

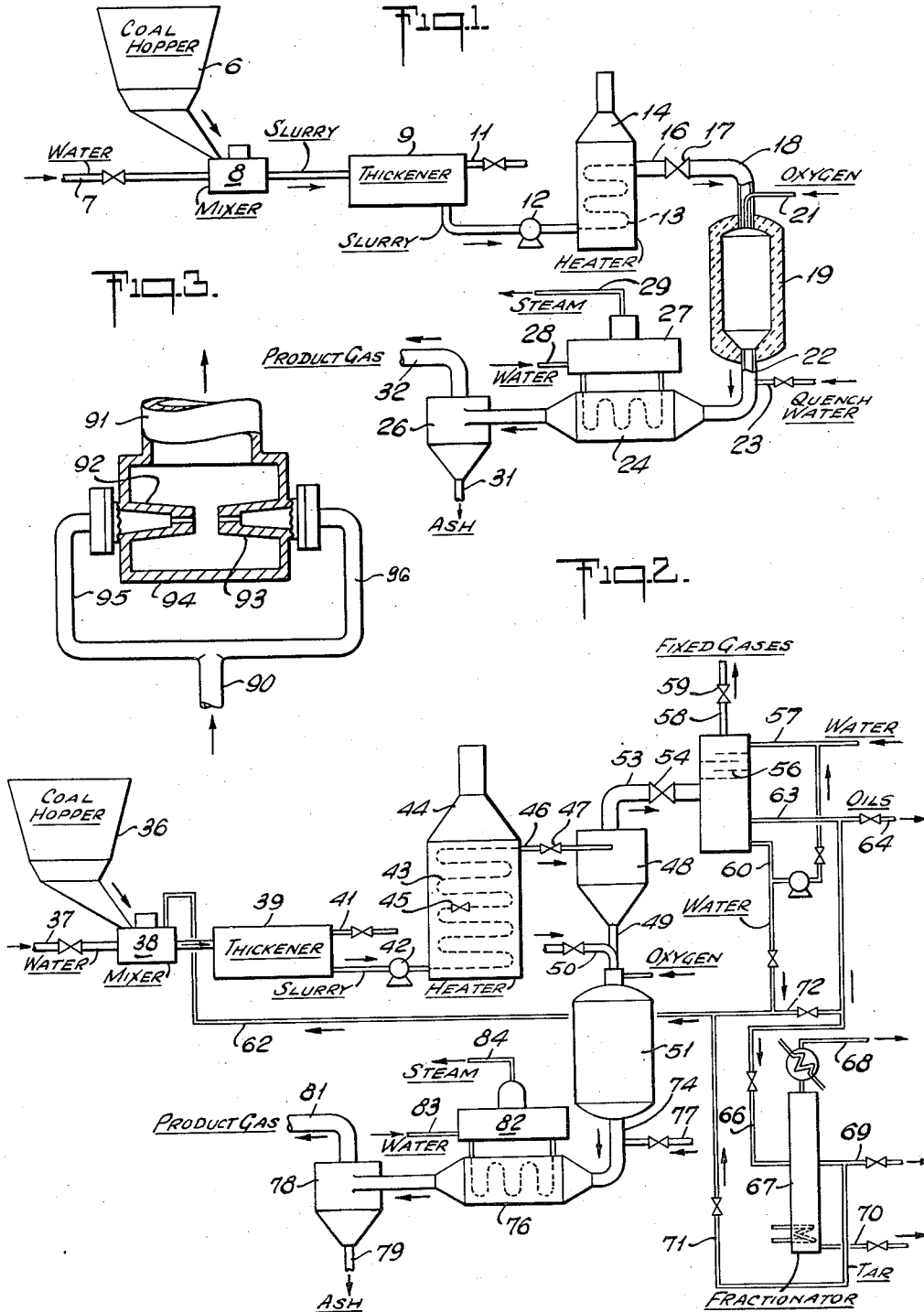
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DU BOIS EASTMAN ET AL

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GASIFICATION OF SOLID CARBONACEOUS MATERIALS

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GASIFICATION OF SOLID CARBONACEOUS MATERIALS

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11 Claims. (Cl. 48—206)

This invention relates to a process for the treatment of solid carbonaceous materials. The process of this invention is particularly applicable to the treatment of solid carbonaceous materials containing volatilizable constituents.

The invention comprises a process for effecting conversion of solid carbonaceous material, and particularly hydrocarbons or other compounds containing carbon and hydrogen, into carbon monoxide and hydrogen by reaction with oxygen under superatmospheric pressure and at relatively high temperature substantially without carbon formation and also with relatively little formation of carbon dioxide and water.

This invention involves a novel method for reducing the particle size of coal and similar carbonaceous materials without resorting to conventional grinding or pulverizing operations.

Another feature of this invention is a novel method for the carbonization of carbonaceous materials containing volatilizable constituents.

In one of its more specific aspects, this invention relates to a process for the generation of a mixture of carbon monoxide and hydrogen, suitable as a source of gaseous fuel or as a source of feed gas for the synthesis of hydrocarbons from coal.

The process of the present invention is especially useful in connection with the generation of carbon monoxide and hydrogen from solid carbonaceous materials by partial oxidation. As applied to the gasification of solid fuels, this invention is particularly suited to the production of a mixture of carbon monoxide and hydrogen which may be used as a source of feed gas for the synthesis of hydrocarbons or as a source of fuel gas.

The gasification of solid fuels by simultaneous reaction with oxygen and steam at elevated temperatures is fairly well known. This type of gasification has been previously carried out successfully at temperatures above about 2,000° F. in reactors containing a large excess of carbon. The solid fuel is generally maintained in a stationary, moving, or dense phase fluidized bed. Due to previous heat treatment, the solid fuel undergoing reaction is substantially completely, if not entirely, in the form of coke or char consisting essentially of carbon and ash. Thus, the steam and oxygen are reacted with coke or char, rather than with raw coal. A number of the commercially attractive fuels are coals containing volatile matter and often having caking tendencies. Caking coals impose a problem in gasification and severely limit the field to which many processes may be applied. Caking tendencies may be eliminated by various treatments. Removal of the volatilizable constituents by distillation, or coking, is generally most satisfactory but costly. The process of the present invention may be used for the gasification of caking type coals without previous coking of the coal.

An object of this invention is to provide an improved process for reducing the particle size of coal and similar carbonaceous materials.

Another object of this invention is to provide an im-

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proved process for the carbonization of carbonaceous materials containing volatilizable constituents.

Still another object of this invention is to provide an improved process for the gasification of solid carbonaceous materials.

A further object is to provide a process for the generation of a mixture of carbon monoxide and hydrogen from solid carbonaceous materials.

A still further object of this invention is to provide improved apparatus for the generation of carbon monoxide and hydrogen from solid carbonaceous materials.

Various solid carbonaceous fuels may be used in the process, e. g., coals, lignite, and the like. 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 feed materials other than coal will be evident to one skilled in the art from the detailed description of this invention and the illustrative examples of its application to coal.

In accordance with this invention, solid carbonaceous material is admixed with a vaporizable liquid and passed through a heating zone. Relatively coarse particles of solid material may be used. The suspension is passed through a heating zone as a confined stream in highly turbulent flow. The heating zone is maintained at an elevated temperature.

In a preferred embodiment, the solid fuel, coal, for example, 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 wherein it is heated to a temperature at least sufficient to convert substantially all of the liquid to vapor. The heating step serves to disintegrate the carbonaceous solid and to form a dispersion of powdered solid in vapor. Volatile constituents may be distilled from the coal in the heating step thereby carbonizing the coal. A gasiform dispersion of powdered solid in vapors is produced as the result of the heating step.

The method of pulverizing solid materials disclosed herein is claimed in our copending application, Serial No. 348,642, filed April 14, 1953, now U. S. Patent 2,735,787.

The powdered carbonaceous solid so produced may be subjected to gasification by reaction with oxygen and steam. Product gas from the gasification reaction may be used as fuel gas or as a source of feed gas for the synthesis of hydrocarbons and oxygenated hydrocarbons.

Numerous vaporizable liquids are suitable for the preparation of the suspension. Water and oils are preferred. 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, e. g., benzene, toluene; paraffins, e. g., hexane, heptane, etc.; naphthenes, e. g., cyclohexane and the like; hydroaromatics, e. g., tetralin, decalin; and mixtures of these various liquids.

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 and are completely vaporizable in the sense in which the term is used herein.

Deposition of coke on the interior surface of the heating coil is minimized by the mechanical action of the solids.

Water and oil mixtures, suitably in the form of emul-

sions, 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. In one embodiment of the process of this invention, volatile constituents distilled from the coal in the heating step are recovered and a suitable fraction used in conjunction with water in making up the slurry. An emulsifying agent may be used as an aid in forming an emulsion of the oil and water in making up the slurry.

Vapors resulting from the volatilization of volatilizable constituents are present in admixture with the vapors generated from the liquid on heating of the slurry. Vapors from the liquid and vaporized volatile constituents from the coal may be separated from the residual carbonaceous solid and desirable components recovered therefrom. The volatile constituents distilled from the feed material are useful for the production of high anti-knock motor fuels, solvents, chemicals, etc., as is known in the art.

The powdered solid particles resulting from the heating step may find use in applications other than as a feed material for gas generation. The powdered solid is an excellent fuel for use in industrial boilers. It may be formed into briquettes to produce a dustless, smokeless fuel for general use. A number of other uses will suggest themselves to those skilled in the art.

A portion of the powdered carbonized material resulting from the heating step may be returned for use in making up the feed slurry. This powdered material aids in reducing the deposition of coke on the heating equipment. Also, because of its state of subdivision, the powdered carbonized material aids in forming a homogeneous mixture when oils are used with the water in forming a slurry.

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

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 (2,000° F.-3,500° 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 requirements is not detrimental in the present process. 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 feed material for the present process. Anthracite silt is a term applied to the fine particles of coal and associated impurities, obtained in the mining and in the breaking, sizing and washing of anthracite. At the present time, anthracite silt represents an undesirable, but inevitable, waste. In mining the coal, large quantities are often found already crushed in the seam due to folding and faulting. The drilling, cutting, and blasting operations on the face of the seam produce a certain amount of fines. When the floor of the chamber slopes steeply, considerable attrition occurs as the coal tumbles down to the loading point. Additional breakage occurs each time the

coal is handled as, for example, when the coal is loaded and unloaded from cars and during its handling in the breaker. In the breaker, the coal is passed over screens for sizing purposes. The coal is washed to remove fines, dust and dirt; these also form a part of the anthracite silt. The dirt or incombustible material associated with the coal increases the ash content of the silt over that of the marketable coal. Silt commonly has an ash content of 10 to 30 weight percent. It is estimated that some 200 million tons of good-grade anthracite silt has accumulated in disposal piles and that some 8 to 10 million tons per year are currently produced. This waste material is an important potential source of gaseous and liquid fuels and organic chemicals.

The size of the coal particles fed to the heating step is not of especial importance to the successful operation of the invention. Particles of a size which may be passed through the conduits without difficulty may be used, e. g., particles having an effective diameter less than one-third the pipe diameter. It is preferable to use particles less than about one-half inch in average diameter; smaller particle sizes are even more readily handled. However, since the heating of the slurry results in disintegration of the coal as a result of attrition in the heater, this process may be used to eliminate costly pulverization by mechanical means. 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 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.

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 200 mesh, the bulk of the material falling within the range of $\frac{3}{32}$ inch to 100 mesh.

The slurry may be made up some distance from the processing site and pumped to the site in a pipeline. An excess of liquid may be used in transporting the coal through the pipe line and the concentration adjusted to the desired value prior to feeding the slurry to the process.

The suspension is conveniently heated by passing it through an elongated externally heated zone of restricted cross-sectional area, most suitably a tubular heating zone. The heating may be carried out in a coil or pipe-still type furnace such as those commonly used for heating liquid streams in the refining of petroleum. 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 about one foot per second. The velocity of gaseous dispersion of powdered coal and vapor, e. g., at the outlet of the coil is within the range of from about 25 to about 500 feet per second, suitably about 60 feet per second.

The temperature at the outlet of the heating coil may range from about 250 to 2,000° 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 1,400° F. or higher is attained at the outlet of the coil; a temperature in the neighborhood of 1,000° F. is generally suitable. 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. The distillation of volatilizable materials is also dependent to some extent on the amount of water in the slurry,

larger amounts of water tending to increase the amount of distillation.

The method of distilling volatilizable constituents from coal as disclosed herein is claimed in our copending application, Serial No. 285,246, filed April 30, 1952, now U. S. Patent 2,761,824.

Pressure, in itself, is not critical in the heating step. The temperature and pressure relationships affecting vaporization are well known. Generally, it is desirable to operate the heating zone at a pressure somewhat higher than the operating pressure of associated processes. In the generation of fuel or synthesis gas, for example, it is often desirable to operate the gasification step at an elevated pressure, for example, 100 to 600 pounds per square inch, often 200 to 300 p. s. i. The heating and pulverizing step of this invention may be operated at a pressure sufficiently above the generator pressure to insure flow to the generator. Generally 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 drop the pressure suddenly in the heating zone or at its outlet to increase the vaporization and disintegration actions of the heating step.

While considerable grinding of the solid particles takes place when the dispersion simply flows at high velocity and turbulently through a long unobstructed tube, it has been found that erosion difficulties are minimized by flowing the dispersion at a relatively low velocity through such a tube and then increasing the turbulence and absolute velocity of particles, or their relative velocities with respect to one another, in a localized zone. One way proposed for locally increasing absolute velocity is to pass the dispersion through a convergent-divergent nozzle at supersonic velocity while the velocity upstream of the nozzle is maintained relatively low, such as 100 feet per second or less, to prevent erosion. Another procedure for locally increasing relative velocities is to divide the slurry stream or the flowing dispersion stream into two parts, and then to impinge the resulting two flowing streams of dispersion against one another at high velocity by passing them through a pair of nozzles which are opposed to one another at 180°, more or less, as described in U. S. 2,846,150.

The process of the present invention is particularly adapted to the gasification of coal by reaction with steam and oxygen. Gasification with steam and oxygen may be employed to produce hydrogen, carbon monoxide, or mixtures of hydrogen and carbon monoxide suitable as a source of fuel gas or as a source of feed gas for the synthesis of hydrocarbons and oxygen-containing compounds. Pulverization and preheating of the coal, and generation and preheating of the steam are accomplished in the single heating step of this invention. Additionally, the coal is subjected to distillation conditions. All of the products of the heating step may be fed into a generator for the production of carbon monoxide and hydrogen. Alternatively, part or all of the vapors may be separated from the powdered solid before it is fed into the generator.

Oxygen of relatively high purity, at least 80 mol percent and preferably at least 95 mol percent, preferably is used, thereby eliminating a large amount of nitrogen from the reactant feed to the gas generator. This materially reduces the heat requirements and also results in a synthesis gas more suitable for the synthesis operation.

The proportion of oxygen charged to the gas generator relative to the hydrocarbon feed appears critical from the standpoint of avoiding free carbon production and excessive carbon dioxide and water formation. Suitable conditions of operation are realized at the preferred temperatures above a minimum of 2,000° F. by initially regulating the oxygen charged to the generator, or as it

can be otherwise stated, the O/C ratio (atomic ratio of total oxygen to total carbon in the feed) within the limits of approximately 1.0 to 2.0, and adjusting the O/C ratio within these limits, so that the residual methane content of the effluent gas from the generator is in the range of 0.05 to 5 mol percent. This principle applies whether the O be from substantially pure oxygen, an oxygen-enriched gas or air and the C be from a solid hydrocarbon as coal, a liquid hydrocarbon as fuel oil or a gaseous hydrocarbon as natural gas.

The total oxygen requirements for the generator, that is, oxygen from the steam as well as free oxygen, must be at least 10 percent in excess of the amount theoretically required to convert the carbon content of the solid fuel to carbon monoxide. In general, satisfactory operation may be obtained with a total oxygen supply of 10 to 80 percent in excess of the theoretical requirements. As the steam preheat temperature is increased, the free oxygen requirements decrease. In general, however, it is necessary to use from about 0.4 to about 1.0 pound free oxygen per pound of coal. From about 0.3 to about 2.0 pounds of steam per pound of coal may be used.

Mixing of the reactants is accomplished entirely within the reaction zone by introducing the separate streams of fuel and oxygen so that they impinge upon each other within the reaction zone while flowing at high velocity, i. e., 100 feet per second or in the range of about 30 to 200 feet per second. Mixing of the reactants in the gas generator may be effectively accomplished by introducing a stream of oxygen and a stream of steam containing powdered coal into contact with one another at relatively high velocity. Inlet velocities of 100 to 200 feet per second give satisfactory mixing with the streams introduced through concentric tubes.

It is preferable to preheat the reactants to a temperature above about 600° F. The oxygen is preferably preheated to a temperature of 600 to 800° F. and the steam and coal, to 600 to 1,200° F. or higher.

Contrary to previous reports to the effect that particles smaller than about 0.05 mm. (50 microns) in diameter tend to escape gasification because of insufficient motion relative to the gaseous reactants, an impalpable powder is preferred for the present process. Particles of solid fuel on the order of 40 microns and smaller are very suitable for gasification; advantageously the largest particles should not exceed 150 microns in average diameter. Pressure is favorable to the gasification reaction. Pressures may range as high as 5,000 to 20,000 p. s. i. g. Contrary to general opinion, elevated pressures on the order of 100 to 600 p. s. i. g. do not result in the production of methane to any appreciable extent. A residence time of the coal particles in the gasification zone of at least one second is required for effective carbon utilization at temperatures of 2,000 to 3,500° F. Substantially complete carbon consumption is obtained with 2 seconds reaction time or residence time at pressures in the range of 100 to 500 pounds per square inch and temperatures of 2,200 to 2,600° F. At higher temperatures, the reaction time is less than at the lower temperatures. With air as the source of free oxygen a somewhat longer residence time is required than is the case with substantially pure oxygen.

The separation of gases or vapors from powdered solid may be effected in a number of ways. Cyclone type separators, filters, and the like are generally effective. A Cottrell precipitator may be used for removal of fine particles. A spray tower is effective for removal of part or substantially all of the condensable vapors and more or less powdered solid, as desired.

Important advantages result from the method of handling the raw coal in the process of this invention. As a dispersion, the coal is readily transported and subjected to elevated pressure. Since the dispersion may be handled as a liquid, troublesome lock hoppers and similar devices are eliminated and replaced simply by the slurry mixer

and pump. The quantity of coal fed to the process thus may be accurately metered.

When the carbonaceous material from the heater is fed directly to a gasification zone, it is advantageous to operate the heater at a pressure corresponding to or slightly higher than the pressure in the gasifier. A generator or gasification zone operated with the powdered coal as feed suitably is operated at a pressure within the range of from about 100 to 600 pounds per square inch, but generator operating pressures are not limited to this range.

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 process, coal is taken as a preferred fuel, water as a preferred liquid for forming the dispersion, and gasification of the resulting powder with oxygen as a preferred modification of the invention.

Fig. 1 of the drawing is a diagrammatic elevational view showing a suitable arrangement of apparatus for carrying out one modification of the process of this invention.

Fig. 2 is a diagrammatic flow sheet illustrating an arrangement of apparatus suitable for carrying out the process of the present invention in accordance with a second modification.

Fig. 3 is a fragmentary sectional view illustrating an arrangement of nozzles effective for sudden pressure reduction with localized high velocity and extreme turbulence resulting in pulverization of the solid particles.

With reference to Fig. 1, coal from a storage hopper 6 and water from line 7 are admixed in a mixer 8 to form a slurry of coal and water. The resulting slurry is passed to a thickener 9 of conventional design wherein the concentrations of water and coal in the slurry are adjusted. Excess water may be discharged from the thickener through line 11, from which it may be returned to the mixer 8. The resulting slurry is withdrawn from the thickener to pump 12, and forced under pressure through heating coil 13 disposed within a furnace 14.

In the furnace, the slurry is heated to a temperature sufficient to vaporize substantially all of the water. The resulting mixture of steam and powdered carbonaceous material is discharged from the coil 13 through line 16. The pressure in the furnace may be controlled by valve 17. Heating the slurry serves to generate steam and at the same time disintegrate the coal particles to form a dispersion of powdered coal in steam at the furnace outlet.

The mixture of powdered coal and steam is passed through line 18 into a synthesis gas generator 19. The synthesis gas generator comprises a pressure vessel provided with a refractory lining and an essentially unobstructed reaction space. The generator is capable of operating at elevated temperatures and pressures. Oxygen for the reaction is supplied through line 21 and passed into admixture with the steam and coal. The resulting products of reaction, comprising carbon monoxide and hydrogen, are discharged from the generator through line 22. Ash from the coal in either solid or molten form is also discharged through line 22.

The generator preferably is of the type disclosed in our U. S. Patent No. 2,582,938. As disclosed in detail in said application, the inverse ratio of the internal surface of the generator to the surface of a sphere of the same volume is at least 0.65. Otherwise stated, the reaction zone is substantially unobstructed and generally cylindrical with a length to radius ratio of about 0.67 to 10. Otherwise stated, the internal surface area of the reaction zone is not more than about 1.5 times the area of the surface of a sphere of equal volume.

Water may be admitted into line 22 through line 23 for the purpose of cooling the reaction products. When operating at temperatures above the fusion point of the residue it is desirable to quench to a temperature below

the solidification point of the ash. Ash as a finely divided solid entrained in the product gas stream is carried with the gases through a heat exchanger 24 to a separator 26.

The heat exchanger 24 suitably is in the form of a waste heat boiler wherein the heat from the reaction products are used to generate steam. Water is supplied to the steam chest 27 of the boiler through line 28. Steam produced by the boiler is discharged through line 29.

The separator 26 may suitably be of the cyclone type. Ash is separated from the product gas in the separator and discharged from the system through line 31. The resulting product gas passes through conduit 32 for use as fuel gas or as a source of feed material for the synthesis of hydrocarbons and oxygen containing organic compounds. The product gas stream may be subjected to further purification operations for removal of ash, sulfur, carbon dioxide, etc.

With reference to Fig. 2, coal from hopper 36 is admixed with water from line 37 in mixer 38. The mixture of coal and water is passed to the thickener 39 where the concentration of solids and liquid in the resulting slurry is adjusted. Excess water is drawn off from the thickener by line 41 from which it may be returned, if desired, to the mixer. The slurry is passed by pump 42 through heating coil 43 in furnace 44. A restriction 45 may be provided in heating coil 43 to permit operation of the latter portion of the coil, relative to flow therethrough, at a pressure somewhat lower than the first portion of the coil. Operation in this manner is sometimes advantageous in that expansion and rapid vaporization may take place as a result of pressure reduction at the restriction. The gasiform stream of steam and powdered coal resulting from the action of the heating coil, is discharged from the heating coil through line 46, provided with a valve 47, and passed into a separator 48.

The separator 48 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 heater is helpful in disintegrating the carbonaceous material. The powdered solid carbonaceous material is separated from at least a portion of the steam and vapors in separator 48 and discharged therefrom through line 49.

Powdered solid carbonaceous material from separator 48, together with sufficient steam for reaction with the carbonaceous material, is passed through line 49 into gas generator 51. If desired, a supplemental carrier gas or gaseous reactant, e. g., tail gas from a hydrocarbon synthesis operation, may be admitted through line 50 into admixture with the solid feed material to the generator. The generator is similar to the generator 19 of Fig. 1. Oxygen for the gasification reaction is supplied to the generator through line 52 into admixture with the steam and solid reactants.

The steam and other vapors separated from the carbonized material are discharged from the separator 48 through line 53. The control of the quantity of steam and vapors passed with the solid carbonized material to the gasification zone is effected by valve 54. From line 53 the gases are discharged into scrubber 56 preferably operated at an elevated pressure.

The scrubber may suitably be a tray type contacting tower wherein the gases are countercurrently contacted with the water. Water is introduced into the scrubber through line 57 at a point near the top of the tower. Fixed gases which may comprise nitrogen and methane are discharged from the scrubber through line 58. The pressure on the scrubber, and if desired, the pressure on the separator 48 and heating coil 43, is controlled by means of a regulating valve 59.

In the scrubber the tar and readily condensable oils distilled from the coal are condensed. Water is withdrawn from the bottom of the scrubber through a line 60 from which it may be recycled to the scrubber through line 61 or passed through line 62 to the mixer 38 for use in making up slurry. The condensed volatile constituents

vaporized in the coil 43, are withdrawn separately as an oil layer from the scrubber through line 63. These oils may be passed through line 64 to storage.

The oils may be passed through line 66 into a fractionation column 67 wherein they are separated into desired fractions, such as a motor fuel fraction, a light oil fraction and a tar fraction; the various fractions being withdrawn from the fractionator through lines 68, 69 and 70, respectively.

A fraction of the oils, for example, the light oil fraction, may be passed to the mixer 38 via lines 71 and 62 for use in making up the feed slurry. Alternatively, a portion of the unfractionated oil product may be passed via line 72 into line 62 and returned to the mixer.

Product gases from the gasification zone are discharged through line 74 into a heat exchanger 76. Water may be supplied to line 74 through line 77 to quench the product gas as described hereinabove in connection with Fig. 1. The residual solid particles comprising mainly ash are separated from the gas stream in separator 78. The ash is discharged through line 79 and product gases disposed of by way of conduit 81. The heat exchanger 76 is preferably in the form of a waste heat boiler with water supplied to the boiler 82 through line 83. Steam generated by the waste heat boiler is discharged from the steam drum through line 84.

Valves 17, 45 and 46 may take the form of orifices, chokes, or nozzles, e. g., venturi nozzles. Fig. 3 illustrates a preferred arrangement of nozzles which may be employed as valve 17 in line 16 of Fig. 1, as valve 45 in heating coil 43, and as valve 47 in line 46. When the opposed nozzle arrangement of Fig. 3 is employed, the dispersion is introduced through inlet 90 and discharged through outlet 91. A pair of nozzles 92 and 93 are arranged to deliver opposed jets of the dispersion at extremely high relative velocity against one another. As illustrated, the nozzles are directed toward one another at an angle of 180°, i. e., they are directly opposed to one another. Although the illustrated arrangement is a preferred one, the nozzles may be arranged so that the jets impinge on one another at an angle of less than 180°; preferably the included angle is at least 90°. More than two nozzles may be arranged so that the jets impinge at a common point. The nozzles are preferably directed so that the point of impingement, measured along the axis of the jet, is not more than 1 inch from the end of the nozzle. The nozzles discharge into chamber 94 in which the high velocities of the jets are largely dissipated, disintegrating the solid particles. Nozzles 92 and 93 should have a relatively small bore or orifice, for example, $\frac{3}{8}$ inch in diameter. The dispersion is supplied to nozzles 92 and 93 at equal pressures by conduits 95 and 96.

In the foregoing detailed description of the invention as illustrated in the figures, the powdered carbonized material is used as feed material for the generation of carbon monoxide and hydrogen by reaction with steam and oxygen. While this is a preferred use for the carbonized material produced in accordance with this invention, it is to be understood that the powdered carbonized material may find other uses.

Example I

Crushed sub-bituminous coal of the following composition was used as feed in carrying out the process of the present invention.

	Weight percent
Carbon	64.86
Water	11.77
Hydrogen	4.69
Oxygen	10.12
Nitrogen	1.14
Sulfur	0.80
Ash	6.62
Heating value, as received, 11,530 B. t. u. per pound.	

Screen analysis (Tyler standard scale):

15.0 wt. percent retained on 40 mesh.
43.2 wt. percent retained on 100 mesh.
9.2 wt. percent retained on 150 mesh.
9.4 wt. percent retained on 200 mesh.
2.0 wt. percent retained on 250 mesh.
4.8 wt. percent retained on 325 mesh.
16.4 wt. percent retained thru 325 mesh.

This coal was mixed with water to form a slurry. The coal and water were fed to the system at the rate of 147 pounds of coal per hour and 273 pounds of water per hour. The slurry was pumped at an inlet pressure of 400 pounds per square inch gauge through a heating coil $\frac{1}{2}$ inch in diameter and 104 feet long.

The mixture of coal and water was heated in the coil to a temperature of 650° F. and the resulting mixture of coal particles dispersed in steam was fed into a gas generator operated at 280 pounds per square inch gauge. The coal was dispersed in the steam in the form of very finely divided powder. The dispersion presented the appearance of a brown fog.

Oxygen at 80° F. was fed into the generator at the rate of 1625 standard cubic feet per hour. The generator operated at 280 pounds per square inch gauge and 2350° F. Ash was recovered from the product as finely divided fly ash by quenching with water.

Product gas of the following composition was produced at the rate of approximately 5200 standard cubic feet per hour:

	Percent by volume
Carbon monoxide	24.2
Carbon dioxide	29.0
Hydrogen	45.6
Nitrogen	0.7
Methane	0.5

Several parallel runs indicated that conversion rates by this process are comparable to those in which natural gas is used in the generation of carbon monoxide and hydrogen. Allowable heating temperatures for the slurry appear to be limited only by the tube metal. The runs also indicate that fine grinding of the coal is not necessary.

Example II

Crushed Colorado bituminous coal from the Somerset Mine in Gunnison County, Colorado, of the following composition is used as feed to carry out our novel process:

Components:	Weight percent
Ash	9.3
Sulfur	0.4
Hydrogen	5.5
Carbon	70.6
Nitrogen	1.5
Oxygen	12.7
Total	100.0
Heating value, as received, 12,627 B. t. u. per lb.	

Crushed particles of this coal, having a maximum size of about $\frac{1}{8}$ inch, are mixed with Santa Maria Valley Crude Petroleum Residuum of 10° API gravity in proportions of 1:1 by weight to form a slurry. The slurry of coal in hydrocarbon oil is pumped at an inlet pressure of 1,200 pounds per square inch gauge through an externally fired heating coil 600 feet in length at a rate of 6,528 pounds per hour.

The slurry of coal in oil is heated in the coil to a temperature of 700° F., and the resulting dispersion of coal particles in oil vapors is fed into a gas generator operated at 250 pounds per square inch gauge and 2,500° F.

A flowing stream of gaseous oxygen, 95 percent pure, at 600° F. is concurrently fed into the generator at a rate of 66,300 standard cubic feet per hour. At the same

time, a flowing stream of steam at a temperature of 750° F. is fed into the generator at a rate of 1,546 pounds per hour.

Product gas issues from the generator at a rate of 326,400 standard cubic feet per hour, is quenched with water, and then has the following composition:

	Mol percent—dry basis
Hydrogen	39.7
Carbon monoxide	52.2
Carbon dioxide	4.1
Methane	2.6
Nitrogen	1.4

This application is a continuation-in-part of our application Serial No. 461,893, filed October 12, 1954, and now abandoned. Said application Serial No. 461,893 was a continuation-in-part of our application Serial No. 49,626, filed September 16, 1948, and now abandoned. Said application Serial No. 49,626 was a continuation-in-part of our application Serial No. 717,267, filed December 19, 1946, and now abandoned.

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.

We claim:

1. In a process for the generation of carbon monoxide and hydrogen from a solid carbonaceous fuel by partial oxidation in an unpacked reaction zone wherein said solid fuel in fine particle form is reacted with free oxygen and steam while suspended in gaseous reactants and reaction products at a pressure within the range of from about 100 to about 600 pounds per square inch gauge and at a temperature within the range of from about 2000 to about 3500° F., the improvement which comprises forming a fluid slurry of solid fuel particles in a vaporizable liquid reactant selected from the group consisting of water and liquid hydrocarbons, introducing said slurry as a continuous stream into an externally heated tubular heating zone at a linear velocity of at least one-half foot per second, effecting vaporization of substantially all of said liquid from said slurry within said heating zone at an elevated pressure in excess of the pressure in said reaction zone thereby forming a stream of dispersion of said solid particles in resulting vapor moving at a velocity in excess of about 25 feet per second, and passing said stream of dispersion into said reaction zone into intimate admixture with gas containing free oxygen at a velocity in excess of about 30 feet per second.

2. A process according to claim 1 wherein said vaporizable liquid is water and said vapor is steam.

3. A process according to claim 1 wherein said vaporizable liquid is a liquid hydrocarbon.

4. A process according to claim 1 wherein said vaporizable liquid is a mixture of water and liquid hydrocarbon.

5. A process according to claim 1 wherein vapor is separated from said dispersion prior to passing dispersion into said reaction zone.

6. A process according to claim 1 wherein said solid fuel is coal.

7. A process according to claim 1 wherein said coal contains volatilizable constituents which are distilled therefrom in said heating zone and oil so separated is admixed with said particles of said solid fuel feed as at least a portion of said vaporizable liquid employed in forming said slurry.

8. A process according to claim 1 wherein said particles of solid fuel are subjected to disintegration by impinging at least two streams of said dispersion upon one another at an angle of at least 90° and with a velocity of each of said streams in excess of 100 feet per second thereby effecting fragmentation of said particles by impact upon one another, and resulting pulverized solid dispersed in vapor passed into said reaction zone.

9. A process as defined in claim 8 wherein said streams of dispersion impinge upon one another at an angle of 180°.

10. A process as defined in claim 1 wherein product gas from said reaction zone is cooled by heat exchange with water to produce steam.

11. A process according to claim 1 wherein said stream of dispersion passed to said reaction zone is at a temperature within the range of 600 to 1400° F.

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