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PROCESS FOR ENRICHMENT OF WATER GAS

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2 Sheets-Sheet 1

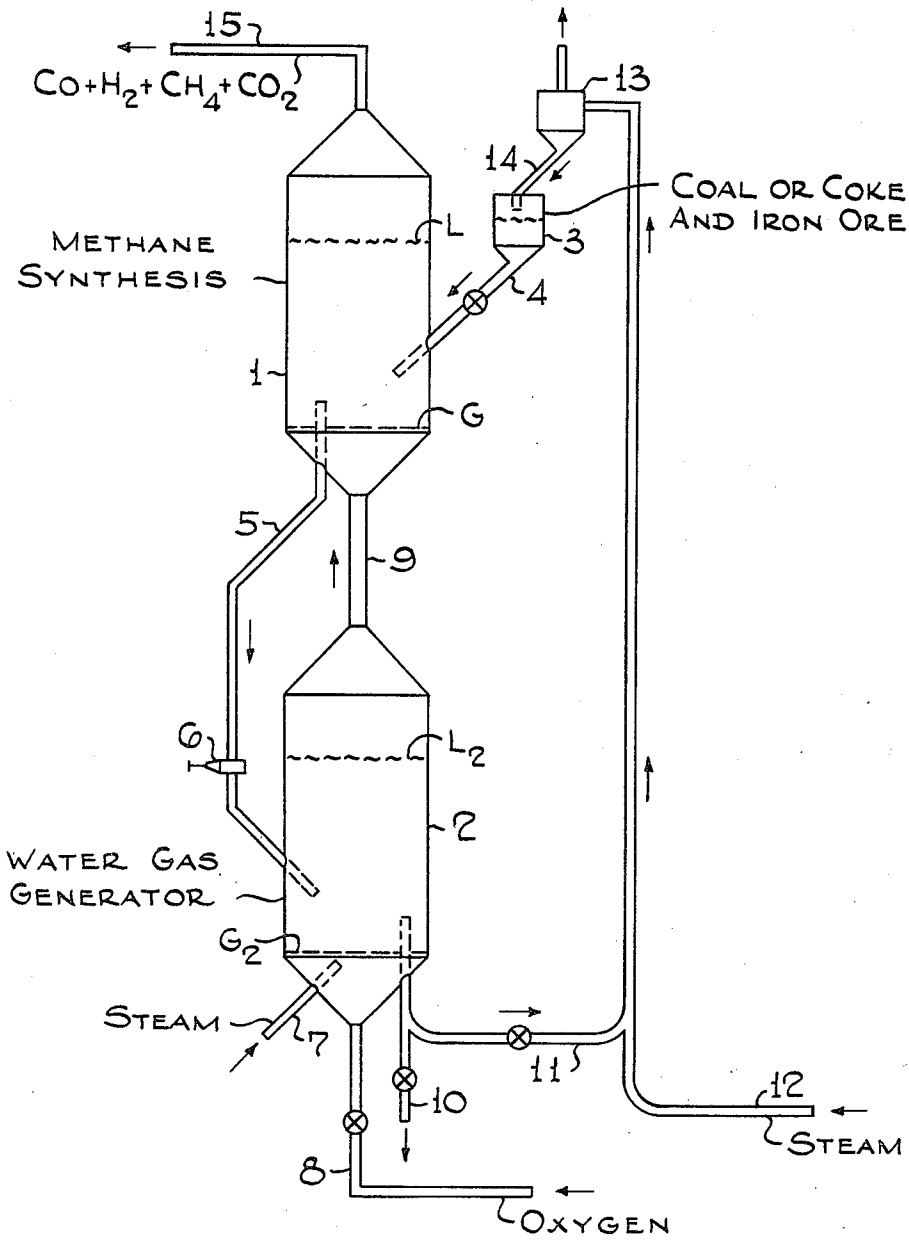


FIG.-1

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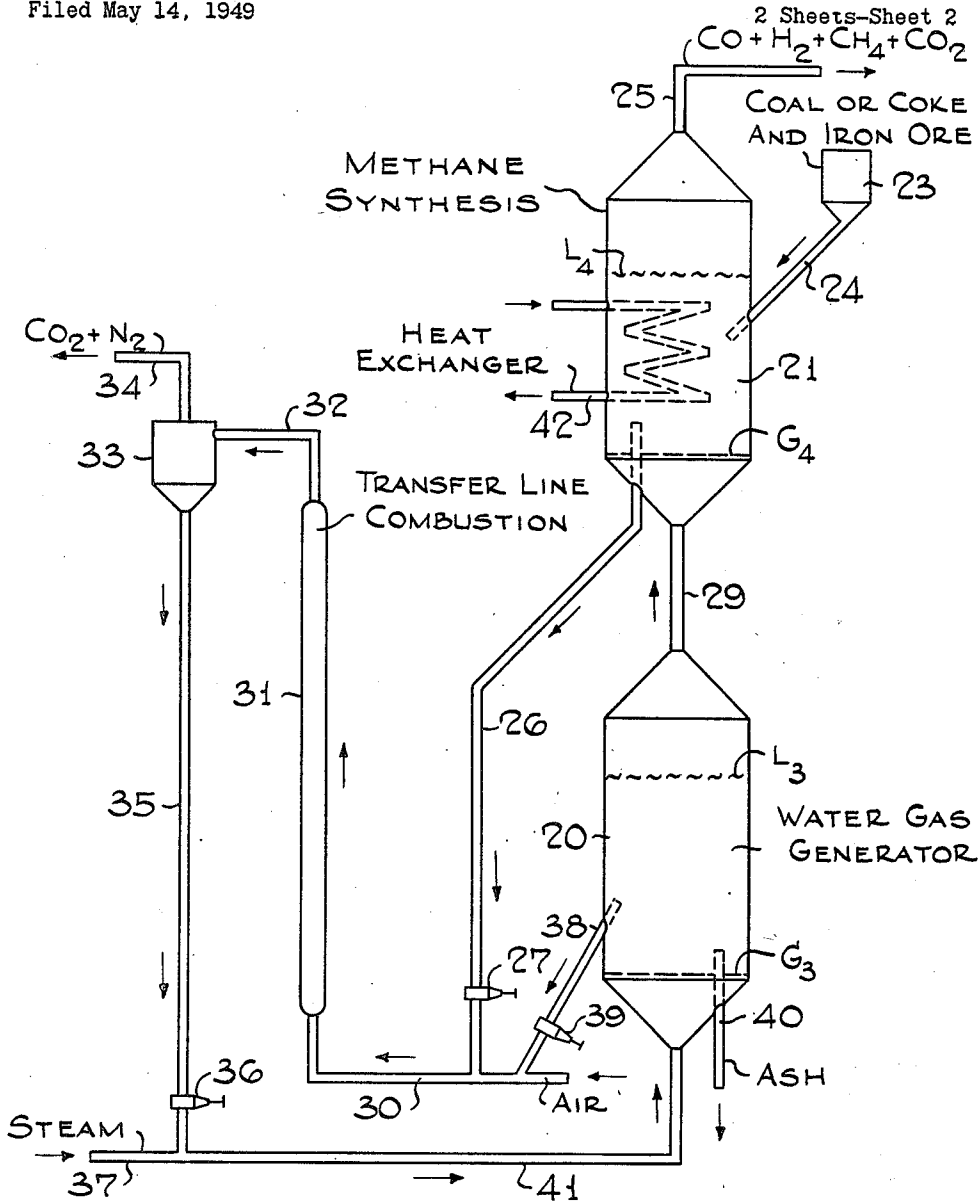


FIG. - 2

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PROCESS FOR ENRICHMENT OF WATER GAS

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Application May 14, 1949, Serial No. 93,208

17 Claims. (Cl. 48—197)

The present invention relates to improvements in the art of converting coal or coke to a city gas containing formed methane and, therefore, of improved heating value.

Prior to this invention it was known that carbonaceous material such as coal, when subjected to the influence of steam at high temperatures, was adapted to generate volatile constituents suitable for use as a fuel and which contained not only hydrogen and carbon monoxide but also methane, the methane being present in greater quantity in the fuel than that corresponding simply to the methane produced by destructive distillation of the coal. In other words, at least a portion of the carbon monoxide and hydrogen reacted to form methane. This process has been practiced abroad commercially and is generally referred to as the Lurgi process.

The present invention constitutes an improvement over the older process in several particulars including the employment of the fluidized solids technique, the use of at least two vessels, and the use of a catalyst to promote the hydrogenation of the oxides of carbon to form methane.

The main object of the present invention, therefore, is to produce a fuel gas of improved heating value in a process which is more economical, more flexible, and in particular, which results in the formation of a fuel gas of increased heating value due to the presence of increased quantities of methane.

Another object of the present invention is to carry out continuously, a treatment of coal or coke in a two-zone process so that the generation of hydrogen and carbon monoxide is carried out in a zone physically separated from a second zone in which methane synthesis occurs. Another object of the present invention is to preheat the fresh charge of carbonaceous material in the methane synthesis zone thus obviating the necessity of preheating coal or coke outside of the said reaction zones.

Other and further objects of the invention will appear in the following more detailed description and claims.

Before proceeding with a detailed description of the process and the preferred embodiment thereof, it should be pointed out that heretofore it has been demonstrated that water gas can be generated from coal or coke by contacting it with steam while the said coal or coke is in the form of a fluidized mass. The gas thus produced, however, has a relatively low B. t. u. value, generally of the order of about 300 B. t. u. per cubic foot. Such gas is suitable as a hydrocarbon synthesis feed gas, but is of too low quality for use as a city gas since the latter requires a higher B. t. u. value.

It has previously been found that the heating value of the water gas thus produced can be increased by contacting the hot gas as it issues from the water gas generating zone with incoming coal or coke in a second zone, whereby methane is synthesized by contact of the carbon monoxide and hydrogen in the water gas with the coal or coke. In such an operation the incoming coal or coke feed contacts the water gas in an initial syn-

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thesis zone in which the coal or coke is formed into a fluidized mass. The solid carbonaceous feed from the initial zone then gravitates into a secondary zone where it is again procured in fluidized form and wherein the water gas is formed by contact of the carbonaceous material with steam at a temperature of about 1800° F. or any known suitable temperature. In order to support the exothermic reaction occurring in this latter zone, commercially pure oxygen is also fed into the said latter zone causing combustion of a portion of the carbonaceous material and the release of heat. Ash of relatively low carbon content is withdrawn from a lower portion of the water gas generation zone and this may be rejected from the system, or the sensible heat thereof may be utilized in any known manner.

It has now been found that increased yields of methane can be obtained in the product gas by including in the coal or coke fed to the carbonization and methane synthesis zone, relatively small amounts of a catalyst adapted to promote the methane synthesis. The yields of methane obtained by passing a mixture of carbon monoxide and hydrogen into contact with a coke formed by low temperature carbonization (800° to 1000° F.) with and without the inclusion of an iron catalyst have been determined by experiment and the results appear hereinafter. At this point it is simply stated that the concentration of methane in the product gas when a catalyst was present was increased over and above that where no catalyst was used. It also was determined that when a catalyst is employed as indicated, the methane synthesis proceeds at a lower temperature than when a catalyst is not employed.

It is an important feature of this invention to employ cheap catalysts, such as iron ores. Another advantage of the present invention is that one may use an iron hydrocarbon synthesis catalyst which has been rejected from a hydrocarbon synthesis process due to permanent loss of activity since at the higher temperatures prevailing in the methane synthesis zone of the present process, this catalyst will possess sufficient activity.

In the accompanying drawing there is shown, diagrammatically, in Fig. 1 an apparatus layout in which a preferred embodiment of the invention may be carried into effect, and in Fig. 2 a modification thereof.

Referring in detail to Fig. 1, numeral 1 refers to a carbonizing (if coal is present) and methane synthesis zone and 2 represents a water gas generation zone. In operating the process, coal or coke and iron ore, which may be at ordinary atmospheric temperature, is charged from hopper 3 through an aerated line 4 into zone 1, the coal or coke and ore having been previously ground to a particle size ranging within the approximate limits of 40 to 400 microns.

It should be stated at this point that the system about to be described is operated under superatmospheric pressure and some suitable means, such as lock hoppers operating in parallel must be employed in feeding the coal or coke. Thus, hopper 3 may receive the coal or coke charge at atmospheric pressure, undergo pressurization to system pressure (or slightly higher) and thereafter its content of coal or coke may be discharged via 4 into carbonizer 1. As indicated, the feed may be continuous by employing two hoppers such as 3, to operate in parallel. Instead of lock or pressurized hoppers, the coal or coke may be brought up to system pressure by means of a plurality of aerated standpipes operating in series.

As stated, the carbonaceous material is formed into a fluidized mass in zone 1 in the usual manner by controlling the superficial velocity of upflowing gas, which as will subsequently more fully appear, passes from lower vessel 2 to vessel 1. The said gas velocities causing the fluidization of the carbonaceous material are within the

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range of from $\frac{1}{2}$ to 5 feet per second. As usual, the reactor is provided with a gas distributing means G, such as a screen or grid, in order to provide for good distribution of the gas entering the zone. Then depending on the superficial gas velocities, (superficial velocity signifies the calculated velocity at the vessel inlet, assuming no solids in said vessel) and the amount of carbonaceous material in the said zone, the bed will have an upper dense phase level at L and above L there will be a dilute phase suspension of solids in gas. Although not actually shown in the drawing, it will be understood by those who are familiar with this technique that it is customary to dispose one or more solids separating devices (e. g. centrifugal separators) in the upper portion of the vessel in order to separate from the issuing gases, entrained solids, which are returned to the fluidized bed by suitable pipes. The product gas eventually issues from reactor 1 through line 15 and CO₂ removed therefrom as by scrubbing with an aqueous alkali solution.

Carbonized solids are withdrawn continuously from zone 1 through an aerated line 5 controlled by valve 6 and charged to zone 2, the water gas generation zone. As previously indicated, both steam, which enters the generator through line 7, and oxygen which enters through line 8, are charged into the said generator below a distribution means G₂ and then proceed upwardly at the superficial velocity rates disclosed above in connection with the description of the operation of zone 1. In this zone the steam reacts with the carbonaceous solids to form water gas, or a mixture of hydrogen and carbon monoxide. Meanwhile, the oxygen reacts with carbonaceous material to form oxides of carbon with simultaneous release of heat. This gaseous mixture proceeds from the fluidized mass upwardly through exit pipe 9 and then is discharged into zone 1 where it undergoes reaction as previously indicated. As in the case of vessel 1, the solids in vessel 2 are procured in the fluidized state by controlling the superficial velocity of the upflowing gasiform material and the result will be as in vessel 1, the forming of a dense fluidized mass of solids in gas which, depending on the amount of solids actually present, will have an upper dense phase level at L₂ above which will be a dilute phase. No attempt is made to separate solids from the dilute phase and they are permitted to pass with the gasiform material from vessel 2 into vessel 1. Ash resulting from the treatment in vessel 2 is withdrawn through line 10 and may be rejected from the system. However, it is preferable to recycle to vessel 1 a portion of this ash since it contains iron catalyst. To this end, therefore, the ash is withdrawn via lines 10 and branch line 11, charged in a current of gasiform material such as steam in line 12 and conveyed pneumatically to a separator 13 where it is separated from the steam or other gas, and thence conveyed via line 14 to hopper 3.

In Fig. 2 there is shown a modification of the apparatus illustrated in Fig. 1, the main difference being that in order to supply heat to the water gas generation zone, solids are withdrawn from the synthesis zone and the water gas zone, and burned in the presence of air in a separate combustion zone and thereafter transferred to the water gas generation zone. This, of course, eliminates the necessity for employing pure oxygen.

Referring in greater detail to Fig. 2, 20 represents the water gas generation zone and 21 the methane synthesis and coking zone. In both zones, as in the case of the apparatus depicted in Fig. 1, the solids are maintained in the form of dense fluidized beds having upper dense phase levels at L₃ and L₄, respectively. As before, coal or coke and iron ore is withdrawn from hopper 23 via line 24 and discharged into the methane synthesis zone where, under the influence of heat, the coal (if that is the material) is converted to coke, and simultaneously, carbon monoxide and hydrogen obtained from water gas generator 20 are at least, in part, converted to methane in the presence of the iron ore also present in the methane synthesis zone. The carbonaceous solids are withdrawn from zones 20 and 21, via lines 26 and 38, respectively, controlled by valves 27 and 39, respectively, and charged into an air stream introduced into the system through line 30 to form therein a suspension which is conducted into a transfer line combustion zone 31 where combustion occurs and, of course, the temperature of the solids is increased.

A transfer line combustor is simply an elongated con-

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duit through which a dilute suspension flows at a rather rapid rate and its function is to cause burning of carbonaceous material to CO₂ predominately, so as to obtain the maximum amount of heat. The fumes are withdrawn from the combustor before there is an opportunity for the CO₂ to be reduced to CO to any substantial degree, and hence, the time element as well as small excess of air are important features of this technique.

Of course, circulation rates between the burner and the water gas set are sufficiently high to support the endothermic reaction therein occurring. The amount of hot solids fed to the water gas generating zone will depend on the degree of steam conversion and the carbonaceous solids residence time. Simple manipulative steps will serve to maintain proper heat supply and temperature conditions so that steam conversions as high as 80% or higher are achieved. Thus, about 75-80 lbs. of hot solids per lb. of steam converted at a solids temperature of about 200° F. higher than that prevailing in the water gas zone, should be delivered to the said water gas zone. These figures apply to a commercial installation and the amounts given are sufficient to support the reaction, for preheat and to offset radiation losses.

The suspension is withdrawn from the combustion zone 31, through line 32 and thence charged into a solids-gas separating device 33 which may be, for example, one or more centrifugal separators wherein the solids are separated from the combustion fumes, thence conveyed via line 35, controlled by valve 36 into a line 37 containing steam to form a suspension of the hot solids in the said steam, which suspension is then conveyed via line 41 into the bottom of water gas generator 20. As previously explained, in connection with the description of Fig. 1, the water gas reaction occurs in 20 and the products pass via line 29 into 21 where at least a portion of the oxides of carbon and hydrogen react to form methane. The product is finally withdrawn from 21, via line 25 and delivered to purification and storage (not shown).

As usual, vessels 20 and 21, respectively, are provided with foraminous members G₃ and G₄, respectively, disposed in the vessels for the purpose of effecting good distribution of the gasiform material passing there-through and into the fluidized beds. And as usual, transfer lines, such as 26 and 35 operating on the stand-pipe principle, are provided with spaced gas taps (not shown) through which fluidizing gas may be introduced for the purpose of effecting smooth flow of the solids in the said standpipes. Attention is directed to the fact that heat exchange cooling coil 42 is shown disposed in the bed of fluidized solids in vessel 21. This provides means for preventing the temperatures therein from reaching too high a value, for the data hereinafter set forth has revealed that the reaction promoting the formation of methane is best performed within a relatively restricted temperature range. This cooling means, although not shown in vessel 1 of Fig. 1, is now disclosed as being desirable in most instances.

Another modification in the invention involves employing a fluidized bed of solids in the combustion vessel in lieu of the transfer line combustion zone 31 shown in Fig. 2. However, it is preferred to use the transfer line combustor since this procedure affords a greater degree of conversion of carbon to carbon dioxide which, of course, means that, as stated, from a given weight of carbonaceous material, a maximum quantity of heat is released. In other words, if a fluidized bed of solids was subjected to combustion in the form of a fluidized bed similar to that shown, say, in vessel 1 of Fig. 1, the combustion would result in the formation of less carbon dioxide and more carbon monoxide, in most instances, than would be the case were a transfer line combustor employed.

Product is recovered overhead through line 25 and before delivering to storage, it is usually treated to remove CO₂. Ash withdrawn from vessel 20, Fig. 2, through line 40, is in part recycled to vessel 21.

As heretofore pointed out, several test runs were made in order to determine the efficiency of the present process and the results of these runs are set forth below in tabular form. In the runs carried out, the coke employed was a commercially available coke produced by low temperature carbonization, that is, carbonizing of bituminous coal at a temperature of the order of 900° F.

Enrichment of water gas with methane

[250 p. s. i. g. pressure, 45% CO + 55% H₂ in Feed (Fixed Bed Unit).]

Catalyst.....	Table I			Table II		Table III
	Coke			Coke + 2.2% Magnetite		Coke + 2.2% Hematite
Run.....	84A	79A	85A	103	102	99
Temperature, ° F.....	1,200	1,500	1,500	1,200	1,500	1,200
Space Vel. v./v./hr. ¹	485	310	465	550	550	550
Prod. Gas Comp., percent:						
CO ₂	1.0	7.8	4.0	20.2	7.2	10.2
CO.....	46.6	37.6	44.0	22.2	37.8	36.8
H ₂	48.5	39.9	43.0	30.0	42.2	36.8
CH ₄	3.6	14.7	9.0	26.7	12.8	16.2
C ₂	0.3			0.7		
Lower heating value ² :						
B. t. u./C. F.:						
Scrubbed for CO ₂ removal.....	324	395	356	509	381	409
Containing CO ₂	321	364	341	406	354	367

¹ Volume of feed gas per hour per volume of bed measured at standard conditions.
² Heat of combustion without condensation of water vapor from product gases.

The foregoing data clearly show that the inclusion of an iron ore in relatively small amounts results in the production in the product gas of increased quantities of methane at the lower temperatures. The data (and the same would be true of fluid operation) show that magnetite is a superior catalyst to hematite but they further show that at 1200° F. hematite results in the production of over four times the quantity of methane in the product as does coke not containing the said hematite. It is evident that the optimum temperature for maximum methane formation using magnetite as the catalyst is lower than for maximum formation with coke alone.

It is evident from the above tabulation that an appreciable increase in the calorific value of the gas can be attained by the removal of carbon dioxide. Consequently, it is preferred to scrub the gas with a solvent such as water or ethanolamine for carbon dioxide removal. Since the gas is generated under pressure, scrubbing can also be conducted under pressure and water is an effective solvent for carbon dioxide under these conditions. When coal is used in place of coke as the feed for the process, additional enrichment of the water gas is obtained by carbonization of the coal with production of coal gas.

It has been observed that the following conditions of operation have been found to give best results. Hence, there is set forth below a tabulation of the preferred range of operating conditions in both the methane synthesis zone and the water gas generation zone. It is to be observed, as previously pointed out, that the system works under superatmospheric pressure. It will also be observed that in the methane synthesis zone for best results which, of course, means maximum production of methane, the temperature range is relatively restricted and critical.

	Methane Synthesis Zone:	Water Gas Generation Zone:
Pressure.....	100-600 p. s. i. g.	100-600 p. s. i. g.
Temperature.....	1,100-1,300° F.	1,500-2,000° F.
Amount of catalyst.....	0.1-5.0%	Not required.
Contact time, Min.....	0.1-2.0	0.1-2.0.
Super. Vel. of Gasiform Material.....	0.5-3.0	0.5-3.0.
Particle Size of Solids.....	40-400 mu.	40-400 mu.
Carbon Concentration.....	60-90%	5-15%.

With respect to the catalyst added with the coal or coke, we prefer to use a cheap material such as an iron ore, for example, magnetite, hematite or siderite. No promoter, such as the alkali metal carbonates used in conventional hydrocarbon synthesis catalysts, is required when operating according to the conditions of the present process. Also no reduction of the catalyst is required prior to its use in the process. While no catalyst is required in the water gas generating zone, the presence of the iron oxide in the carbonaceous material fed to this zone has no deleterious effect on the water gas reaction.

It has been found that high concentrations of steam in the water gas have an adverse effect on the methane

synthesis. Consequently, we prefer to operate at relatively high steam conversion in the water gas generator, for example, above about 80%.

Numerous modifications of the present invention not specifically mentioned herein will occur to those who are familiar with this art without departing from the spirit thereof.

What is claimed is:

1. A continuous process for producing a fuel gas of improved heating value which comprises charging cold, powdered carbonaceous material and finely divided oxidic iron ore catalytic material to an initial methane synthesis zone, maintaining said carbonaceous solids and oxidic iron ore catalytic material in the form of a fluidized mass having a lower, dense phase suspension and an interface separating an upper, dilute phase suspension, contacting the dense fluidized suspension of carbonaceous material and oxidic iron ore catalytic material with gasiform material containing hydrogen and carbon monoxide at temperatures of about 1100°-1300° F. and at pressures of about 100 to 600 lbs. per sq. inch for a period sufficient to convert a substantial amount of hydrogen and carbon monoxide to normally gaseous hydrocarbons including methane, withdrawing a mixture of hot solids comprising carbonaceous material and oxidic iron ore catalytic material from the methane synthesis zone and charging said mixture to a water gas generation zone, maintaining the mixture of solids in said water gas generation zone, in the form of a fluidized mass having a lower, dense phase suspension and an interface separating an upper, dilute phase suspension, charging gasiform material containing steam through said dense phase suspension in said water gas generation zone, maintaining said water gas generation zone at temperatures of about 1500°-2000° F. and at pressures of about 100-600 lbs. per sq. inch for a period sufficient to convert a substantial part of said carbonaceous solids and gasiform reaction material into gasiform material containing carbon monoxide and hydrogen, charging the latter gasiform material directly to the first-named, methane synthesis zone as the aforesaid gasiform contacting material and recovering from said first-named zone a gaseous fuel containing carbon monoxide, hydrogen and methane.

2. The method set forth in claim 1 in which heat necessary to support the endothermic reaction taking place in the water gas generation zone is supplied by charging hot solids to said zone.

3. The method set forth in claim 1 in which solid residue is withdrawn from the water gas generating zone and recycled to the methane synthesis zone.

4. The method set forth in claim 1 in which the carbonaceous material is withdrawn from the methane synthesis zone, partially burned in the presence of air in a separate combustion zone to increase its temperature to at least water gas generating temperatures and thereafter charging the thus heated carbonaceous material to the water gas generation zone.

5. The method set forth in claim 1 in which a cooling fluid is circulated in indirect heat exchange relationship with the material undergoing conversion in the methane synthesis zone.

6. A continuous process for producing a fuel gas of improved heating value which comprises charging cold powdered carbonaceous material and finely divided oxidic iron ore catalytic material to an initial methane synthesis zone, maintaining said carbonaceous solids and oxidic iron ore catalytic material in the form of a fluidized mass having a dense, lower phase suspension and an interface separating a dilute phase suspension, contacting the dense fluidized suspension of carbonaceous material and oxidic iron ore catalytic material with a gas containing hydrogen and carbon monoxide at temperatures of about 1100-1300° F. and at pressures of about 100 to 600 lbs. per sq. inch for a period sufficient to convert a substantial amount of hydrogen and carbon monoxide to normally gaseous hydrocarbons, including methane, withdrawing a mixture of hot solids comprising carbonaceous and oxidic iron ore catalytic material from the methane synthesis zone and charging said mixture to a water gas generation zone, maintaining the mixture of solids in the water gas generation zone in the form of a fluidized mass having a dense lower phase suspension and an interface separating a dilute phase suspension, charging steam and oxygen through said dense phase suspension in said water gas generation zone, maintaining said water gas generation zone at pressures of about 100-600 lbs. per sq. inch and at temperatures of about 1500-2000° F., by the combustion of a portion of the carbonaceous material with the oxygen, maintaining contact between the steam and said dense phase suspension in said water gas generation zone for a period of time sufficient to convert a substantial part of said carbonaceous solids and steam into gasiform material containing carbon monoxide and hydrogen, charging the latter gasiform material directly to the first-named, methane synthesis zone as the aforesaid gasiform contacting material and recovering from said first-named zone a gaseous fuel containing carbon monoxide, hydrogen and methane.

7. A continuous method for producing a fuel gas of improved heating value which comprises charging powdered coke and finely divided oxidic iron ore catalytic material to an initial methane synthesis zone, maintaining the said coke and oxidic iron ore catalytic material in the form of a fluidized bed having a lower dense phase suspension and an interface separating an upper dilute phase suspension in said initial zone, contacting the dense phase suspension with a gas containing hydrogen and carbon monoxide at temperatures of about 1100-1300° F. and at pressures of about 100-600 lbs. per sq. inch for a sufficient period of time to effect at least partial conversion of said hydrogen and carbon monoxide to normally gaseous hydrocarbons including methane, withdrawing a mixture of hot solids comprising coke and oxidic iron ore catalytic material from said methane synthesis zone and charging said mixture to a water gas generating zone, maintaining the mixture of solids in said water gas generation zone in the form of a fluidized bed having a lower, dense phase suspension and an interface separating an upper, dilute phase suspension, charging gasiform material including steam through said dense phase suspension in said water gas generation zone, maintaining said last-named zone at temperatures of about 1500-2000° F. and at pressures of about 100-600 lbs. per sq. inch, maintaining contact between said gasiform material and said dense phase suspension for a sufficient period of time to effect the conversion of substantial quantities of said coke and gasiform material into gasiform product containing carbon monoxide and hydrogen, charging the latter gasiform product directly to said methane synthesis zone as the aforesaid gasiform contacting material, and recovering from said methane synthesis zone a fuel containing carbon monoxide, hydrogen and methane.

8. The method of claim 7 in which the iron oxide is in the form of magnetite.

9. The method set forth in claim 7 in which solid residue is withdrawn from the water gas generating zone and recycled to the methane synthesis zone.

10. The method set forth in claim 7 in which the carbonaceous material is withdrawn from the methane synthesis zone, partially burned in the presence of air in a separate combustion zone to increase its temperature to at least water gas generating temperatures and thereafter charging the thus heated carbonaceous material to the water gas generation zone.

11. The method set forth in claim 7 in which a cooling fluid is circulated in indirect heat exchange relationship

with the material undergoing conversion in the methane synthesis zone.

12. The continuous method of producing a fuel gas of improved heating value which comprises charging powdered coal and finely divided oxidic iron ore catalytic material to an initial methane synthesis zone, maintaining the said powdered coal and oxidic iron ore catalytic material in the form of a fluidized bed having a lower, dense phase suspension and an interface separating an upper dilute phase suspension in said zone, contacting the dense phase suspension with a gas containing hydrogen and carbon monoxide at temperatures of about 1100-1300° F. and at pressures of about 100-600 lbs. per sq. inch for a sufficient period of time to carbonize said coal and to effect at least partial conversion of the hydrogen and carbon monoxide to methane, withdrawing a mixture of hot solids comprising carbonized coal and oxidic iron ore catalytic material from said methane synthesis zone, charging said mixture of solids to a water gas generation zone, maintaining the mixture of solids in said water gas generation zone in the form of a fluidized bed having a lower, dense phase suspension and an interface separating an upper, dilute phase suspension, charging a gasiform material including steam through said dense phase suspension in said water gas generation zone, maintaining said last-named zone at temperatures of about 1500-2000° F. and at pressures of about 100-600 lbs. per sq. inch, maintaining contact between said gasiform material and said dense phase suspension in said water gas generation zone for a sufficient period of time to effect the conversion of substantial quantities of said gasiform material and said carbonized coal into gasiform product containing carbon monoxide and hydrogen, charging the latter gasiform product directly to said methane synthesis zone as the aforesaid gasiform contacting material, and recovering from said methane synthesis zone a fuel containing carbon monoxide, hydrogen and methane.

13. The method set forth in claim 12 in which the iron oxide is in the form of magnetite.

14. The method set forth in claim 12 in which solid residue is withdrawn from the water gas generating zone and recycled to the methane synthesis zone.

15. The method set forth in claim 12 in which the carbonaceous material is withdrawn from the methane synthesis zone, partially burned in the presence of air in a separate combustion zone to increase its temperature to at least water gas generating temperatures and thereafter charging the thus heated carbonaceous material to the water gas generation zone.

16. The method set forth in claim 12 in which a cooling fluid is circulated in indirect heat exchange relationship with the material undergoing conversion in the methane synthesis zone.

17. A continuous method of producing a fuel gas of improved heating value which comprises charging powdered coke and finely divided oxidic iron ore catalytic material to an initial methane synthesis zone, maintaining the said coke and said oxidic iron ore catalytic material in the form of a fluidized bed having a lower, dense phase suspension and an interface separating an upper, dilute phase suspension in said initial zone, contacting the dense phase suspension with a gas containing hydrogen and carbon monoxide at temperatures of about 1100-1300° F. and at pressures of 100-600 lbs. per sq. inch for a sufficient period of time to effect at least partial conversion of said hydrogen and carbon monoxide to normally gaseous hydrocarbons including methane, withdrawing a mixture of hot solids comprising coke and oxidic iron ore catalytic material from said methane synthesis zone and charging said mixture to a water gas generation zone, maintaining the mixture of solids in said water gas generation zone in the form of a fluidized bed having a lower, dense phase suspension and an interface separating an upper, dilute phase suspension, charging gasiform material including steam and oxygen through said dense phase suspension in said water gas generation zone, maintaining said last-named zone at pressures of about 100-600 lbs. per sq. inch and at temperatures of about 1500-2000° F. by the combustion of a portion of the coke with the oxygen, maintaining contact between the steam and the dense phase suspension in said water gas generation zone at said temperatures and pressures for a sufficient period of time to effect conversion of substantial quantities of said coke and steam to gasiform

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product containing carbon monoxide and hydrogen, charging the latter gasiform product directly to said methane synthesis zone as the aforesaid gasiform contacting material, and recovering from said methane synthesis zone a fuel containing carbon monoxide, hydrogen and methane.

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