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PROCESS FOR THE PRODUCTION OF FUEL GAS FROM CARBONACEOUS SOLID FUELS

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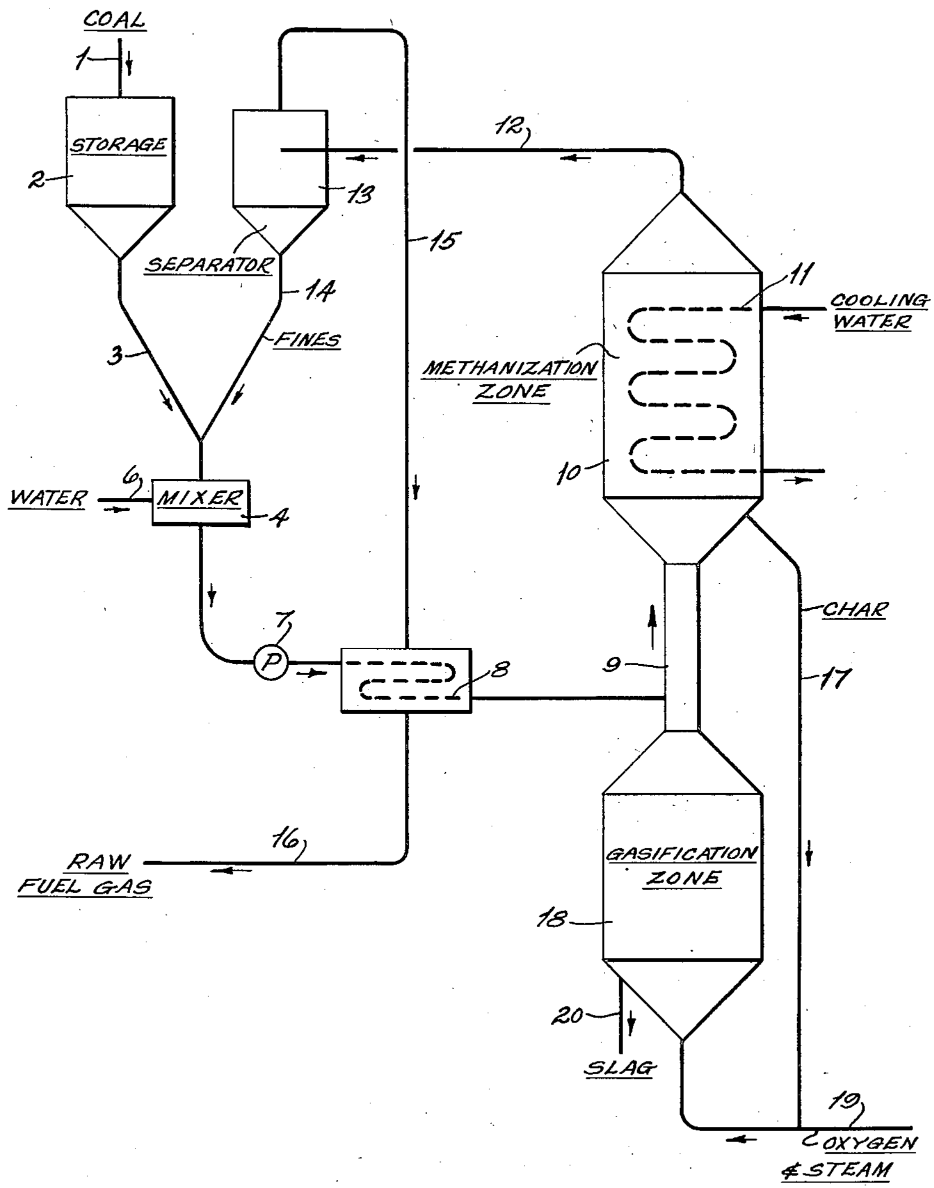

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PROCESS FOR THE PRODUCTION OF FUEL GAS FROM CARBONACEOUS SOLID FUELS

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5 Claims. (Cl. 48—202)

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This invention relates to a process for the production of fuel gas from a carbonaceous solid fuel. In one of its more specific aspects this invention relates to an improved process for the distillation of coal and the simultaneous methanization of carbon monoxide and hydrogen to produce a fuel gas of relatively high heating value. The process of this invention may be applied to the gasification of coke, oil shale, and various grades of coal including anthracite, lignite, and bituminous coals.

An object of this invention is to provide an improved process for the gasification of solid carbonaceous fuels.

Another object of this invention is to provide for the production of fuel gas from solid fuels.

Still another object of this invention is to provide for the distillation of volatilizable constituents from solid carbonaceous materials containing volatilizable constituents.

A further object of this invention is to provide for the methanization of carbon monoxide and hydrogen to produce a fuel gas of high heating value.

In a copending application of du Bois Eastman and Leon P. Gaucher, Serial No. 49,626, filed September 16, 1948, (D#31,208), a novel process for pulverizing carbonaceous solids is disclosed. In accordance with the method disclosed in said application, particles of a solid carbonaceous material, particularly coal, are admixed with a liquid to form a suspension and the suspension passed as a confined stream through a heating zone. The carbonaceous solid is heated in the heating zone to an elevated temperature. Heating of particles of coal under these conditions results in rapid disintegration of the particles to powder.

In accordance with the present invention, this novel step of heating and pulverizing solid carbonaceous material is employed in connection with gasification of the resulting powdered fuel with oxygen and steam and conversion of the resulting carbon monoxide and hydrogen to fuel gas. The gasification with steam and oxygen is carried out in a flow type gas generator at a temperature within the range of from about 2000 to about 3000° F. Hot gases from the gasification step are used to supply heat for carbonization of the fuel in a fluidized bed in a separate carbonization and methanization zone. The methanization zone is operated at a temperature within the range of from about 900 to about 1800° F. and preferably within the range of from about 1000 to about 1500° F. Additional heat is liberated by the methanization reaction, i. e., the reaction of

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carbon monoxide and hydrogen to produce methane. Methane produced by this reaction and that liberated from the fuel by distillation serve to enrich the product gases. Heat from the gasification is also used for heating the slurry to vaporize the liquid and preheat and vaporize the carbonaceous solid.

An important distinction over processes of the prior art is the combination of an unobstructed, flow type generator and a fluid bed carbonization zone. The results obtained by this combination are quantitatively different from those obtained by fluid bed gasification processes and those employing moving beds. In the flow type generator, the quantity of solid fuel supplied to the generator is just sufficient to react with the gases. Slag may be withdrawn from the generator as a liquid or solid ash may be separated from the product gases. Free heat transfer by radiation is achieved so that the entire reaction zone operates at essentially a single uniform temperature. For best results the internal surface area of the generator, as compared with the surface of a sphere of equal volume, is less than 1.5 times the surface area of the sphere.

Methanization is most effectively carried out at a temperature considerably below the temperature effective for rapid and efficient gasification. The fluidized bed of solid fuel and resulting char provides an ideal reaction zone for the production of methane from carbon monoxide and hydrogen, since the entire reaction zone may be maintained at a uniform desired temperature. As there is no appreciable consumption of the coal particles in the fluidized bed and no ash production, there is no problem of carbon loss as in the conventional fluid bed gasifier. Heat transfer surfaces may be provided in the methanization zone for accurate control of the temperature therein. Heat from the methanization zone may be used to vaporize the slurry feed stream.

Since the bed of solid particles of carbonaceous material in the methanization zone is maintained in a highly turbulent condition, fresh coal is rapidly dispersed in a large volume of carbonized coal or char. Under these conditions, a raw caking coal passes through the plastic stage with a minimum of agglomeration. Heat transfer surfaces are kept clean by the abrasive action of the fluidized particles.

The process of this invention produces a fuel gas of equal or higher heating value than comparable processes in which gasification with steam and oxygen is carried out in a dense phase, e. g., in a fluidized or moving bed, with an appreciable saving in oxygen and steam. The permissible oxygen-to-steam ratio in the generator is considerably higher than for the conventional dense phase gasification reactors while, at the same time, the oxygen-to-fuel ratio is lower. Since oxygen and, to a lesser extent, steam requirements are significant factors in the cost of synthetic fuel production, the present process materially improves the economy of the production of fuel gas of high heating value.

The overall steam requirements for the process range from about 0.8 to about 2.0 pounds per pound of solid fresh fuel while the free oxygen requirements range from about 0.1 to about 0.8 pounds per pound of solid fresh fuel. Pressures may vary from about 150 to about 750 pounds per square inch gauge, or higher.

In a preferred embodiment of this invention, coal in particle form is mixed with sufficient water to form a fluid suspension or slurry. The slurry is passed through a tubular heating zone wherein it is heated to a temperature at least sufficient to vaporize the water. Combined water contained in the coal need not be completely removed in the heating step. The heating step produces a dispersion of powdered coal in steam and at the same time may distill some of the volatilizable constituents from the coal.

The quantity of liquid admixed with the coal to form the suspension may vary considerably depending upon process requirements and the feed material. A minimum of about 35 percent water by weight is required to form a fluid suspension of coal. The liquid content of the suspension may be controlled by first mixing the solid with a quantity of liquid in excess of the required quantity and adjusting the consistency to the desired value by removal of excess liquid in a conventional thickener. The suspension is readily pumped with suitable equipment, e. g., with a diaphragm type pump, of the type commonly used for handling similar suspensions of solids. The suspension may be made up at a point some distance away from the processing site and pumped to the site in a pipeline.

A catalyst for the methanization reaction, for example, iron oxide, may be added to the slurry. Also fluxing agents, e. g., lime, silica, alumina, etc., may be added to decrease the fusion temperature of the ash.

Some coals require substantial theoretical amounts of steam for the production of hydrogen and carbon monoxide by reaction with steam and oxygen at temperatures within commercially attainable limits (2000° F. to 3000° F.). Others contain water in sufficient quantity or even in excess of the theoretical requirements. Anthracite is an example of the former, requiring a considerable quantity of steam, for example, 30 percent by weight. Lignite is an example of the latter, often containing more than the theoretical requirement of water. Water in excess of the theoretical requirement is not detrimental to the gasification reaction. While anthracite, because of its relatively high steam requirement, is an excellent feed material for the process of this invention, lignite may also be used.

Anthracite silt may advantageously be used as a feed material for the present process. Anthracite silt is a term applied to the fine particles of coal and associated impurities, obtained as a by-product in the mining, handling, and sizing of anthracite coal. Anthracite silt may be used in the present process without preliminary grinding. It ranges in size from about $\frac{3}{16}$ inch average diameter, to about 200 mesh, the bulk of the material falling within the range of $\frac{3}{32}$ inch to 100 mesh.

The size of the coal particles fed to the heating step is not of especial importance to the successful operations of the invention. Particles of a size which may be passed through the heater tubes without difficulty may be used, i. e., particles having an effective diameter less than one-third the pipe diameter. Generally, it is preferable to use particles less than about one-quarter inch in average diameter. Since the heating of the dispersion under turbulent flow conditions results in disintegration of the coal, costly pulverization by mechanical means is eliminated. It is contemplated in most applications of this process that the coal will be reduced only to a particle size such that it may be readily handled as a suspension or slurry. The coal may be crushed mechanically to about one-fourth inch in average diameter with a relatively small expenditure of power. Further mechanical reduction in size becomes progressively more expensive, pulverization requiring large expenditures of power. It is evident that this process possesses important advantages over conventional methods which involve separate pulverization and carbonization.

The linear velocity of a liquid suspension at the inlet to the heating coil should be within the range of from about ½ foot to about 10 feet per second, suitably about 1 to 2 feet per second. The velocity of gaseous dispersions as at the outlet of the coil depends upon the pressure and temperature of the dispersion.

The temperature at the outlet of the heating coil may range from about 250 to 1500° F. or higher. The temperature preferably is at least sufficient to insure substantially complete vaporization of liquid present in the dispersion by the time it is discharged from the heating zone. Preferably a temperature within the range of 600 to 1400° F. is attained at the outlet of the coil. The higher temperatures, within practical limits, are usually advantageous. The extent of carbonization, i. e., distillation of volatilizable constituents from the coal, may be controlled by control of the temperature.

Pressure, in itself, is not critical in the heating step. The temperature and pressure relationships affecting vaporization are well known. It is desirable to operate the heating zone at a pressure somewhat higher than the operating pressure of the gasification zone. In the generation of fuel or synthesis gas, it is often desirable to operate the gasification step at an elevated pressure, for example, 300 to 600 pounds per square inch. The heating and pulverizing step may be operated at a corresponding pressure sufficient to insure flow through the heating coil and into the generator at the desired rate. A considerable pressure drop takes place in the heating zone due to resistance to flow. This drop may be on the order of, for example, 100 pounds per square inch. Often it is desirable to reduce the pressure suddenly in the heating zone or at its outlet to enhance the vaporization and disintegration actions of the heating step.

Part of the vapors may be separated from the powdered solid before it is fed into the generator or part of the solid may be separated from the gasiform dispersion. Separation of powdered solids from gases or vapors may be effected in a number of ways. A cyclone separator is generally effective for removal of solids from gases.

Very fine particles may be separated with a Cottrell precipitator. Less desirable are separators of the filter or liquid contact type.

A number of advantages are obtained by this method of operation. Pulverization and preheating of the coal, and generation and preheating of the steam for the gasification reaction may be accomplished in a single heating step. Additionally, the coal may be subjected to distillation conditions. When dispersed in a liquid to form a slurry, the carbonaceous solid may be readily transported and subjected to elevated pressure. Since the slurry may be handled as a liquid, troublesome lock hoppers and similar devices are eliminated and replaced simply by a slurry mixer and a pump. Another advantage results from the fact that, in a dispersion, the quantity of coal fed to the process may be accurately metered.

The invention will be more readily understood from the following detailed description and the accompanying drawing. In the detailed description of illustrative operations involving the present invention, coal is taken as a preferred fuel and water as a preferred liquid for forming the dispersion.

The figure is a diagrammatic elevational view illustrating a preferred method of carrying out the process of the present invention.

With reference to the figure, coal in particle form is introduced through line **1** into storage hopper **2** from which it may be passed through line **3** into mixer **4**. Sufficient water to form a fluid slurry of coal in water is admitted to the mixer through line **6**. The slurry is withdrawn from the mixer **4** to a pump **7** and forced under pressure through a heating coil **8** wherein it is heated to a temperature at least sufficient to vaporize the water. The resulting dispersion of powdered coal in steam is introduced into conduit **9** and thence into vessel **10**.

Vessel **10** is a pressure vessel wherein hot gases comprising carbon oxides and hydrogen resulting from the gasification of solid fuels with oxygen and steam are contacted with fresh coal and its char in a dense phase fluidized bed. A cooling coil **11** is provided in vessel **10** to remove excess heat therefrom and to control the temperature at which the methanization zone is operated. In the vessel **10**, carbon monoxide and hydrogen interact in the presence of the solid fuel to produce methane. At the same time, volatilizable materials are distilled from the coal and admixed with the gases resulting from the gasification with steam and oxygen and the methanization reaction.

The resulting mixture of gases passes through line **12** to a cyclone separator **13**. In the separator **13**, solid particles of coal which may be carried over from the fluidized bed in vessel **10** are separated from the gases. The fine particles so recovered are passed through line **14** to mixer **4** into admixture with particles of fresh coal from line **3**. The gases from separator **13** pass through line **15** into heat exchange with the slurry in the heating coil **8** to provide at least a portion of the heat required for heating the slurry. The gases are then discharged from the system through line **16** as raw fuel which, after suitable purification steps for the removal of water, condensible oils and tars, is suitable for industrial and household heating.

Char from the vessel **10** is withdrawn through line **17** and introduced into the gasification zone **18** into admixture with oxygen and steam entering through line **19**. The gasification zone is operated as a flow generator with the reactants in dilute phase. The resulting gases from the gasification zone pass through line **9** into vessel **10**. Slag is discharged from the gasification zone **19** through line **20**.

Example

Buckwheat coal having the following analysis is used in the process of this invention:

Proximate Analysis	Percent as Received	Percent Dried at 105° C.	Percent Moisture and Ash Free	Percent Dry and Mineral Matter Free
Moisture	3.3	-------	-------	-------
Volatile Matter	4.7	4.9	5.7	-------
Fixed Carbon	78.1	80.7	94.3	95.9
Ash	13.9	14.4	-------	-------
Ultimate Analysis:				
Ash	13.9	14.4	-------	-------
Sulfur	0.6	0.6	0.7	-------
Hydrogen	2.5	2.3	2.6	-------
Carbon	76.7	79.3	92.7	-------
Nitrogen	0.8	.8	0.9	-------
Oxygen	5.5	2.6	3.1	-------
Caloric Value, B. t. u. per lb	12,730	12,730	14,870	15,040

A slurry is made up using one pound of water per pound of coal. The slurry is charged through a heating coil wherein it is heated to about 1100° F. and charged into a fluidized bed of char in a methanization zone maintained at about 1160° F. and 600 pounds per square inch gauge. The slurry is passed in indirect heat exchange with the fluidized bed of char in the methanization zone.

The gasification zone is operated at about 2320° F. and 600 pounds per square inch gauge. Steam and oxygen are preheated to about 620° F. and admixed with char drawn directly from the methanization zone. The quantities of steam and oxygen fed to the gasifier correspond to 0.773 pound steam and 0.760 pound of an oxygen concentrate containing 99.2 percent oxygen and 0.8 percent nitrogen, by volume, per pound of raw coal, as received, fed to the system. The slag is withdrawn from the gasifier as a liquid in an amount corresponding to 0.150 pound per pound of feed.

The char from the methanization zone amounts to about 0.907 pound per pound of raw coal. About 0.021 pound of recovered fines is separated from the product gas and admixed with the fresh feed.

The gas from the gasification zone at 2320° F. has the following approximate composition:

	Volume percent
Hydrogen	26
Carbon monoxide	49
Water vapor	15
Carbon dioxide	10

All of this gas passes to the methanization zone.

The total product gas from the methanization zone has the following approximate composition:

	Volume percent
Hydrogen	11
Methane	12
Water vapor	44
Carbon monoxide	3
Carbon dioxide	30

In addition, the raw gas contains small amounts of nitrogen and sulfur compounds.

The total product gas is treated for removal of water, carbon dioxide, and sulfur compounds. A purified fuel gas is obtained in an amount equivalent to about 14.2 standard cubic feet per pound of raw coal of the following composition:

	Volume percent
Hydrogen	40
Methane	46
Carbon monoxide	12
Nitrogen	1
Water vapor and carbon dioxide	1

The fuel gas has a gross heating value of about 611 B. t. u. and a net heating value of 548 B. t. u. per standard cubic foot.

Obviously many modifications and variations of the invention as hereinabove set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In a process for the generation of fuel gas from a solid carbonaceous fuel containing volatilizable constituents, the improvement which comprises admixing said solid carbonaceous fuel in particle form with sufficient water to form a fluid suspension, passing said suspension through a heating zone at an elevated temperature such that substantially all of the water is vaporized thereby forming a dispersion of coal in steam, passing the resulting dispersion into a fluidized bed of solid carbonaceous material in a methanization zone into contact with carbon monoxide and hydrogen at a temperature within the range of from about 900 to about 1800° F. whereby carbon monoxide and hydrogen are converted to methane and volatilable constituents of said solid carbonaceous material are distilled therefrom, withdrawing carbonaceous material from said methanization zone and passing it into contact with oxygen and steam in dilute phase in a gasification zone maintained at a temperature within the range of from about 2000 to about 3000° F., passing the resulting gases comprising carbon monoxide and hydrogen from the gasification zone into the methanization zone as the source of carbon monoxide and hydrogen therefor, and discharging the gaseous products of the methanization zone as the raw product fuel gas.

2. A process as defined in claim 1 wherein at least a portion of the heat requirements of said heating zone is obtained from said methanization zone by indirect heat exchange.

3. A process as defined in claim 1 wherein said methanization zone is maintained at a temperature within the range of from about 1000 to about 1500° F.

4. A process as defined in claim 1 wherein the gasification zone and methanization zone are operated at a pressure within the range of from about 150 to about 750 pounds per square inch gauge.

5. In a process for the generation of fuel gas from a solid carbonaceous fuel containing volatilizable constituents, the improvement which comprises admixing said solid carbonaceous fuel in particle form with sufficient water to form a fluid suspension, passing said suspension through a heating zone at an elevated temperature such that substantially all of the water is vaporized thereby forming a dispersion of coal in steam, separating at least a portion of the steam from the solid carbonaceous particles, passing the solid carbonaceous particles into a fluidized bed of solid carbonaceous material in a methanization zone into contact with carbon monoxide and hydrogen at a temperature within the range of from about 900 to about 1800° F. whereby carbon monoxide and hydrogen are converted to methane and volatilizable constituents of said solid carbonaceous material are distilled therefrom, withdrawing carbonaceous material from said methanization zone and passing it into contact with oxygen and steam in dilute phase in a gasification zone maintained at a temperature within the range of from about 2000 to about 3000° F., passing the stream separated from the solid carbonaceous particles to the gasification zone to supply at least a portion of the steam thereto, passing the resulting gases comprising carbon monoxide and hydrogen from the gasification zone into the methanization zone as the source of carbon monoxide and hydrogen therefor, and discharging the gaseous products of the methanization zone as the raw product fuel gas.

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