reduction of the iron oxide by the producer gas to metallic iron. Since this reaction is exothermic it may be desirable to withdraw heat by any conventional means such as a cooling coil 44. The particle size of the iron oxide which may be supplied to regenerator 40 by any means known per se such as screw conveyor 45 before starting up the process, is preferably somewhat smaller than that of the carbonaceous feed and may fall within the approximate range of 150–300 mesh to establish proper fluidization at gas flow conditions similar to those outlined in connection with chambers 10 and 20. Flue gas practically free of combustible constituents is withdrawn overhead from dense phase 42, passed through a conventional gas-solids separator 47 provided with solids return line 49, and leaves the system through line 50 either to be vented or to be used for preheating and/or aeration purposes in the system.

Solid fluidized reduced iron passes downwardly from dense phase 42 through standpipe 51 provided with control valve 53 and enters line 55 where it is suspended in steam and passed to the lower section of hydrogen generator 60 through a distributing device 57. The conditions of gas and solids flow to hydrogen generator 60 are so controlled that a dense fluidized solids phase 62 having an upper level 63 is formed therein and kept at a steam reducing temperature of about 750°–1100° F. to form the desired amount of hydrogen. Heat required for this reaction may be supplied as sensible heat of the reduced metal from the high temperature zone 42. In general, solid circulation rates of about 0.1 to 5 lbs. of reduced metal per cu. ft. of steam depending on the temperature difference between phases 42 and 62 are suitable for this purpose. Solid fluidized oxidized iron is withdrawn downwardly from zone 62 through pipe 65 carrying control valve 67 and passed into line 37 and regenerator 40 as outlined above.

Hydrogen which may contain some unconverted steam passes overhead from zone 62, is freed of entrained solids in conventional separator 69 provided with solids return pipe 71, and is withdrawn through line 73 wherein it may be mixed with "blue water gas" supplied from water gas generator 10 by way of lines 16 and 75, to establish the desired ratio of hydrogen and carbon monoxide in the final synthesis gas mixture.

The embodiment of my invention illustrated by the drawing permits of numerous modifications. For example, heat may be supplied to generator 10 by a partial combustion of carbonaceous material within generator 10 by the direct supply of relatively small amounts of an oxidizing gas in such a manner as to maintain overall reducing conditions in generator 10. The conditions of temperature, steam and oxygen supply in generator 10 may also be so controlled as to produce predominantly carbon monoxide. Hydrogen-containing solid fines may be used in place of coke, or hydrogen-containing solid, liquid and/or gaseous fuels may be introduced into heater-burner 20 to enrich the producer gas with hydrogen, if desired. Part or all of the water-gas produced in generator 10 may be introduced through line 77 into the hydrogen generator 60 to reduce iron circulation and to supply additional heat as sensible heat of the water-gas and/or heat of the reaction between its components and metal oxide formed in zone 62. Instead of feeding solids to the bottom of chambers 10, 20, 40 and 60 by means of a carrier gas any other conventional means of conveying fluidized solids such as pressurized feed hoppers, mechanical conveyors, etc. may be used. Means for the removal of ash may be provided at any suitable point of the solids cycle of the water-gas producing system. For instance, separator 11 may be operated in stages so that light ash may be rejected through line 79. It will be understood that the operation of the entire system may be made fully continuous by continuously feeding solid and gaseous starting materials, maintaining a continuous solids circulation and withdrawing continuously water-gas, hydrogen, flue gas and ash from the system. Other modifications and variations within the scope of my invention will appear to those skilled in the art.

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

EXAMPLE

The following conditions of my process have been found useful for manufacturing 100,000 C. F./hr. of gas containing two moles of hydrogen per mole of carbon monoxide.

Operation of water gas generator and heater burner

	Water Gas Generator	Heater Burner
Operating Conditions:		
Feed	Coke Containing 90% Carbon–10% Ash.	
Temperature, ° F	1,800	1,940
Pressure, p. s. i. g	200	200
Carbon Reacting, #/hr	1,113	640
Steam Used, #/hr	1,690	475
#Carbon Circulated/# Carbon Reacted	100	
Air, #/hr		4,315
Gas Produced, C. F./hr. (@ S. C.)	67,500	82,000
Gas Composition Leaving Vessel:		
CO	49+	33
CO_2	<2	1
H_2	49+	12
O_2	Nil	<1
N_2	Nil	54

Operation of hydrogen generator and metal regenerator

	Hydrogen Generator	Metal Regenerator
Operating Conditions:		
Temperature, °F.	800	1,350
Pressure, p. s. i. g.	190	190
# Fe Reacting/hr.	3,864	
# Fe_3O_4 to Reduce/hr.		5,330
Steam Added, #/hr.	1,650	
Gas Leaving Vessel, C. F./hr.	100,000	82,000
Gas Composition Leaving Vessel:		
CO	33	Nil
H_2	66	Nil
CO_2	<1	34
H_2O		12
N_2		54
O_2		<1

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

I claim:

1. The continuous process of producing mixtures of hydrogen and carbon monoxide serving as feed gas to a hydrocarbon synthesis process and containing controlled molecular proportions of hydrogen from solid carbonaceous materials and steam which comprises continuously feeding fresh finely divided carbonaceous solids to a heated water gas generation zone, subjecting said finely divided solid carbonaceous material, in the form of a dense, turbulent bed of solids fluidized by an upwardly flowing gas and resembling a boiling liquid having a well defined upper level, to a water gas reaction with steam in said zone to produce a hot stream of water gas, continuously circulating solid carbonaceous residue of the water gas reaction to a heating zone and subjecting it therein in the form of a similarly fluidized bed of solids to incomplete combustion with air and steam to produce a hot combustible gas containing about 25% to 35% of carbon monoxide and about 10% to 15% hydrogen, continuously supplying a part of the heat generated by said combustion to said water gas reaction in the form of sensible heat of solid combustion residue returned from said heating zone to said water gas generation zone, continuously subjecting steam to a reducing treatment at a steam reducing temperature with a finely divided reduced metal oxide maintained in a similarly fluidized bed of solids to form hydrogen and finely divided metal oxide, continuously regenerating said reduced metal oxide in a separate regeneration zone by reducing said metal oxide in a similarly fluidized bed of solids heated to a temperature higher than said steam reducing temperature by said hot combustible gas and reduced thereby producing a completely burned vent gas substantially free of carbon monoxide, continuously supplying to said steam reducing treatment at least a part of said hot water gas together with reduced metal oxide from said regenerating zone substantially at said higher temperature, controlling the molecular ratio of hydrogen to carbon monoxide in the gas from said steam reducing treatment by controlling the amounts of hot water gas and steam fed thereto together with said reduced metal oxide, mixing said gas with any remaining water gas by-passing the steam reducing treatment, and recovering the hydrogen enriched mixture.

2. The process as claimed in claim 1 in which said metal is iron and said metal oxide approximates the composition Fe_3O_4.

3. The process as claimed in claim 1 in which a small amount of steam is added to said oxidizing gas.

4. The continuous process of producing mixtures of hydrogen and carbon monoxide serving as feed gas to a hydrocarbon synthesis process and containing more than equimolecular proportions of hydrogen from solid carbonaceous materials and steam which comprises continuously feeding fresh finely divided carbonaceous solids to a heated water gas generation zone, subjecting said finely divided solid carbonaceous material, in the form of a dense turbulent bed of solids fluidized by an upwardly flowing gas and resembling a boiling liquid having a well defined upper level, to a water gas reaction with steam in said zone to produce a hot stream of water gas, continuously circulating solid carbonaceous residue of the water gas reaction to a heating zone and subjecting it therein in the form of a similarly fluidized bed of solids to incomplete combustion with air and steam to produce a hot combustible gas containing about 25% to 35% of carbon monoxide and about 10% to 15% of hydrogen, continuously supplying a part of the heat generated by said combustion to said water gas reaction in the form of sensible heat of solid combustion residue returned from said heating zone to said water gas generation zone, continuously subjecting steam to a reducing treatment at a steam reducing temperature with a finely divided reduced metal oxide maintained in a similarly fluidized bed of solids to form hydrogen and finely divided metal oxide, continuously regenerating said reduced metal oxide in a separate regeneration zone by reducing said metal oxide in a similarly fluidized bed of solids heated to a temperature higher than said steam reducing temperature by said hot combustible gas and reduced thereby producing a completely burned vent gas substantially free of carbon monoxide, continuously supplying hot reduced metal oxide from said regenerating zone to said steam reducing treatment substantially at said higher temperature, passing at least a portion of said hot water gas into said hydrogen generation zone to supply additional heat for said steam-reducing treatment, mixing said water gas and said hydrogen, and recovering the hydrogen-enriched mixture.

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