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COMPLETE SPECIFICATION

An Improved Method of Producing Normally Gaseous Fuels from Carbon-containing Materials

We, 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, and 100, West 10th Street, Wilmington, Delaware, both in the United States of America, 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 art of producing valuable fuels, particularly to improvements in the production of normally gaseous fuels from carbonaceous materials. More specifically, it concerns the manufacture of a fuel gas of high heating value from gas mixtures containing carbon monoxide and hydrogen which are obtained by the gasification of solid carbonaceous materials, such as coal, coke from coal or oil, lignite, peat, tar sands, shale and the like. A particularly advantageous solid carbonaceous material which may be used is the residue from a carbonization process, and preferably a residue from a carbonization process operated according to the so-called "fluidized solids" technique. The invention is of special merit in, and certain of its novel features particularly apply to, combinations with processes for gasifying naturally occurring carbonaceous materials having an appreciable content of material other than carbon. However, in a broader sense, it may be applied to gas mixtures containing substantial proportions of carbon monoxide and hydrogen obtained from any source.

The present invention is particularly intended to fill the need for a process to make high heat-content gas by the most economical means and is particularly adapted to the economies inherent in a continuous process. Further, the invention is particularly adapted to be used at the source of naturally occurring solid carbonaceous materials, at which geographical location it is frequently desirable to convert such materials into a more readily usable fuel gas which may be more easily handled and transported than coal. Thus, the method of this invention can be used to convert low grade coal to a gas which is substantially all methane and which can be more readily transported in gaseous or liquid form.

The production of fuel gases of gross heating values of 500 to 600 B.Th.U./cu.ft. or more from carbonaceous materials such as coal has been carried out heretofore on a large scale. One such method is to distill coal containing a considerable amount of hydrogen in order to make coal gas consisting mainly of high heat-content gaseous hydrocarbons and hydrogen. In this process, part of the hydrogen content of the coal is recovered in by-products, such as ammonia, benzene, toluene, creosote oils, and the like. The major part of the carbon content of the coal is obtained as solid coke. The process is usually carried out in coke ovens by a batch method which does not permit of efficient temperature control and which does not give maximum yields of higher value products.

Another method for manufacturing gas from high carbon-content materials involves contacting the feed material with steam at a high temperature to obtain a product gas containing carbon monoxide and hydrogen. The raw material may be either a high carbon-content coal or coke from coke ovens or petroleum processes. Heat may be supplied by mixing air and/or oxygen with the steam to cause combustion of part of the carbonaceous charge or a batch of carbon-containing material may be blown alternately with air and steam while segregating the products from the different blows. In the latter method heat is stored up in the batch of solid material during the "air" blow and utilized for the "water gas" reaction during the "steam" blow. The product gas from the "air" blow contains principally oxides of carbon, and, if air is used, also some nitrogen. The product gas from the "steam" blow is the so-called "blue-water" gas which contains about 30—40% of carbon monoxide, 40—50% of hydrogen, 3—5% of carbon dioxide and, when using air in the "air" blow, 4—10% of nitrogen.

To increase the heat-content of "blue-water" gas, high boiling liquid hydrocarbons, such as gas oil, are usually injected into the gas generator at a suitable point for thermally cracking these hydrocarbons to principally gaseous products. However, this method is expensive because of the high cost of the gas oil and it usually yields a gas of only about 500 B.Th.U./cu.ft.

It is also known to convert "blue-water" gas into a gas of higher heat content by reacting carbon monoxide with hydrogen to form largely methane in the presence of fixed bed catalysts at about 500°—700° F. This reaction is highly exothermic and must be carried out within a narrow temperature range in order to obtain the optimum yield of methane. This combination of factors leads to difficulties because the heat evolved by the reaction tends to cause undesirable high temperatures in some parts of the fixed bed, which tendency is not effectively counteracted by the known means of heat removal. Furthermore, the equipment required is excessively expensive. Therefore, the process has not been commercially successful on a large scale.

It is the purpose of the present invention to enhance the heating value of combustible gas mixtures containing carbon monoxide and hydrogen by passing such a mixture through a conversion zone containing a highly turbulent, dense, fluidized mass of finely divided hydrogenation catalyst, the choice of catalyst and conversion conditions of temperature, pressure and throughout being adapted to yield a product containing predominantly normally gaseous hydrocarbons.

The above conversion reaction is highly exothermic and heretofore the synthesis feed gas has been admitted to the conversion zone at a temperature substantially below synthesis temperature in order to utilize the cooling effect of the feed gas. Synthesis feed gas so introduced has a chilling effect on the catalyst with the result that at the point of gas entry temperatures conducive to the formation of high molecular weight hydrocarbons prevail. Although the proper gas-forming synthesis temperature is rapidly attained, due to the high turbulence of the catalyst, it has been found that the localized temperatures conducive to the formation of for the formation in appreciable quantities of the high molecular weight products which are converted subsequently to coke, thereby contributing to a premature over carbonization of the catalyst.

The present invention employs a process of this latter type but overcomes the disadvantage outlined by preheating the synthesis gas feed to the conversion zone to substantially the conversion temperature prevailing therein. The synthesis gas feed may be preheated in any desired manner, preferably by utilizing the heat of reaction generated in the conversion zone. Where a two stage process hereinafter described and involving an initial gasification stage for the production of the synthesis feed gas is employed, preheating of the synthesis gas feed to the conversion stage may be conveniently achieved by utilizing the heat of solids removed from the gasification zone.

Thus according to the invention a preheated gas mixture containing carbon monoxide and hydrogen is passed, at conversion conditions conducive to the formation of predominantly gaseous hydrocarbons, through a reaction zone containing finely divided solid conversion catalyst in the form of a relatively dense turbulent mass fluidized by the gaseous reactants and reaction products. The dense mass resembles a boiling liquid as regards uniformity of temperature and flow characteristics. As a result, the temperature throughout the reaction zone may be readily maintained uniform and constant at any desired level by the supply and removal of heat at any point of the catalyst zone, whereby the yields of gaseous hydrocarbons are greatly increased. In addition, the fluid state of the catalyst facilitates and simplifies continuous operation, as will appear hereinafter.

The reactants, including carbon monoxide and hydrogen, preferably enter at the bottom of the reaction zone and the reaction products are withdrawn overhead. However, a portion of the reactants may be fed at any other point below the well-defined upper level of the fluidized catalyst mass. If the carbon monoxide and hydrogen in the feed gas are not in the desired proportion, make-up gas from another source may be added, preferably at the bottom of the zone. The reaction products are withdrawn overhead through equipment designed to remove the suspended catalyst and return it to the reaction chamber. This equipment may consist of a preferably enlarged space in the upper part of the reaction chamber in which the velocity of the rising gas is such as to permit the solid particles to drop back into the dense mass, followed by mechanical separators, for example, of the cyclone type, and/or electrical precipitators, and, if desired, by water washing.

The conversion catalyst may be any hydrogenation catalyst capable of catalyzing the hydrogenation of carbon monoxide to gaseous hydrocarbons, particularly methane, including iron group metals, particularly nickel, oxides and sulfides of metals of the fifth and sixth groups of the Periodic Table, and the like, either alone or in mixture or supported on carrier materials, such as kieselguhr, clay, alumina and natural or synthetic siliceous gels. The particles have preferably a diameter of less than 150 microns comprising not more than, say, 60% of particles of 0—20 micron diameter. Good results are generally obtained with a particle size range of from 5 to 100 microns, at superficial gas velocities of 0.1 to 2 ft. per second, resulting in an apparent density of the fluidized catalyst mass of 5 to 150 lbs./cu.ft., depending on the particle size and shape, the true density of the catalyst and the velocity, density and viscosity of the gas throughout the reaction zone.

The reaction pressure may vary from about atmospheric to as high as 2000 lbs./sq.in., depending partly upon the disposition of the products. For example, if it is desired to transport the product gas to the consumer through a high pressure pipe line or as a compressed liquid, it may be desirable to operate the reaction zone at a pressure slightly above the inlet pressure of the pipe line or slightly above the condensing pressure, for example, 600 lbs./sq.in.

Since heat is liberated by the reaction, heat must be withdrawn from the reaction zone. This may be accomplished by several means. A cooling medium may be caused to flow through a heat exchange surface supported within the reaction zone in contact with the fluidized catalyst mass. Or, a stream of fluidized catalyst may be withdrawn from the reaction zone, passed through a heat exchanger in heat exchange with a cooling medium, and then returned to the reaction zone. Since the fluidized catalyst mass behaves in many ways like a liquid, the stream of fluidized material may be withdrawn through a conduit from any point below the upper level of the dense catalyst phase and passed to a point of equal or higher pressure level by means of standpipes wherein a stream of finely-divided solids is led downwardly through a vertical column of a height such as to produce at the bottom of the column a pressure equal to that required to force it through a restricted path into a less dense suspension and in this form to its final destination. The downward flow of the relatively dense vertical catalyst column may be facilitated and the density flowing suspension may be reduced by the addition of any suitable gas, preferably the gaseous reactants. The heat of reaction may be removed in a further optional manner by withdrawing a stream of fluidized catalyst, conducting it through a vertical downward column and restricted path as described above, adding to the stream a cooling gas in direct contact, separating the cooling gas from the suspended catalyst by mechanical or other suitable means and returning the catalyst to the reaction chamber as, for example, through a vertical downward column leading back into the reaction chamber and discharging below the upper level of the dense mass.

To give the optimum yield of gaseous hydrocarbons, particularly methane, the reaction temperature should be maintained at a substantially constant value within the approximate range of 500° F. to 700° F., preferably between about 500° and 575° F., if gas decomposition and carbon deposits on the catalyst are to be avoided. However, in some cases it may be preferred to operate within a temperature range of 575° to 700° F., in which case provision must be made for removing carbon from the catalyst, either periodically or continuously. For this purpose, a stream of fluidized catalyst may be withdrawn from the reaction zone, suspended in air, and conducted to an oxidation chamber in which the carbon is burned off the catalyst. This chamber may be similar in construction and operation, to the reaction chamber described above, catalyst separated from air and combustion gases being returned to the reaction chamber. If the catalyst leaving the oxidation chamber contains metal oxide, it may be desirable to reduce the oxide before returning the catalyst for further use. In this case, a stream of fluidized catalyst may be withdrawn from the oxidation chamber through a standpipe mixed with a stream of hydrogen, and passed to a reduction chamber, in which the oxide is reduced to the metal. Construction and operation of this chamber may again be similar to those of the reaction chamber. Reduced catalyst may be returned to the reaction chamber by any conventional means. In both the oxidation and reduction chambers the temperature may be maintained at any desired level by adding or removing heat by methods similar or analogous to those used in controlling the temperature in the reaction chamber.

If a reduced metal catalyst, particularly metallic nickel is used, the feed gas, before entering the reaction chamber, is preferably desulfurized by any conventional process. For example, the gas may be contacted with a caustic soda solution to remove H_2S, SO_2 and SO_3. In other cases, for example when it is undesirable to employ special desulfurization equipment or when the desulfurization is incomplete, the sulfur may be periodically or continuously removed from the catalyst in a manner similar to the removal of carbon described above.

Normally, the product gases from the reaction chamber will contain small amounts of carbon monoxide and hydrogen because the conversion to methane is reversible and cannot go beyond the equilibrium point. Therefore, it may be desirable to pass the product gases through one or more additional reaction zones and to remove water, between the reaction zone, in order to react additional amounts of carbon monoxide and hydrogen. The removal of water may be accomplished by any suitable means such as condensation by cooling.

As an alternative to using two or more successive reaction zones, a single reaction zone may be used with a part of the product gas stream continuously recycled through water removal equipment back to the reaction zone.

The final composition of the product gas depends largely upon that of the feed gas. Ordinarily, each mol of carbon monoxide converted to methane will consume approximately 1—3 mols of hydrogen. Thus, in the case of normal water gas there is a deficiency of hydrogen leaving some carbon monoxide unconverted. However, due to the preponderance of methane, the heating value of the product gas is still considerably greater than that of pure carbon monoxide of pure hydrogen, or mixtures thereof. The amount of carbon monoxide in the product gas may be reduced by adding hydrogen from an external source to the feed gas so as to increase the ratio of hydrogen to carbon monoxide from, say, 1.3:1 up to about 2:1 or 3:1.

The product gas may be freed simultaneously of by-product carbon dioxide and water, for example by means of a cooler condensing the water in which the carbon dioxide is dissolved, preferably under pressure. Further carbon dioxde removal may be accomplished by washing the gas with a caustic soda solution or by other conventional means.

While mixtures of carbon monoxide and hydrogen, such as blue water gas of any origin, may be used in this process, this invention affords the greatest advantages in connection with the carbonization and gasification of coal or other solid carbonaceous material, resulting in the highly desirable production of high B.Th.U. fuel gas from the non-carbonizable constituents of these solid fuels. More specifically, this invention includes the use of gas mixtures containing carbon monoxide and hydrogen obtained in such processes for the gasification of finely-divided solid carbonaceous materials, as apply to the fluid solids technique. Expressed in broad terms, these processes among other features utilize the flow characteristics of fluidized solids to transport continuously heat generated by partial combustion of the carbonaceous solids in the form of sensible heat of the fluidized solids between conversion zones exhibiting substantial temperature gradients. It has been found that, due to the continuity of the procedures and the particular temperature gradients involved, these or similar fluid processes may be made to cooperate with particular advantage in the production of fuel gas in accordance with this invention.

Having set forth the general nature and objects, the invention will be best understood from the more detailed description hereinafter in which reference will be made to the accompanying drawing which is a partly schematic and a partly diagrammatic illustration of an apparatus suitable for carrying out a preferred modification of the present invention.

Referring now to the drawing, finely-divided carbonization coal or the like is fed to hopper 1 by means of screw conveyor 2 and fluidized with the aid of air, dry steam or any inert gas admitted through line 3 to the bottom of hopper 1. Fluidizing gas is taken overhead after separation of solids fines in separator 4. The fluidized coal in the form of a dense suspension resembling a liquid is passed through standpipe 5 to dispersing chamber 8. The flow through pipe 5 may be facilitated by the injection of small amounts of fluidizing gas through lines 6. In chamber 8 the solids are picked up by an oxidizing gas, such as air and/or oxygen, supplied by pump 10 through line 12 provided with heater 11 for preheating during the starting period. The suspension of coal in air is passed from chamber 8 through line 14 to coker 16 under the pseudo-hydrostatic head of the fluidized solids column in line 5. The coal in coker 16 is maintained at carbonization temperatures of about 700°—1200° F. in the form of a turbulent, dense, fluidized mass of solids having an upper level 15. Just enough oxidizing gas is supplied to support a partial combustion sufficient to supply the heat required for the carbonization of the coal charged. Fluid carbonization products are withdrawn overhead through gas-solids separator 17 and line 18 and passed to a conventional products recovery system (not shown).

Solid fluidized coke is withdrawn downwardly through standpipe 20, further fluidized if desired by gas supplied through lines 21, and passed to dispersing chamber 22 where it is picked up by oxidizing gas and/or steam or other fluidizing gas supplied by lines 24 or 26 and passed at about the temperature of the coking zone through line 28 to gas generator 30 under the pressure of the fluidized solids column in line 20. A mixture of oxidizing gas and steam, which may be preheated during the starting period in heater 31, is supplied through line 32 to generator 30 in which the coke is subjected in the form of a fluidized, turbulent mass having an upper level 34 to a gasification reaction with steam at temperatures within the approximate limits of 1200°—2000° F. The absolute and relative amounts of oxidizing gas and steam are such as will produce just enough heat by combustion to supply the heat required by the reaction between the coke and steam to form carbon monoxide and hydrogen in the desired amounts and proportions. Air may be used as the oxidizing gas when producer gas is the fuel gas desired, while the production of blue water gas requires the use of oxygen or air enriched with oxygen in order to reduce the nitrogen content of the fuel gas. Blue water gas, however, is better suited for the present process and high nitrogen concentrations in the product gas should be avoided.

A major portion of the solid gasification residue, which may now be substantially free of carbonaceous matter, is withdrawn downwardly from generator 30 and passed at about the temperature of the gasification zone through standpipe 36 to preheater 37, if desired, after further fluidization by way of lines 35. Preheater 37 serves to preheat steam and/or oxidizing gas, preferably by direct contact with the hot gasification residue. The preheated gases are supplied through lines 39, 40 and 26 to the reaction zones 16 and 30. A minor portion of the fluidized hot gasification residue is passed through line 42 to preheater 44 to preheat the feed gas for the subsequent catalytic conversion, as will appear more clearly hereinafter.

A gas mixture consisting chiefly of carbon monoxide and hydrogen with the hydrogen preferably preponderating, and containing small amounts of carbon dioxide, nitrogen and sulfur compounds, is withdrawn overhead from generator 30 through gas-solids separator 46 and line 48 and passed through waste heat boiler 50 to a gas purification system schematically indicated at 52. Steam produced in boiler 50 may be fed to the generator 30 through lines 51 and 32. In the purification system 52 the gas is desulfurized and freed of other impurities, such as carbon dioxide, by any conventional means. The gas which now consists substantially of carbon monoxide and hydrogen in the proper proportions is passed to the catalytic conversion stage as outlined below.

Purified water gas which has lost most of its sensible heat in the gas purification system is passed through line 54, if desired, enriched with hydrogen through line 55, and conducted to preheater 44 where it is heated to a conversion temperature of between 500° and 575° F., preferably in direct heat exchange with hot solid gasification residue withdrawn from gasification zone 30. The preheated gas leaves preheater 44 through line 56 and enters catalytic reactor 60 through lines 57 and 58 and the conical base 61 of reactor 60.

Reactor 60 is a cylindrical vessel preferably provided with a conical base 61 and enlarged cylindrical top section 62. The conical base 61 is separated from the cylindrical main section by a distributing grid 63. A limited amount of finely-divided catalyst preferably metallic nickel supported on silica gel having a particle size between 50 and 200 mesh, is supplied to reactor 60 through screw conveyor or other conveying means 64. The catalyst is converted by the incoming gas feed into a dense, ebullient fluidized mass of solids having nearly perfect heat distribution characteristics resulting in a substantially uniform temperaure throughout the catalyst bed which has a well-defined upper level 65. In order to accomplish this condition of the catalyst bed, the superficial velocity of the gases passing through the reactor should be maintained between the approximate limits of 1 to 10 ft. per second, depending to some extent on the pressure which may vary between atmospheric pressure and 2000 lbs, per sq. in.

Due to their excellent distribution within the catalyst phase, the gases react immediately and completely to form methane from available carbon monoxide and hydrogen in a strongly exothermic reaction tending to raise the catalyst temperature. In order to maintain the reaction temperature constant at the optimum level of approximately 550° F., fluidized catalyst is continuously withdrawn from a point above grid 63 through standpipe 68 which may be supplied through lines 69 with additional fluidizing gas, such as feed gas or steam. The catalyst passes through slide valve 70 to dispersing chamber 72 where it is picked up by further feed gas coming from line 56 through line 73 or by other fluidizing gas, such as steam, supplied through line 74. The catalyst suspension has now a lower density but still the characteristics of a pseudo-liquid. This suspension is passed under the pressure of the catalyst column in line 68 to a waste heat boiler or other cooler shown at 76, to give off a substantial portion of its sensible heat and to be adjusted to the temperature desired for cooling the reaction zone, and if desired the sensible heat imparted to the waste heat boiler or other cooler may then be used for preheating the feed gases to reactor 60. The temtemperature desired for cooling the reaction zone depends on the amount of catalyst withdrawn, the size of the reactor and the reaction conditions to be maintained in the reactor. In general, good results are obtained when the temperature of the catalyst suspension leaving cooling means 76 is by about 50—100° F. lower than the desired reaction temperature. The cooled catalyst still under the pressure of standpipe 68 is forced back through line 78 into reactor 60 at a point either below or above grid 63 or both. In any case, complete mixing and uniformity of temperature will be immediately accomplished due to the turbulent state of the fluidized catalyst mass. Spent catalyst may be continuously or periodically withdrawn through line 71 and replaced through feeder 64 by fresh catalyst.

Reacted gas passes upwardly through reactor 60 and enters the enlarged section 62 where its superficial velocity decreases to such an extent that most of the entrained catalyst fines are separated and returned to the fluidized catalyst bed. The gas now contains about 30—50% of methane, depending on the porportion of hydrogen available in the feed gas, the remainder being steam, higher molecular hydrocarbon gases, small amounts of carbon dioxide and some unconverted reactants. From reactor section 62 the product gas passes through line 80 to gas-solids separating means 82 which may be of the centrifugal and/or electrical type. Any catalyst fines not removed from the gas in section 62 are separated by separator 82 and either returned to the reaction zone through line 83 or removed from the system through line 84. Product gases free of solids leave separator 82 through line 86 and pass through a heat exchanger 87 and the combined steam-condensing and gas-purifying system 88 to storage or consumer. If desired the heat exchanger 87 may be utilized to provide indirect heat exchange to feed gases admitted from line 54. Further instead of recovering the whole of the product gases from the conversion zone for storage or consumer a substantial portion thereof may be continuously recycled to the conversion zone. In system 88 carbon dioxide may be removed by spraying with water or dilute alkali lyes. The gas passed to storage contains 90—95% of methane and has a heating value of about 900 B.Th.U. per cu.ft.

The embodiment of this invention described above permits of many variations and modifications apparent to those skilled in the art. With respect to the production of the feed gas for the catalytic conversion stage, in general all modifications and variations made possible by the application of the fluid solids technique may be applied in this process insofar as the continuity of the process is maintained and sufficient waste heat is available to preheat the purified feed gas for the catalytic conversion to substantially conversion temperature. The danger of overheating is completely eliminated through the efficient temperature control by means of circulating cooled catalyst.

To mention a few of the possible modifications, other solid carbonaceous materials may be used in place of coal, for example, oil shale, oil tar sands or coke, if no volatile carbonization products are desired. The coking and gasification reactions may be carried out successively in a single reactor. Heat may be supplied to the coker by circulating hot solid gasification residue from the generator to the coker. Also, the heat-generating combustion may be carried out in a separate burner and hot solid combustion residue may be circulated to the coker and/or generator to supply the heat required therein. The fluidization conditions of particle size and gas velocity in tthe coking, gasification and combustion zones may vary within wide limits, good results being in general obtained at fluidization conditions similar to those described in connection with the catalytic reactor. Other modifications of this stage of this process are possible within the scope of the present invention.

The equipment illustrated by the drawing may also be used with mixtures of carbon monoxide and hydrogen derived from sources in addition to the fluid coal gasificaton processes described above. For example a feed gas containing carbon monoxide and hydrogen may be supplemented by a coal gas mixture obtained by the carbonization of finely divided carbonaceous material (preferably in a fluidized state) and containing carbon monoxide, carbon dioxide, methane and hydrogen. Such feed gases may be supplied by line 55 and the total gas mixture passed through heat exchanger 87 to pick up some of the heat of reaction of the product gases leaving reactor 60 through line 86. Leaving heat exchanger 87 the feed gases may pass through line 90 to heat exchanger 92 riding on line 90 to pick up further heat of reaction from steam superheated in waste heat boiler 76 and supplied to heat exchanger 92 through line 94. Either heat exchanger may be by-passed by way of lines 54, 53 and 91. If the feed gas temperature approaches reaction temperature the gas may be fed through line 58 and conical base 61 to reactor 60. Due to the turbulent condition of the fluidized catalyst mass, the feed gas will very rapidly attain the desired conversion temperature which may be kept at the desired level by an appropriate control of the catalyst cycle described above. Any suitable preheating means (not shown) for the feed gas and/or the catalyst may be provided particularly for starting up the process.

In order further to illustrate this invention, the following example is given, which should not be construed as limiting the same in any manner whatsoever.

EXAMPLE.

As an example of the operation of this process, the charge consists of one ton per hour of a West Virginia semi-bituminous coal ground to particles of mostly 5—100 microns diameter and having the following analysis:

	% by weight	lbs./hr.
Water as moisture	24.5	490
Ash	2.0	40
Carbon	66.6	1332
Hydrogen	3.5	70
Sulfur	0.6	12
Nitrogen	1.2	24
Oxygen	1.6	32
	100.0%	2000 lbs./hr.

The charge is picked up by a stream of compressed coal gas amounting to 4000 cu.ft./hr. measured at atmospheric temperature and 17 lbs. per sq. in. gauge pressure and led into a coking chamber in which the average upward velocity of the gas is 1 ft. per second. The temperature in the coking chamber is maintained at 1100° F. by injecting a stream of 7000 lbs. per hour of ash at 1800° F. from a separate combustion chamber. A stream of gas including net volatile products and recycle coal gas and a stream of a dense suspended solids mass including net coke product and recycle ash are withdrawn from the coking chamber.

The net volatile products comprise:

	lbs./hr.
Water	490
Tar	200
Light Oil	11
Ammonia	2
Gas:	
CO_2	30
H_2S	7
N_2	12
H_2	5
CO	18
CH_4	37
C_2H_4	3
C_2H_6	13
C_3H_6	4
C_3H_8	7
C_4H_8	5
C_4H_{10}	3
Liquid hydrocarbons	13

The net coke products amount to 1140 lbs./hr. The volatile products are processed to remove the water, tar, light oil, ammonia, H_2S, CO_2, and liquid hydrocarbons. A portion of the remaining coal gas is recycled as previously mentioned and the remainder is sent to the catalytic methanation process. The net products and recycle ash are split in a 55:45 ratio, the larger portion going to a water gas chamber and the smaller portion to the combustion chamber. About 1100 lbs./hr. of steam is used to suspend the coke and the recycle ash stream and to accomplish the water-gas reaction which is carried out at 1300° F. and slightly superatmospheric pressure, the heat being supplied by a stream of 36,000 lbs./hr. of ash at 1800° F. from the combustion chamber. Water gas and a suspended solids mass including all the ash from the original coal are withdrawn from the gas generator.

The gas comprises:

	lbs./hr.
CO	1100
CO_2	399
Nitrogen	2
H_2S	2
H_2O	162
Hydrogen	125

The ash amounts to 40 lbs./hr. The net product total ash from the original coal is withdrawn from the system at this point and all other ash fed into the water gas generator is returned to the combustion chamber.

The other 45% of the net coke and recycle ash from the coking chamber is suspended in air and transported to the combustion chamber which is maintained at 1800° F. A total of 79,500 standard cu.ft./hr. of air is used for the supply and operation of the combustion chamber from which a flue gas consisting principally of carbon dioxide and nitrogen, and a stream of hot ash are withdrawn. The latter is returned in part to the coking chamber and in part to the water-gas generator.

The purified gas from the coking chamber and the water gas (after removal of water, CO_2 and sulfur compounds) from the water-gas chamber are next combined, preheated and fed into the methanation reactor at substantially the temperature prevailing therein. The latter is operated at slightly superatmospheric pressure while the previous coking and water-gas chambers are operated at sufficiently higher pressures to cause their gas products to flow into the methanation reactor. Suspended catalyst is maintained in the methanation reactor in the form of reduced nickel deposited on small particles of kieselguhr of about 5 to 100 microns in diameter. The temperature in the methanation chamber is maintaned at about 570° F. by withdrawing a fluidized stream of suspended catalyst, circulating it through a cooler to remove about 2 million BTh.U/hr. and returning it to the reaction chamber. The gas withdrawn from the methanation reactor is purified by cooling and caustic scrubbing to remove water and carbon dioxide. The net product gas comprises:

	lbs./hr.
CH_4	403
CO	311
CO_2	Negligible
Hydrogen	5
Ethane to Butane	40
Water	18
Nitrogen	14

Its average gross heat content is about 800 BTU/standard cu.ft.

Higher hydrogen content raw materials tend to give a final product gas having a higher methane content, and a higher heating value. Omission of the coal gas feed to the methanation step will give a smaller volume of methanation gas product of higher heating value.

For purposes of simplification, the heat recovery means have not been described in the above example. It will be apparent to any one skilled in the art that heat can be recovered from the process to change the overall heat balance so as to reduce the amount of feed to the combustion chamber and to increase the yield of final product gas per ton of coal. Alternatively, a part or all of the heat recovered may be used to generate steam or for any other useful purpose.

From the above description, it will be understood that we may convert carbonizable and non-carbonizable fuels, such as coal, coke from oil, and coal, shale, tar sands, cellulosic materials, and the like completely to crude tar, benzol, ammonia, liquid and liquefiable fuels and a high B.Th.U fuel gas suitable for compressing, pumping through lines, heating purposes and for enriching fuel gases of lower BTU value.

This invention is not to be limited to any specific examples presented here, all such being intended solely for purposes of illustration.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of fuel gases of high heating value which comprises passing a gas mixture containing carbon monoxide and hydrogen at conversion conditions of temperature, pressure and through-put conducive to the predominant formation of normally gaseous hydrocarbons, particularly methane, to a conversion zone containing a highly turbulent, dense, fluidized mass of finely divided solid hydrogenation catalyst capable of promoting the conversion of carbon monoxide and hydrogen predominantly to said normally gaseous hydrocarbons at the conversion conditions, preheating the said gas mixture to substantially said conversion temperature prior to its entry to the conversion zone, withdrawing heat from the conversion zone to maintain the conversion temperature at the desired level, and recovering normally gaseous hydrocarbons from the conversion zone.

2. A process according to Claim 1, wherein the temperature in the conversion zone is controlled by withdrawing part of the fluidized catalyst therefrom, cooling the withdrawn catalyst, and returning the cooled catalyst to the conversion zone at a rate adapted to establish the desired reaction temperature in the conversion zone.

3. A process according to Claim 2, wherein the catalyst is withdrawn downwardly from the conversion zone in the form of a vertical column of dense fluidized catalyst, said dense catalyst being suspended in a fluidizing gas to form a catalyst suspension of relatively low density and the suspension thus formed being returned to the conversion zone under the pseudo-hydrostatic pressure of said vertical column.

4. A process according to Claim 2 or 3,

wherein the gas mixture is preheated to the desired reaction temperature by the heat of reaction generated in the conversion zone.

5. A process according to Claim 4, wherein the gas mixture is preheated by passing it in indirect heat exchange with hot catalyst or hot gaseous reaction products removed from the conversion zone.

6. A process according to any one of Claims 1—5, which comprises preheating a gas mixture containing about 1.3—3 volumes of hydrogen per volume of carbon monoxide to a temperature falling within the approximate limits of 500° and 700° F., passing said preheated gas mixture at a superficial velocity of about 0.1—2 ft. per second upwardly through a conversion zone containing a highly turbulent, dense, fluidized mass of finely divided nickel catalyst having a particle size of less than 150 microns, with not more than about 60% of the particles having a size of 0—20 microns, so that said mass has an apparent density of about 5—150 lbs. per cu.ft., withdrawing a gas rich in methane overhead from said conversion zone and withdrawing heat from said conversion zone to maintain a temperature therein within the above quoted range.

7. A process according to any one of the preceding claims, wherein said gas mixture is passed to the conversion stage from a gasification zone in which a finely divided fluidized mass of solid carbonaceous material is reacted with steam at gasification temperatures to produce a gas mixture containing carbon monoxide and hydrogen.

8. A process according to Claim 7, wherein the gas mixture passed to the conversion zone is preheated by passing it in indirect heat exchange with hot solids removed from the gasification zone.

9. A process according to any one of the preceding claims, wherein coal gas containing carbon monoxide, carbon dioxide, methane, and hydrogen, obtained by the carbonization of finely divided solid carbonaceous material, preferably according to the fluidized solid technique, is added to the gas mixture feed to the conversion zone.

10. A process according to Claim 9, wherein said coal gas is purified and freed from water, sulphur, and nitrogen compounds before being passed to the conversion zone.

11. A process according to any one of the preceding claims, wherein the product fuel gas obtained from the conversion zone is passed through at least one additional conversion zone operated at conditions similar to those of said first mentioned conversion zone and water is removed from the product gas between conversion zones.

12. A process according to any one of Claims 1—10, wherein a substantial portion of the product fuel gas is continuously recycled to the conversion zone.

13. A process according to any one of the preceding Claims, wherein the catalyst comprises metals of the iron group, or oxides or sulphides of metals of groups V and VI of the Periodic Classification alone or admixed with each other or supported on carrier materials.

14. A process according to Claim 13, wherein the said carrier material comprises kieselguhr, clay, alumina, or natural or synthetic siliceous gels.

15. A process according to Claim 14, wherein the catalyst comprises nickel supported on kieselguhr.

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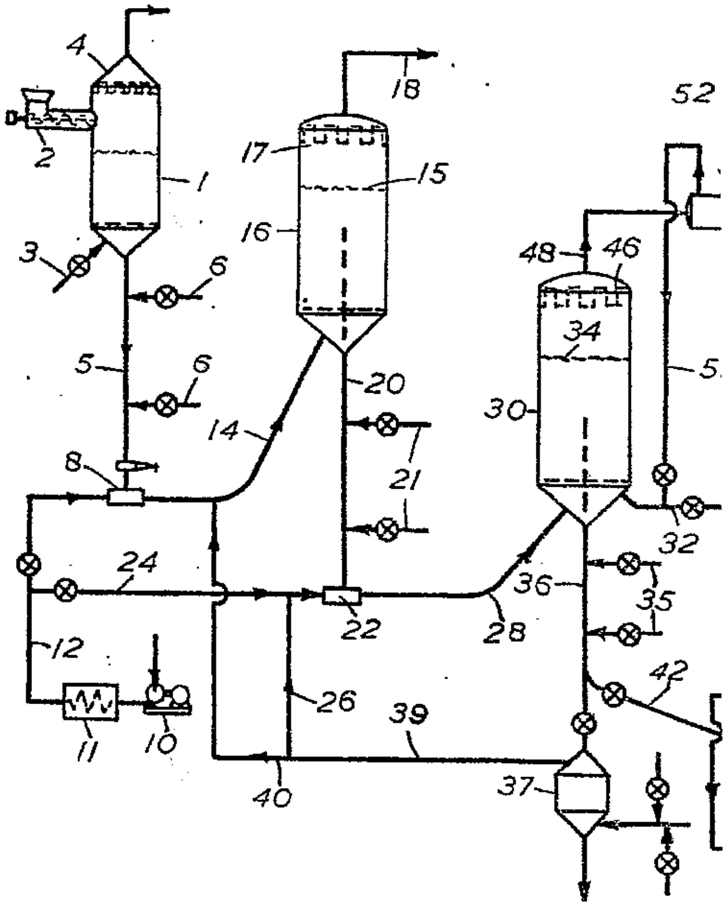

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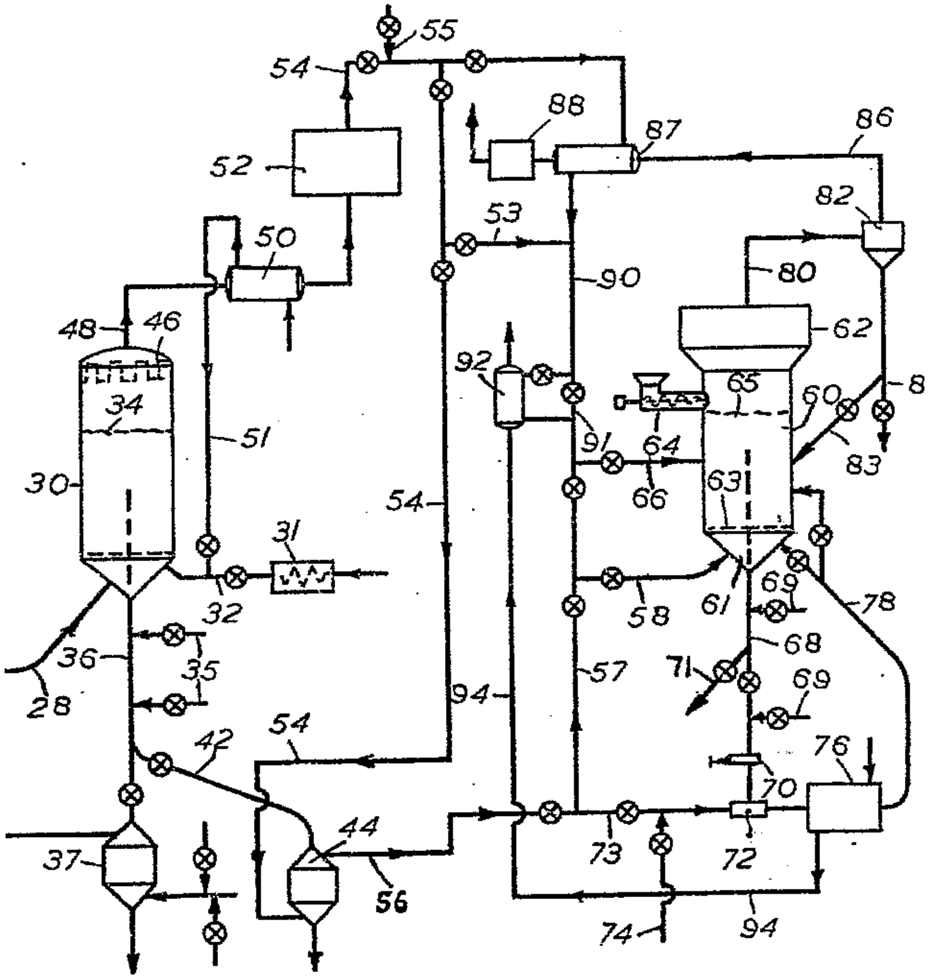

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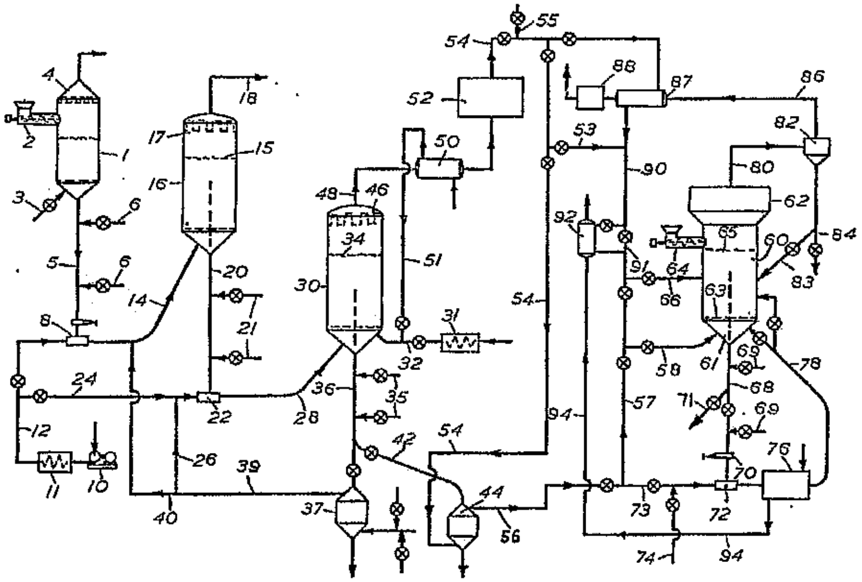

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