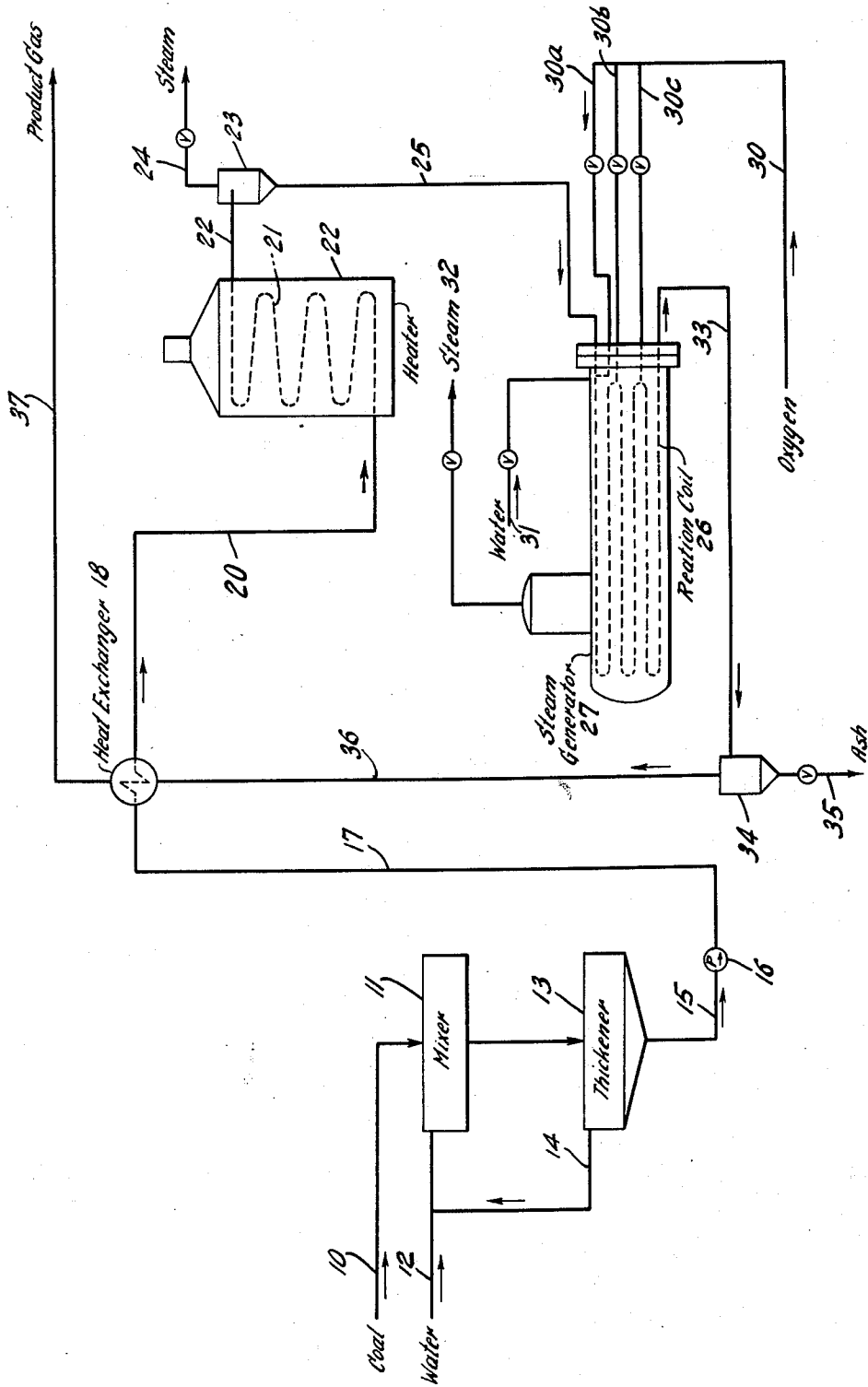


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MANUFACTURE OF SYNTHESIS GAS
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MANUFACTURE OF SYNTHESIS GAS

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This invention relates to a method for the gasification of solid carbonaceous fuels. In one of its more specific aspects it relates to the manufacture of synthesis gas from solid carbonaceous fuels.

The invention comprises a process for effecting gasification of solid carbonaceous fuels by reaction with oxygen under turbulent flow conditions in an elongated reaction zone of restricted cross-sectional area. According to the process of this invention, a dispersion of solid carbonaceous fuel in a gasiform carrier is mixed with uncombined oxygen and passed as a confined stream at a velocity in excess of about 50 feet per second, preferably in excess of 100 feet per second, through an elongated reactor of restricted cross-sectional area to effect reaction between said solid carbonaceous fuel and said oxygen and produce a gas comprising carbon monoxide and hydrogen.

The process of the present invention is especially useful in connection with the generation of carbon monoxide and hydrogen from solid carbonaceous fuels by partial oxidation. Coke, coal of various grades, for example, lignite, bituminous, and anthracite coals, oil sand, tar sand, and oil shale are suitable as fuels for the process. The mixture of carbon monoxide and hydrogen produced by this process may be used as a source of feed gas for the synthesis of alcohol or hydrocarbons, as a source of fuel gas, or for the manufacture of hydrogen useful for ammonia synthesis.

The gasification of solid fuels by reaction with oxygen and steam at temperatures above about 2000° F. is well known. Processes are well known for the gasification of a solid fuel maintained in a bed within the reaction zone wherein the fuel bed may be in the form of a stationary bed, a moving bed, or a bed of fluidized solids. More recently, means have been developed for the partial oxidation of solid carbonaceous fuels by reaction of said fuels with an oxygen containing gas in a closed unobstructed reaction zone at a temperature within the range of about 2000 to about 3500° F. such as is described in the co-pending application of Du Bois Eastman and Leon Gaucher Serial No. 490,214, filed February 24, 1955, now Patent No. 2,864,677. I have now found that coal may be gasified in a reaction zone having an exceptionally high ratio of length to diameter under conditions of highly turbulent flow at temperatures considerably below those heretofore employed.

For the sake of simplicity, in the following detailed description of the invention, the process will be described as applied to treatment of coal. The application of the present invention to solid carbonaceous fuels other than coal will be evident to one skilled in the art from the detailed description of this invention and the example of its application to coal.

In accordance with this invention, solid carbonaceous material is admixed with a carrier fluid and passed through a heating zone. Relatively coarse particles of solid material may be used. The suspension is passed as a confined stream in highly turbulent flow through a heat-

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ing zone maintained at an elevated temperature. Gases, vapors, or liquids may be used as the suspending medium; vaporizable liquids, particularly water and hydrocarbons and mixtures thereof, are preferred. Suitable gases include hydrocarbon gases, for example, methane, natural gas, refinery gases, synthesis tail gas, coal gas, hydrogen, carbon monoxide, carbon dioxide, nitrogen, steam, and mixtures composed of or comprising the above-mentioned gases. After preheating the dispersion of fuel particles in gasiform carrier fluid with little or no reaction taking place, uncombined oxygen, for example, air or oxygen in concentrated form, is mixed with the dispersion and the gasification reaction carried out as described in more detail hereinafter.

In a preferred embodiment, the solid fuel in particle form is admixed with a liquid which may be converted to vapor form on heating. Sufficient liquid is employed to form a slurry or suspension of the solid. The suspension is passed through a tubular heating zone, for example, a heating coil, wherein it is heated and substantially all of the liquid converted to vapor. A dispersion of powdered solid in vapor is formed in the heating step, and at the same time, some disintegration of the solid takes place. The extent of disintegration depends upon the characteristics of the solid, the length of the heating coil, and the velocity of the dispersion in the coil. Some volatile constituents may be distilled from the coal in the heating step. A gasiform dispersion of powdered solid in vapors is produced as the result of the heating step. The pulverization of solid materials by this method is covered by U.S. Patent 2,735,787 to Du Bois Eastman and Leon Gaucher. In the preparation of the dispersion, it is preferable to use particles less than about one-fourth inch in average diameter; smaller particle sizes are even more readily handled. Since disintegration of the coal may be accomplished in the preheater as taught in the patent to Eastman and Gaucher, this may be used to eliminate costly conventional mechanical pulverization. The solid fuel may be crushed mechanically to about one-fourth inch in average diameter with a relatively small expenditure of power. Further reduction in size becomes progressively more expensive, pulverization requiring large expenditures of power.

Numerous vaporizable liquids are suitable for the preparation of the suspension. Water and oils are preferred. Water, petroleum and coal oils, petroleum and coal distillates, and related organic compounds are preferred oils for use in the process. Specific examples of vaporizable liquids suitable for use in the present process include water; gasoline, kerosene, naphtha, and gas oil fractions of petroleum distillates; a light oil, middle oil or tar fraction of a coal distillate; aromatics, for example, benzene, toluene; paraffins, for example, hexane, heptane, and so forth; naphthenes, for example, cyclohexane and the like; hydroaromatics, for example, tetralin, decalin; and mixtures of these various liquids.

Water and oil mixtures, suitably in the form of emulsions, may be used in preparing the suspension. Various oils or tars may be used in conjunction with water in making up the suspension. An oil or tar fraction derived from the coal is especially useful in making up the suspension.

The quantity of liquid admixed with the coal to form the slurry may vary considerably depending upon process requirements and the feed material. A minimum of about one part water per part of coal by weight is required to form a slurry. The liquid content of a coal-water slurry, for example, may be controlled by first mixing the coal with a quantity of water in excess of the required quantity and adjusting the water content by removal of excess water in a conventional thickener. The slurry is readily pumpable with suitable equipment, e.g.,

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with a diaphragm type pump or similar equipment commonly used for handling similar suspensions of solids.

Substantial amounts of steam may be used in the production of hydrogen and carbon monoxide by reaction with oxygen at temperatures within the limits of this process. Some lignites already contain water in sufficient quantity to meet the theoretical steam requirements of the process.

The suspension is fed into the heated tube at a rate sufficient to maintain dispersion of the solid particles in the fluid. The linear velocity of slurry at the inlet to the heating coil should be within the range of from about one-half to about ten feet per second; suitably above about one foot per second. The velocity of gaseous dispersion of powdered coal and vapor, for example, at the outlet of the coil is within the range of from about 50 to about 500 feet per second, suitably above about 100 feet per second.

The temperature at the outlet of the heating coil may range from about 250 to 1400° F. The temperature should be at least sufficient to insure substantially complete vaporization of liquid present in the dispersion at the pressure existing in the heating zone. Preferably a temperature within the range of 600 to 1200° F. is attained at the outlet of the coil; a temperature in the neighborhood of 1000° F. is generally suitable.

The temperature and pressure relationships affecting vaporization are well known. The heating zone is at a pressure somewhat higher than the pressure of the associated reaction zone. In the generation of fuel or synthesis gas, it is desirable to operate the gasification step at an elevated pressure, for example, 100 to 600 pounds per square inch gauge. The heating step is operated at a pressure sufficient to effect flow through the tubular reaction zone.

Oxygen of relatively high purity, at least 80 mol percent and preferably at least 95 mol percent is used, thereby largely eliminating nitrogen from the reactant feed to the gas generator.

Oxygen is reacted with the powdered fuel in a tubular reaction zone. Turbulent flow conditions are maintained in the tubular reaction zone by imparting a velocity in excess of about 50 feet per second, preferably in excess of 100 feet per second to the reactants. The reaction pressure may range from about atmospheric to about 600 pounds per square inch gauge or higher. The reaction temperature is maintained in the range of about 1500 to about 2000° F. The temperature of the reaction zone may be controlled by cooling the external surface of the reaction zone or by introducing one of the reactants, preferably oxygen, at a plurality of points in the reaction zone, or both means of cooling may be employed. Advantageously, the exothermic heat of reaction may be employed for the generation of steam by disposing the tubular reaction zone within a steam generator. Alternatively, the heat of reaction may be employed for preheating gas or steam, for example, for superheating steam. A tubular reactor within a steam generator or superheater has several advantages in addition to the generation of useful steam. Advantageously, the steam generation pressure can be selected and controlled at a level such that the pressure of the steam generator balances the pressure within the tubular reaction zone and thereby substantially reduces the stress applied to the tubular reactor. The use of balanced pressures is particularly significant in view of the high temperatures employed in gasification.

An advantage of the process of this invention is that rapid and complete reaction is facilitated by the maintenance of turbulent flow conditions.

Another advantage of the process of this invention is that substantially complete reaction is effected at relatively low temperature. Under the low temperature reaction conditions employed, fusion of the ash present in coal is avoided. The deposition of a slag of ash on the

reactor surfaces is effectively avoided and the solid ash is readily separated from the gaseous products.

A further advantage of the process of this invention is that the reactor inherently provides a large contact surface for the reactants which facilitates the control of reaction temperature.

Another advantage of the use of a tubular reaction zone is that it may readily be disposed within a shell maintained at high pressure in order to balance the internal and external pressure.

Another advantage of the process of this invention is that exothermic reaction effects internal heating and the reaction zone may have a considerably higher temperature than the temperature of the tube wall which confines the reaction zone.

The accompanying drawing diagrammatically illustrates one form of the process of this invention. Although the drawing illustrates one arrangement of apparatus in which the process of this invention may be practiced, it is not intended to limit the invention to the particular apparatus or material described.

Coal feed 10, from an external source not shown, is introduced into mixer 11 wherein it is mixed with a vaporizable liquid such as water introduced through line 12 to form a slurry of coal and water. The resulting slurry is passed to thickener 13 wherein the concentrations of coal and water in the slurry are adjusted. Excess water is returned to the mixer through line 14. The resulting slurry is withdrawn from the thickener through line 15 and is forced by pump 16 through line 17 to heat exchanger 18 wherein the slurry is preheated by heat exchange with effluent products. Preheated slurry is then passed through line 20 to heating coil 21 disposed in heater 22.

In the heating coil the slurry is heated to a temperature sufficient to vaporize substantially all of the water. The resulting mixture of coal dispersed in steam is discharged from coil 21 through line 22 to separator 23. Separator 23 may be operated at substantially the same pressure as that existing at the outlet of the heating coil or at a somewhat lower pressure. A pressure drop at the outlet of the heating coil is helpful in disintegrating the coal. A portion of the steam is separated from the coal steam dispersion in separator 23 and is withdrawn through line 24 for external use. A dispersion of the coal in the remaining steam is withdrawn from separator 23 through line 25 and passed to tubular reaction coil 26 which is disposed in steam generator 27. Oxygen from an external source not shown in line 30 is introduced to the inlet of the reaction coil through line 30a. Additional oxygen to maintain and control reaction temperature to effect substantially complete conversion of the coal to synthesis gas is introduced as necessary through lines 30b and 30c at intermediate points within the reaction coil. Water is introduced to the steam generator through line 31 and is converted to steam which is discharged through line 32 for external use not shown. Effluent product from reaction coil 26 is discharged through line 33 and passes to ash separator 34 which may suitably be of the cyclone type. Ash is separated from the product gas in the separator and discharged from the system through line 35. The resulting product gas passes through line 36 to heat exchanger 18 where it supplies a part of the heat required for heating the slurry feed. Cool product gas from heat exchanger 18 is discharged through line 37 for further purification or use.

Example

Bituminous coal at a rate of 7,680 pounds per hour is crushed so that 70 percent passes through a 200 mesh screen. The crushed coal is combined in a mixer and thickener with 15.63 gallons per minute of steam con-

densate. The coal on a dry basis has the following ultimate analysis:

| | Weight percent |
|----------------|----------------|
| Sulfur ----- | 2.6 |
| Nitrogen ----- | 1.5 |
| Carbon ----- | 77.3 |
| Hydrogen ----- | 4.9 |
| Oxygen ----- | 5.4 |
| Ash ----- | 8.3 |

This slurry of coal and water is passed through a heat exchanger and externally fired tubular heater, at a heater inlet pressure of 1200 p.s.i.g., where it is heated to an exit temperature of 750° F. The resulting dispersion of coal in steam is passed through a cyclone separator where 4,500 pounds per hour of steam are separated and the remaining 3,300 pounds per hour of steam containing the original 7,680 pounds of coal are charged to a reaction coil. Oxygen of 95 percent purity at a temperature of 300° F. is added at a rate of 78,000 standard cubic feet per hour to the coal-in-steam dispersion.

This mixture of reactants is passed through the reaction coil at an average linear velocity of 450 feet per second. Reaction takes place between the oxygen, steam and coal to produce gaseous products comprising principally carbon monoxide and hydrogen. The exothermic heat of reaction is absorbed by the generation of steam in a steam generator which surrounds the reaction coil and maintains the temperature of the reactants in the coil at about 1625° F. The effluent from the reactor coil is directed to a cyclone where ash and unconverted coal is separated in the amount of 966 pounds per hour from the gaseous products. After suitable heat exchange and cooling for the condensation of unreacted steam, a dry synthesis gas is produced in the amount of 280,000 standard cubic feet per hour having the following analysis:

| Constituent: | Mol percent |
|--------------------------------------|---------------|
| Carbon monoxide ----- | 56.0 |
| Hydrogen ----- | 33.3 |
| Carbon dioxide ----- | 7.1 |
| Methane ----- | 0.5 |
| Nitrogen and argon ----- | 2.3 |
| Hydrogen and carbonyl sulfides ----- | 0.8 |
| Total ----- | 100.00 |

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

I claim:

1. A process for the gasification of a solid carbonaceous fuel which comprises forming a slurry of particles of said carbonaceous fuel in water, passing said slurry as a confined stream through an externally heated elongated heating zone to vaporize substantially all of the water in said slurry and to form a dispersion of particles of said carbonaceous fuel in steam, withdrawing said dispersion from the heating zone at a velocity of at least 50 feet per second, introducing the particles of solid carbonaceous fuel dispersed in steam into an elongated reaction zone, introducing gas comprising uncombined oxygen into the reaction zone with the dispersion, imparting a velocity in excess of about 50 feet per second and at least as great as the velocity at which the dispersion is removed from the heating zone to the resulting stream

of particles dispersed in steam and said gas in the elongated reaction zone to effect highly turbulent flow in the reaction zone, passing the stream of solid particles dispersed in steam and said gas through said elongated reaction zone at a pressure within the range of about atmospheric to about 600 p.s.i.g. and at an autogenous temperature within the range of from about 1500° F. to about 2000° F. thereby effecting a reaction between said uncombined oxygen and substantially all of said solid particles of said dispersion to yield a product gas comprising hydrogen and carbon monoxide, said velocity in excess of about 50 feet per second being maintained in the reaction zone until said reaction is substantially complete and discharging product gas comprising carbon monoxide and hydrogen from said reaction zone.

2. The process of claim 1 in which said product gas is passed in indirect heat exchange with said slurry to preheat the latter before it is introduced into the heating zone.

3. The process of claim 1 in which the slurry is formed at substantially atmospheric pressure and is passed to the heating zone at superatmospheric pressure.

4. A process for the gasification of a solid carbonaceous fuel which comprises forming a slurry of particles of said carbonaceous fuel in water, passing said slurry as a confined stream through an externally heated elongated heating zone to vaporize substantially all of the water in said slurry and to form a dispersion of particles of said carbonaceous fuel in steam, withdrawing said dispersion from the heating zone at a velocity of at least 50 feet per second, introducing the particles of solid carbonaceous fuel dispersed in steam into an elongated reaction zone, introducing gas comprising uncombined oxygen into the reaction zone with the dispersion, imparting a velocity in excess of about 100 feet per second and at least as great as the velocity at which the dispersion is removed from the heating zone to the resulting stream of particles dispersed in steam and said gas in the reaction zone to effect highly turbulent flow in the reaction zone, passing the stream of solid particles dispersed in steam and said gas through said elongated reaction zone at a pressure within the range of about atmospheric to about 600 p.s.i.g. and at an autogenous temperature within the range of from about 1500° F. to about 2000° F. thereby effecting reaction between said uncombined oxygen and substantially all of said solid particles of said dispersion to yield a product gas comprising hydrogen and carbon monoxide, said velocity in excess of about 100 feet per second being maintained in the reaction zone until said reaction is substantially complete and discharging product gas comprising carbon monoxide and hydrogen from said reaction zone.

5. The process of claim 4 in which the internal and external pressure of the reaction zone are substantially equal.

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