

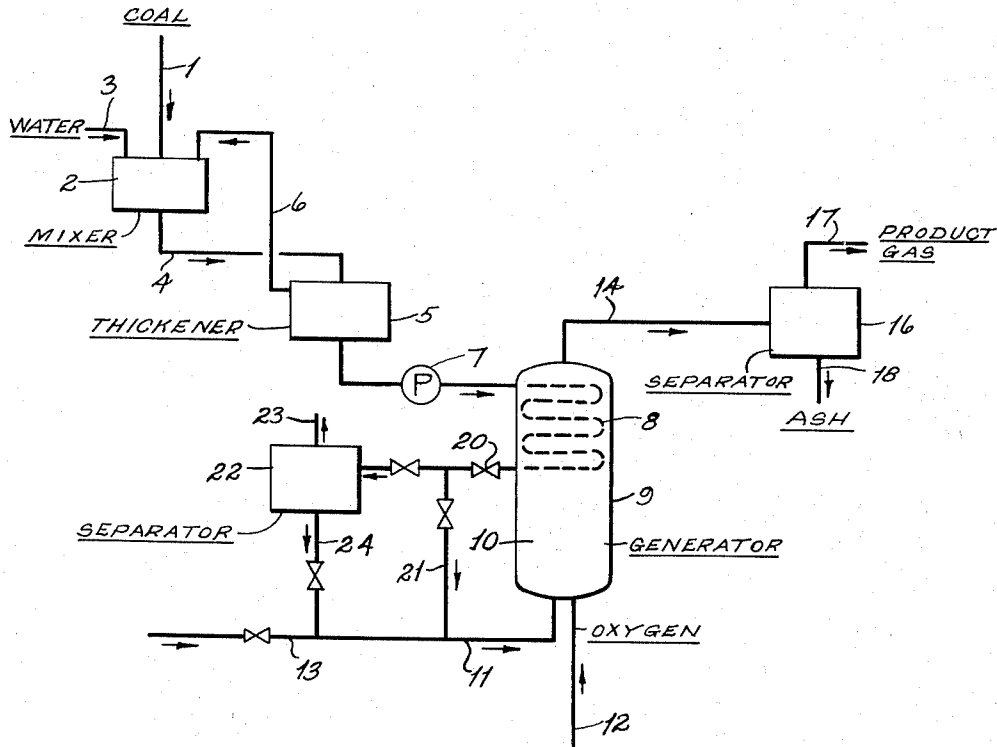
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F. B. SELLERS

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PROCESS FOR GASIFYING CARBONACEOUS SOLIDS

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INVENTOR.

F. BURTON SELLERS

BY

Samuel Stryker
J. H. Williams
ATTORNEYS

UNITED STATES PATENT OFFICE

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PROCESS FOR GASIFYING CARBONACEOUS SOLIDS

Frederick Burton Sellers, New York, N. Y., assignor to Texaco Development Corporation, New York, N. Y., a corporation of Delaware

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This invention relates to a process for the gasification of solid carbonaceous materials.

The process of this invention is particularly applicable to the treatment of coal, e. g., anthracite, bituminous coal, or lignite. In one of its more specific aspects, this invention relates to an improved method of generating a mixture of carbon monoxide and hydrogen from a solid carbonaceous fuel by reaction with oxygen. The process of this invention is particularly suited to the production of water gas, fuel gas, or feed gas for the synthesis of hydrocarbons by the Fischer-Tropsch reaction.

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

Another object is to provide an improved process for the generation of a mixture of carbon monoxide and hydrogen by reaction of a solid carbonaceous material with oxygen.

Still another object of this invention is to provide an improved process for the generation of carbon monoxide and hydrogen by the reaction of coal with steam and oxygen.

In a copending application of Du Bois Eastman and Leon P. Gaucher, Ser. No. 49,626, filed September 16, 1948, 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 fluid to form a suspension and the suspension passed as a confined stream in turbulent flow 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 powder with oxygen and steam. Preferably the gasification step is carried out with an oxygen concentrate, e. g., commercial oxygen containing 95 per cent or more oxygen by volume. The gasification reaction is exothermic and is carried out at an elevated temperature, e. g., 2000 to 2600° F. In the present invention heat from the gasification reaction is used to supply heat to the heating zone for heating and disintegrating the carbonaceous material.

The fluid used for suspension may be a gas, vapor, or liquid which is substantially inert or innocuous with respect to reaction with the car-

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bonaceous material under the conditions existing in the heating zone. Suitable gases include hydrocarbon gases, such as methane, ethane, ethylene, natural gas, refinery gases, synthesis tail gas, coal gas, and the like, hydrogen, carbon monoxide, carbon dioxide, nitrogen, steam, and mixtures composed of or comprising the above-mentioned gases. Water and hydrocarbon oils are preferred liquids for use in the process. Suitable liquids include water, gasoline, kerosene, naphtha, and gas oil fractions of petroleum distillates; light oil, middle oil, or heavy oil fractions of coal distillates; aromatic hydrocarbons, e. g., benzene, toluene; paraffins, e. g., hexane, heptane, etc.; naphthenes, e. g., cyclohexane, methylcyclohexane, and the like; hydroaromatics, e. g., tetralin, decalin; and mixtures of these various materials. An oil fraction derived from the coal is especially useful in making up the suspension. Preferably, the liquid used is at least partly vaporizable on heating in the heating step.

Water and oil mixtures, suitably in the form of emulsions, may be used in preparing the suspension. Emulsifying agents may be used as an aid in the preparation of an emulsion.

When oil is used in the preparation of the suspension it is sometimes advantageous to subject the oil to cracking during the heating step. Oils which undergo thermal decomposition on heating, producing vapors and residual carbonaceous solid, are suitable for use in the process of this invention.

In a preferred embodiment of this invention, coal in particle form is admixed with a liquid which may be converted to vapor form on heating. Sufficient liquid is employed to form a fluid suspension or slurry. The suspension is passed through a tubular heating zone incorporated in a gas generator wherein it is heated to a temperature at least sufficient to convert substantially all of the liquid to vapor. Combined water need not be completely removed from the carbonaceous material. The heating step produces a gasiform dispersion of powdered solid in vapor. Volatile constituents may be distilled from the coal in the heating step, thereby carbonizing the coal.

A portion of the powdered carbonaceous material resulting from the disintegration in the heating step may be separated from the gases or vapors and returned for use in making up the feed suspension. This powdered material, because of its state of subdivision, aids in producing a uniform suspension and reduces the

quantity of liquid required to form a pumpable fluid suspension.

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 per cent liquid by weight is required to form a fluid suspension with water. 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.

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 per cent 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. Excess water has an effect on the generator temperature and oxygen requirements.

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 $\frac{1}{16}$ inch average diameter, to about 200 mesh, the bulk of the material falling within the range of $\frac{1}{32}$ 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 $\frac{1}{2}$ 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, should be within the range of from about 25 to about 200 feet per second, suitably about 50 to 100 feet per second.

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 or all 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. All of the products of the heating step may be fed into the gasification zone for the production of carbon monoxide and hydrogen. 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

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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 to a mixer 2. Sufficient water to form a suspension of coal and water is admitted through line 3. The resulting suspension is passed through line 4 to a thickener 5 of conventional design wherein excess water is removed and the relative proportions of water and coal in the suspension adjusted to the desired value. Excess water may be discharged from the thickener through line 6 and returned to the mixer. The suspension is withdrawn from the thickener 5 to a pump 7 and forced under pressure through a heating coil 8 disposed in a vessel 9.

Vessel 9 preferably is a pressure vessel comprising a gasification zone 10 wherein solid carbonaceous fuel is reacted with oxygen in the presence of steam at an elevated temperature and pressure to produce a mixture of carbon monoxide and hydrogen. The reaction zone is substantially unobstructed and preferably of such dimensions that the ratio of the internal surface of the reaction zone to the surface of a sphere of the same volume is less than about 1.5.

Solid carbonaceous material is fed into the gasification zone through line 11. Oxygen is admitted to the gasification zone by line 12. Steam or other desired reactants may be introduced through line 13.

The reaction of powdered carbonaceous solid and oxygen is exothermic and releases large quantities of heat. The gasification zone preferably is maintained at a temperature within the range of from about 2000 to 2600° F. The hot gases, comprising predominantly carbon monoxide and hydrogen are passed over the coil 8 and discharged from the vessel 9 through line 14. The hot product gases from the gasification zone pass in indirect heat exchange with the suspension passing through the heating coil 8. The gases from the gasification zone may be passed to a suitable separator 16 for separation of ash from product gas. The product gas is discharged through line 17 and ash through line 18.

The pressure within the heating zone or coil 8 is at least sufficiently in excess of the pressure in the gasification zone to result in flow of the discharged material from the coil into the gasification zone. Considerable pressure drop takes place in the heating coil due to resistance to flow. An additional pressure drop may be provided as desired to aid in vaporization and pulverization, by valve 20. The suspension, comprising vapors and powdered solids, discharged from the coil 8 may be passed directly to the gasification zone through lines 21 and 11. Alternatively, part or all of the mixture may be passed to a suitable separation zone 22 wherein at least a part of the gas or vapor is separated from the powdered solid. The gas is discharged from the separation step through line 23. The solids and unseparated gases may be passed through lines 24 and 11 to the gasification zone.

Example

Crushed sub-bituminous coal containing 65 per cent carbon by weight, 12 per cent water, and 7 per cent ash, was mixed with sufficient water to

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form a readily fluid slurry. The slurry was pumped at the rate of 192 pounds of coal per hour into a heating coil $\frac{1}{2}$ inch in diameter and approximately 100 feet long wherein the mixture of water and coal was heated to 730° F. The resulting gasiform stream of powdered solid and steam from the heating coil was discharged directly and without pressure reduction into a gasification zone operated at a pressure of 205 pounds per square inch gauge. Oxygen at atmospheric temperature was fed to the gasification zone at the rate of 1750 standard cubic feet per hour. The temperature within the gasification zone was about 2500° F.

In a run of approximately four hours duration, product gas was made at the rate of about 6,200 standard cubic feet per hour. The composition of the product gas was 19.5% carbon dioxide, 41.7% carbon monoxide, 37.2% hydrogen and 1.6% miscellaneous gases.

Obviously many modifications and variations of the invention as hereinbefore 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 production of carbon monoxide and hydrogen by reaction of a solid carbonaceous fuel with steam and substantially pure oxygen within a closed reaction zone maintained at an elevated pressure, the improvement which comprises passing as a continuous stream in turbulent flow through a tubular heating zone within said reaction zone at a pressure in excess of the pressure in said reaction zone a suspension of particles of said fuel in a liquid which is substantially inert with respect to reaction with said fuel under the conditions existing in said heating zone, vaporizing said liquid within said heating zone by heat exchange with said reaction thereby forming a dispersion of particles of said fuel in vapor within said heating zone and removing heat from said reaction zone, and continuously introducing resulting dispersion of solid carbonaceous fuel in vapor into said gasification zone as reactant for the production of carbon monoxide and hydrogen.

2. A process as defined in claim 1 wherein said liquid is a hydrocarbon oil.

3. A process as defined in claim 1 wherein said liquid is water.

4. In a process for the production of carbon monoxide and hydrogen by reaction of a solid carbonaceous fuel with steam and substantially pure oxygen within a closed reaction zone maintained at a pressure within the range of from about 300 to about 600 pounds per square inch gauge, the improvement which comprises passing as a continuous stream in turbulent flow through a tubular heating zone within said reaction zone a suspension of particles of said solid carbonaceous fuel in water, vaporizing said water within said heating zone by heat exchange with products of said reaction thereby forming a dispersion of particles of said fuel in steam and heating said dispersion while removing heat from said reaction zone, passing the resulting dispersion of fuel in steam into said reaction zone into admixture with substantially pure oxygen for the production of carbon monoxide and hydrogen, and maintaining a pressure within said heating zone sufficiently above the pressure within said reaction zone to produce the desired rate of flow

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through said heating zone and into said reaction zone.

FREDERICK BURTON SELLERS.

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