

[54] FUEL GAS FROM SOLID CARBONACEOUS FUELS

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[58] Field of Search: 48/201, 202, 210, 215, 48/197 R

[56] References Cited

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| 3,607,157 | 9/1971 | Schlinger | 48/202 |
| 3,715,195 | 2/1973 | Tassoney et al. | 48/197 R |
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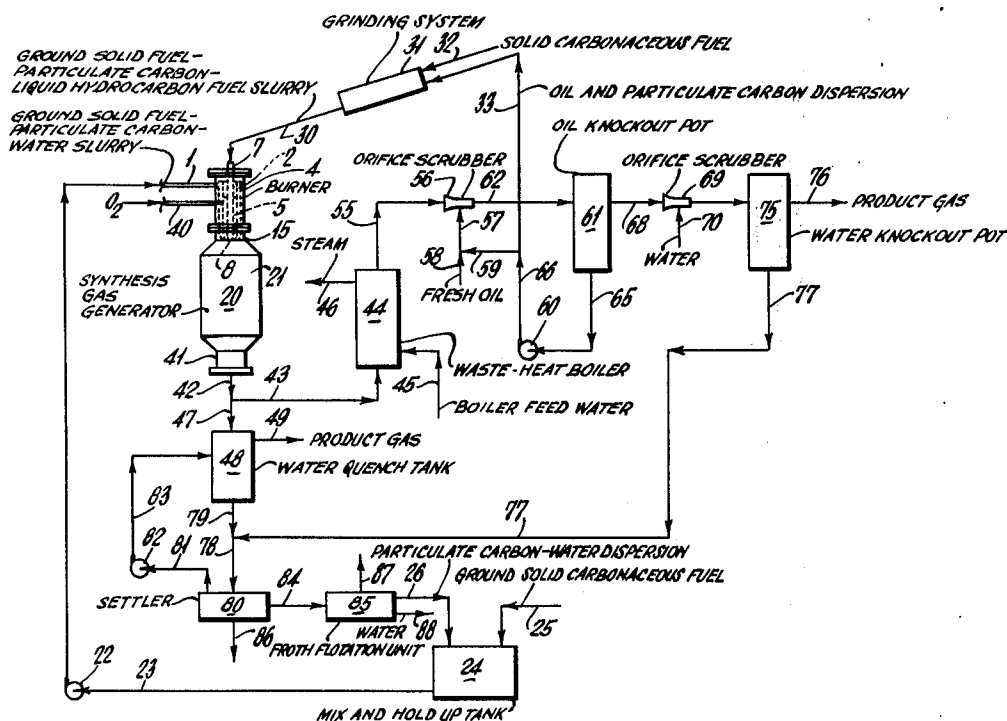
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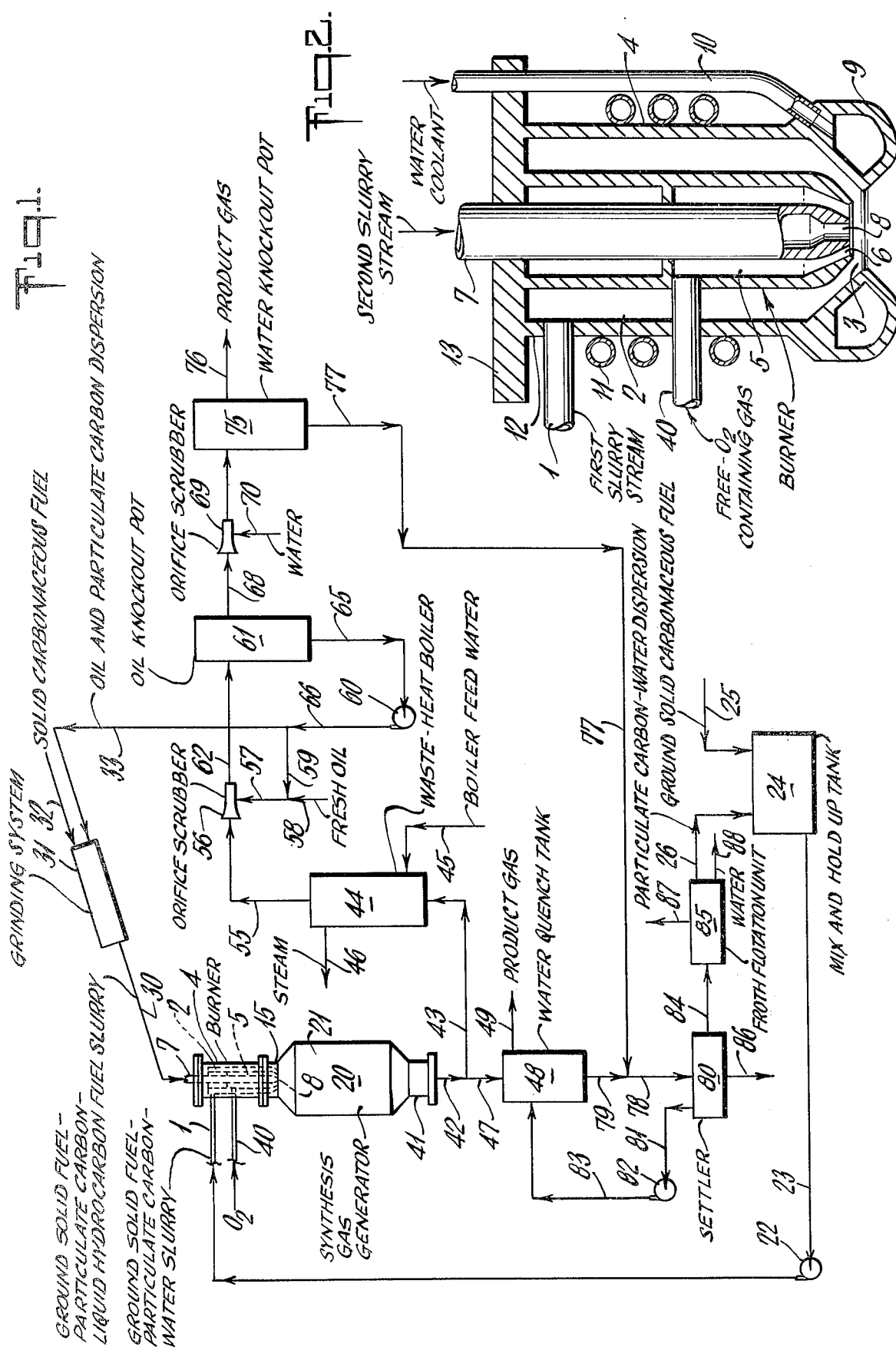
[57] ABSTRACT

This is a continuous partial oxidation process for pro-

ducing fuel gas or synthesis gas from solid carbonaceous fuels. In the process, two separate solid carbonaceous slurry feed streams (with the liquid vehicle being water in one slurry stream and liquid hydrocarbon fuel in the other) along with a separate stream of free-oxygen containing gas which is interposed between said slurry streams, are simultaneously introduced into a reaction zone of a free-flow noncatalytic gas generator where the three streams impinge and mix together to form an atomized dispersion that reacts by partial oxidation at an autogenous temperature in the range of about 1,500° to 3,500°F. and a pressure in the range of about 1 to 250 atmospheres. The effluent gas stream from the reaction zone is split into two streams which are separately cooled and cleaned to produce two separate gaseous streams one gaseous stream saturated with water and the other gaseous stream containing less than 15 mole % water. By the subject mixed mode operation, the weight ratios of water to fuel, oxygen to fuel, and liquid hydrocarbon fuel to total solid fuel may be lowered. This provides a more suitable, and economical gas generator operation.

6 Claims, 2 Drawing Figures





FUEL GAS FROM SOLID CARBONACEOUS FUELS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a continuous process for the manufacture of fuel and synthesis gas from solid carbonaceous fuels.

2. Description of the Prior Art

Because of increasing oil prices and decreasing supplies of natural gas, it is now necessary to use other natural fuel resources which were previously uneconomical. While large deposits of comparatively low cost coal and oil shale exist in this country, these solid carbonaceous materials may not be in a convenient form for many uses. Often these materials contain excessive amounts of sulfur compounds which limit their use as a fuel. In the subject improved process, slurry streams of a solid carbonaceous fuels may be burned more efficiently than previously in a synthesis gas generator.

SUMMARY

By the subject invention, two different and separate slurry streams of solid carbonaceous fuels are simultaneously brought together in a single free-flow gas generator where by partial oxidation they are efficiently converted into synthesis gas or into a clean fuel gas which may be burned without contaminating the environment.

The two pumpable slurry reactant streams are simultaneously passed through a double annulus type burner mounted in a gas generator. One slurry stream comprises a solid carbonaceous fuel with water as the liquid carrier and the other slurry stream comprises a solid carbonaceous fuel with a liquid hydrocarbon fuel as the carrier. One slurry stream is passed through the central conduit of the burner while the other slurry stream is passed through the outer annulus of the burner. Simultaneously, a reactant stream of free-oxygen containing gas is passed through the intermediate annulus passage of the burner thereby flowing between the other two streams. The three reactant streams are introduced simultaneously into the refractory lined reaction zone of the free-flow noncatalytic gas generator where they impinge, atomize, and mix together. The velocity of each of the slurry streams is in the range of about 1 to 500 feet per second. The velocity of the free oxygen containing gas is in the range of about 100 feet per second to sonic velocity.

Partial oxidation reaction takes place in the reaction zone of the gas generator at an autogenous temperature in the range of about 1,500° to 3,500°F. and a pressure in the range of about 1 to 250 atmospheres. The effluent gas leaving the gas generator is split into two streams. The first split stream of gas is cooled in a waste-heat boiler to produce steam. This cooled gas stream is then scrubbed with liquid hydrocarbon fuel or optionally water to remove entrained particulate solids. Optionally, by conventional gas purification procedures, acid-gases may be removed to produce a clean dry synthesis gas or fuel gas. The second split stream of effluent gas from the gas generator is introduced into a quench tank where it is cooled and scrubbed with water. A process gas stream saturated with water is produced thereby which may be introduced into a water-gas shift conversion zone where the H_2/CO mole ratio of the gas stream is increased.

By the subject invention, it was unexpectedly found that readily available solid carbonaceous fuels may be more economically converted into a clean fuel gas having a gross heating value in the range of about 75 to 400 BTU per SCF or into synthesis gas. Improved performance may be shown by reduction in the following weight ratios: water to fuel, oxygen to fuel, and liquid hydrocarbon to total solid fuel.

BRIEF DESCRIPTION OF THE DRAWING

The invention will be further understood by reference to the accompanying drawing in which

FIG. 1 is schematic representation of a preferred embodiment of the process.

FIG. 2 is a diagrammatic representation in vertical cross section of a preferred burner for simultaneously introducing the two slurry streams and one free-oxygen containing gas stream into the gas generator.

DESCRIPTION OF THE INVENTION

By means of the subject process, two gaseous streams each comprising principally hydrogen and carbon monoxide, and optionally at least one member of the group carbon dioxide, water vapor, methane, nitrogen, argon, carbonyl sulfide, and hydrogen sulfide are produced. One of said gaseous streams may be saturated with water vapor while the other stream may contain a maximum of 15 mole % H_2O . Particulate carbon and optionally acid gas are removed from the gas streams.

The product gas stream may be considered fuel gas or synthesis gas depending on the specific gas application. Typical compositions (in mole %) of the product gas stream are shown in Table I.

TABLE I

| | Product | | Gas |
|--------|---------|----|------|
| H_2 | 8.0 | to | 60.0 |
| CO | 8.0 | to | 70.0 |
| CO_2 | 1.0 | to | 50.0 |
| H_2O | 2.0 | to | 50.0 |
| CH_4 | 0.0 | to | 30.0 |
| COS | 0.0 | to | 0.7 |
| H_2S | 0.0 | to | 1.0 |
| N_2 | 0.0 | to | 85.0 |
| A | 0.0 | to | 2.0 |

The solid carbonaceous fuel employed in the subject process gas is selected from the group consisting of coal, coke from coal, coal char, petroleum coke, oil shale, tar sands, pitch, particulate carbon, and mixtures thereof. With the exception of particulate carbon which has a particle size of less than 10 microns, all of the other solid carbonaceous fuels are preferably ground to a particle size so that 100% of the material passes through an ASTM E 11-70 Sieve Designation Standard 425 μm (Alternative No. 40) and at least 80% passes through an ASTM E 11-70 Sieve Designation Standard 75 μm (Alternative No. 200) 1,000 μm = 1 mm.

The coal may be any type e.g. anthracite, bituminous and lignite. Coke from coal is the strong porous residue comprising carbon and mineral ash formed when coal e.g. bituminous is heated in the absence of air in a coke oven. Coal char may be made by the pyrolysis of coal at a temperature in the range of about 600° to 1,600°F. with or without the presence of air, hydrogen or synthesis gas. For example, char may be produced in a fluidized bed retort-see coassigned U.S. Pat. No. 3,715,301. Petroleum coke consists of dehydrogenated and con-

densified hydrocarbons of high molecular weight in the form of a matrix of considerable physical extent. It principally comprises carbon and contains dispersed throughout a very minor amount of petroleum-based asphaltic-like compounds. Raw petroleum coke suitable for use as a starting material in the process of this invention may be produced by the "delayed coking" process or by a similar process for converting heavy residual fuel oil into gasoline, gas oil, and coke. A typical delayed coking process is described in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Vol. 15, Inter-Science Publisher 1968, pages 20-23. Calcined petroleum coke and fluid coke are also suitable as a starting material. Pitch is a black amorphous solid or semi-solid residue obtained from the distillation of tars and tar products. Particulate carbon or free carbon soot may be found entrained in the effluent gas stream from the partial oxidation gas generator in the amount of about 0 to 20 weight percent (basis weight of carbon in the fuel). This particulate carbon is both oleophilic and hydrophobic. It has an Oil Absorption No. of more than 1, and usually one gram of particulate carbon will absorb 2-3 cc of oil.

Some typical solid carbonaceous fuels are described further in Table II.

TABLE II

| TYPICAL SOLID CARBONACEOUS FUELS | | | | | |
|--------------------------------------|-------|-------------------------|--------------|-------------------|-----------------------|
| | Coal | Bituminous Coal Coke | Coal Char | Petroleum Coke | Particulate Carbon |
| Proximate Analysis, Wt.% (dry) | | | | | |
| Volatile Matter | 38.6 | 2.0 | 3.5 | 5.0 | 3.0 |
| Fixed Carbon | 50.0 | 88.0 | 76.4 | 94.3 | 93 |
| Ash | 11.4 | 10.0 | 20.1 | 0.7 | 4.0 |
| TOTALS | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Ultimate Analysis, Wt.% (dry) | | | | | |
| C | 67.2 | 78.9 | 76.8 | 88.4 | 95.2 |
| H | 5.2 | 7.5 | 1.4 | 7.0 | 1.6 |
| N | 1.3 | 1.1 | 1.2 | 2.1 | 0.2 |
| S | 3.8 | 1.1 | 3.1 | 1.5 | 0.6 |
| O | 11.1 | 7.2 | 0.1 | 0.4 | — |
| Ash | 11.4 | 4.2 | 17.4 | 0.6 | 2.4 |
| TOTALS | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

The solid carbonaceous fuels that are used in the subject process are first ground to the proper size and mixed with a liquid vehicle to produce a pumpable slurry. Thus, a first reactant slurry stream may comprise a solid carbonaceous fuel-liquid hydrocarbon fuel slurry having a solids content in the range of about 30 to 65 weight percent and preferably about 45 to 60 wt. %. This first slurry feedstream is prepared by mixing together a liquid hydrocarbon fuel with a solid carbonaceous fuel selected from the group consisting of coal, coke from coal, coal char, fluid or delayed petroleum coke, calcined petroleum coke, oil shale, tar sands, pitch, particulate carbon, and mixtures thereof. The liquid hydrocarbon fuel is selected from the group consisting of petroleum distillate, gas oil, residual fuel oil, reduced crude, whole crude, asphalt, coal tar, coal oil, shale oil, tar sand oil, and mixtures thereof. Preferably, the liquid hydrocarbon fuel is scrubbing fluid which was used subsequently in the process and which contains particulate carbon scrubbed from the effluent gas stream from the gas generator.

The second reactant slurry stream comprises a solid carbonaceous fuel-water pumpable slurry having a solids content in the range of about 30 to 65 weight percent and preferably about 45 to 60 wt. %. This second slurry feedstream is prepared by mixing together a solid carbonaceous fuel or mixtures thereof as previously described with water.

The third reactant stream comprises a free-oxygen containing gas selected from the group consisting of air, oxygen-enriched air, i.e. at least 22 mole % oxygen, and substantially pure oxygen i.e. at least 95 mole % oxygen (the remainder comprising N₂ and rare gases). Substantially pure oxygen is preferred in order to reduce the amount of nitrogen and other gaseous impurities in the product gas.

The three reactant streams previously described are introduced simultaneously into the reaction zone of a conventional free-flow gas generator preferably by way of a double annulus burner. The gas generator is free from packing and catalyst. It is a vertical steel pressure vessel lined on the inside with refractory, such as described in coassigned U.S. Pat. No. 3,097,081. A suitable multiple annulus burner is shown in coassigned U.S. Pat. No. 3,705,108. However, the feedstream and velocities for the subject process differ from those dis-

closed in said patent.

In the subject invention, either the first or second reactant slurry stream is passed into the reaction zone by way of the central nozzle of the triple orifice burner shown in FIG. 2 of the drawing for coassigned U.S. Pat. No. 3,705,108. Simultaneously, the other slurry stream is passed through the outer coaxial annular nozzle that is disposed about an intermediate coaxial annular nozzle which in turn is disposed about said central nozzle. The third reactant stream comprising free-oxygen containing gas is passed simultaneously through said intermediate coaxial annular nozzle. The first and second reactant slurry streams are in liquid phase at a temperature in the range of about 40° to 700°F. as they pass through the burner at a velocity at the burner tip in the range of about 1 ft. per sec. to 500 ft. per sec. and preferably about 5 to 250 feet per second. The third reactant stream comprising free-oxygen containing gas is at a temperature in the range of about 40° to 1,500°F. as it passes through the burner at a velocity in the burner tip in the range of about 100 ft. per sec. to sonic velocity and preferably about 200 to 450 ft. per sec. By

this arrangement, the free-oxygen containing gas emerges at the burner tip as a hollow conical shaped stream which is directed towards the longitudinal axis of the burner, and which is interposed between said first and second slurry reactant stream. By this means the free-oxygen containing stream may deeply penetrate the two slurry streams and provide thorough mixing. The intermediate and outer annular channels are inclined slightly inwardly with respect to the longitudinal axis of the burner, making an angle in the range of about 10° to 70°. When the first and second slurry streams impinge together near the tip of the burner, the solid particles in the two streams contact each other and are furthered reduced in size. The intermediate high velocity jet stream of free oxygen containing gas contacts the other two streams to form a fog of minute solid particles. A substantially homogeneous and uniform dispersion of fine particles of solid carbonaceous fuel in atomized liquid hydrocarbon fuel, H₂O, and oxygen is produced. By this means the combustion efficiency is improved, and there may be a reduction in the weight ratios steam to fuel, oxygen to fuel and total liquid hydrocarbon fuel to solid carbonaceous fuel.

The relative proportions of solid carbonaceous fuel, liquid hydrocarbon fuel, water, and oxygen in the feed-streams to the gas generator are carefully regulated to convert a substantial portion of the carbon, e.g. at least 80 wt. % to carbon oxides e.g. CO and CO₂ and to maintain an autogenous reaction zone temperature in the range of about 1,500° to 3,500°F., preferably in the range of about 1,800° to 2,800°F. The pressure in the reaction zone is in the range of 1 to 250 atmospheres. The time in the reaction zone in seconds is the range of 0.5 to 50, and preferably 1.0 to 10. The weight ratio of steam to total fuel (solid carbonaceous fuel plus liquid hydrocarbon fuel) in the reaction zone is in the range of about 0.1 to 1.3, and preferably 0.2 to 0.50. The atomic ratio of oxygen in the free oxygen containing gas to carbon in the total fuel is in the range of about 0.6 to 1.6, and preferably 0.8 to 1.4. It is common practice to express ratios in this manner as the denominator of the ratio is one and the numerator is the range specified e.g. 0.6 to 1.6.

0.1 to 3 parts by weight and preferably 0.5 to 1.5 parts by weight of said solid carbonaceous fuel-liquid hydrocarbon fuel slurry are introduced into the reaction zone per part by weight of solid carbonaceous fuel-water slurry.

About 0.8 to 12 parts by weight and preferably 2 to 12 parts by weight of total solid carbonaceous fuel are reacted in the gas generator per part by weight of liquid hydrocarbon fuel.

The effluent gas stream from the reaction zone is split into two streams for cooling, cleaning, and for removing entrained solids. One gas stream is cooled in a waste-heat boiler and the other is cooled by quenching in water in an quench vessel. If desired, acid gases i.e. H₂S, COS, CO₂, and mixtures thereof may be removed from the effluent gas stream. By this means fuel gas may be produced which may be burned without contaminating the environment. Also, the heating value may be increased. Alternately, the product gas may be used as a synthesis gas feed which does not affect sulfur-sensitive catalysts.

The effluent gas stream leaving the synthesis gas generator has the following composition in mole %: H₂ 8.0 to 60.0, CO 8.0 to 70.0, CO₂ 1.0 to 50.0, H₂O 2.0 to 50.0, CH₄ 0 to 30.0, H₂S 0.0 to 1.0, COS 0.0 to 0.7

N₂ 0.0 to 85.0, and A 0.0 to 2.0. Entrained in the effluent gas stream is about 0.5 to 20.0 weight percent of particulate carbon (basis weight of carbon in the feed to the gas generator). As previously mentioned the effluent gas stream is then split into two gas streams which are separately cooled.

The first split stream of effluent gas comprising about 5 to 95 volume percent and preferably about 75 to 95% of the total volume of effluent gas from the gas generator is cooled to a temperature in the range of about 200° to 1,800°F. and preferably from 400° to 600°F. by indirect heat exchange with water in a waste heat boiler. Steam is simultaneously produced at a temperature in the range of about 400° to 650°F. The particulate carbon is scrubbed from the first split stream of effluent gas by conventional methods using a liquid hydrocarbon fuel scrubbing liquid. For example, as shown in coassigned U.S. Pat. No. 3,639,261 the process gas stream may be passed through a venturi or jet scrubber, such as described in Perry's Chemical Engineers' Handbook, Fourth Edition, McGraw Hill, Co., 1963, pages 18-55 to 56 and scrubbed with a scrubbing fluid selected from a liquid hydrocarbon fuel as previously described or a dispersion of particulate carbon and liquid hydrocarbon fuel. Then in a conventional oil knockout pot, the process gas stream is separated from a dispersion of particulate carbon-liquid hydrocarbon fuel containing from about 1 to 20 wt. % solids which is removed from the bottom of the knockout pot and mixed with ground solid carboniferous fuel in a conventional grinding system. The aforesaid first slurry feedstream is produced thereby and is introduced into the synthesis gas generator as previously described.

Any particulate carbon and other entrained solids such as a small amount of ash if any remaining in the process gas stream may be removed in a second scrubbing stage. In such event, the process gas stream may be passed through an orifice scrubber similar to that previously described in the first scrubbing stage and scrubbed with water. Then in a water knockout pot, a clean product gas containing less than five mg of particulate carbon per 100 SCF of gas is separated from a water dispersion containing from about 0.001 to 0.2 wt. % of entrained solids. This dispersion may be subsequently concentrated in a manner to be further described and used as a portion of the feed to the gas generator. Gaseous impurities may be removed from the process gas stream by conventional procedures.

The previously mentioned second split stream of effluent gas from the gas generator is cooled by direct quenching in water in a quench tank such as shown in coassigned U.S. Pat. No. 2,896,927. As the process gas stream bubbles through water maintained at a temperature in the range of about 50° to 450°F. substantially all of the particulate carbon and other entrained solids such as ash are scrubbed from the process gas stream and water is vaporized. Product gas saturated with water leaves near the top of the quench tank. Optionally, this gas stream may be subjected to water-gas shift reaction to increase the H₂/CO ratio. H₂O and any gaseous impurities may be then removed by conventional methods.

A water dispersion of particulate carbon and ash containing about 0.1 to 2.0 wt. % of solids from the bottom of the water quench tank, is mixed with the dispersion of water and entrained solids e.g. particulate carbon, from the previously described water knockout pot. By conventional liquid-solids separation proce-

dures e.g. settling, filtration, and centrifuge clarified water is separated from said dispersion. For example, the dispersion may be passed into a settling tank from which the following three streams are removed: a stream of coarse ash which is removed from the bottom of the tank, a water dispersion stream of fine ash and particulate carbon containing about 1.0 to 20 weight percent of solids which is removed and passed into a conventional froth flotation process, and a clarified water stream which is recycled to the water quench tank. A two-stage flotation system may be used to resolve said water dispersion into separate streams of water, a stream of ash, and a concentrated particulate carbon-water slurry stream.

This concentrated particulate carbon-water slurry stream contains about 10.0 to 40.0 weight percent of solids and is passed into a hold up tank from whence it provides liquid for slurry make-up or for wet grinding of the solid fuel. Ground make up solid carbonaceous fuel may be introduced in said mix and hold up tank. For example about 20 to 70 weight percent of solid fuel introduced into mix and hold up tank comprises said solid carbonaceous fuel make-up. A pumpable mixture of solid fuels and water containing 30 to 65 wt. % solids from said mix and hold up tank is preferably introduced into the gas generator as said first reactant slurry stream.

Optionally, the product gas stream from the water knockout pot or the product gas stream from the water quench tank may be submitted to additional cleaning and conventional purification steps to remove any remaining solids or at least one material from the group consisting of H_2O , CO_2 , CH_4 , H_2S , COS , A , and N_2 .

DESCRIPTION OF THE DRAWING AND EXAMPLES

A more complete understanding of the invention may be had by reference to the accompanying schematic drawing which shows in FIG. 1 the previously described process in detail. Quantities have been assigned to the various streams so that the following description in Example 1 may be also serve as an example of the subject invention.

EXAMPLE I

On an hourly basis about 2,750 lbs. of a ground solid carbonaceous fuel-particulate carbon-water slurry feed in line 1 in liquid phase at a temperature of about 60°F. are passed through the outer annular passage 2 and discharged into the reaction zone of synthesis gas generator 20 by way of converging outer annular orifice 3 of double annulus burner 4 at a velocity of 80 feet per second.

An enlarged vertical cross sectional view of burner 4 is shown in FIG. 2. Double annulus burner 4 is more fully described in coassigned U.S. Pat. No. 3,705,108. Other features of the burner include concentric intermediate annular passage 5 which leads to concentric converging intermediate annular discharge nozzle 6 and central conduit 7 which leads to central nozzle or orifice 8. At the tip of the burner is hollow annular cooling chamber 9 through which cooling water is introduced by way of line 10. Tubing 11 through which cooling water is passed, encircles the outside barrel 12 of burner 4. By means of mounting plate 13, burner 4 is attached to the upper flange of burner housing 14. Housing 14 is attached to flanged inlet 15 of vertical free-flow noncatalytic partial oxidation synthesis gas

generator 20 having a 33 cubic feet refractory lined reaction chamber 21.

The aforesaid solid carbonaceous fuel-particulate carbon-water slurry is pumped into line 1 by means of pump 22. This water slurry comes from line 23 and mix and hold up tank 24. In Run No. 1, its composition in weight percent comprises Utah bituminous coal ground to a particle size so that 100% of the material passes through an ASTM E11-70 Sieve Designation Standard 425 μm and at least 80% passes through an ASTM E 11-70 Sieve Designation Standard 75 μm 49.0, particulate carbon (produced subsequently in the process) 1.0, and water 50.0. The materials which are introduced into tank 24 and mixed together therein comprise ground make-up Utah bituminous coal from line 25, and a concentrated dispersion of particulate carbon and water containing 10 weight percent of solids from line 26. The Utah bituminous coal has the following ultimate analysis in wt. %: C 78.9, H 7.5, N 1.1, S 1.1, O 7.2, and Ash 4.2. Gross Heating Value of the coal is 15,737 BTU/lb.

Simultaneously, about 4,125 lbs. of a ground solid carbonaceous fuel-particulate carbon-liquid hydrocarbon fuel slurry feed in line 30, in liquid phase, at a temperature of about 200°F. are passed through central conduit 7 of burner 4 and are discharged into the gas generator reaction zone 21 through central nozzle 8 at a velocity of about 50 ft. per sec. The solid fuel-liquid hydrocarbon fuel slurry in line 30 for Run No. 1 is prepared by grinding together in conventional grinding system 31, 2,063 lbs. of Utah bituminous coal make-up (as previously described) from line 32, and 2,062 lbs. of a dispersion from line 33 containing 0.4 wt. % solids and comprising particulate carbon and 13.7° API California Reduced Crude make-up. The reduced crude has the following ultimate analysis in wt. %: C 85.8, H 11.26, S 1.98, O 0.11, and N 0.80, Ash 0.05, and a Heat of Combustion of 18,410 BTU per lb.

Simultaneously, about 5,417 lbs. of substantially pure oxygen (99.7 mole % O_2) feed in line 40 at a temperature of about 100°F. are passed through intermediate annular passage 5 and discharged into the gas generator reaction zone 21 through converging intermediate annular nozzle 6 at a velocity of about 350 ft. per sec. By this arrangement of feedstreams, a stream of substantially pure oxygen gas is discharged from the burner and is interposed between the oil-slurry stream and the water-slurry stream. Upon discharge from burner 4, the three reactant streams contact each other in the reaction zone with such force as to pulverize the particles of bituminous coal. The slurry streams are atomized and thoroughly mixed with the oxygen stream.

Reaction takes place in reaction zone 21 of synthesis gas generator 20 at an autogenous temperature of about 2,600°F., and a pressure of about 28 atmospheres. The residence time in the reaction zone is 2 seconds. 241,400 standard cubic feet per hour (SCFH) of effluent stream of synthesis gas leave gas generator 20 by way of flanged exit 41 and line 42 with the following composition in mole % for Run No. 1: H_2 33.5, CO 53.1, CO_2 3.4, H_2O 9.3, CH_4 0.1, COS 0.02, H_2S 0.2, N 0.3, A 0.1, and 4.0 wt. % of particulate carbon (basis weight of total carbon in the feedstock to the gas generator).

The effluent stream of synthesis gas in line 42 is split from two streams. The first split stream of effluent gas is passed through line 43 and into waste heat boiler 44

where it is cooled to a temperature of 630°F. by indirect heat exchange with boiler feed water, entering through line 45 at a temperature of 200°F. and leaving through line 46 as steam at a temperature of 590°F. The second split stream of effluent gas is passed through line 47 and is cooled by direct quenching in water in a quench tank 48. Quench tank 48 is further described in coassigned U.S. Pat. No. 2,896,927. The product gas leaving quench tank 48 by way of line 49 is saturated with water. Optionally, the product gas in line 49 may be introduced into a conventional gas cleaning and purification zone (not shown in the drawing) where any remaining solids are removed and one or more gaseous impurities from the group CO₂, H₂S, COS, A, CH₄, H₂O, and N₂ may be removed.

Particulate carbon in the aforesaid first split stream of effluent gas leaving waste heat boiler 44 by line 55, may be removed by passing said effluent gas stream through a conventional orifice scrubber 56. The scrubbing fluid which enters scrubber 56 by way of line 57 is a mixture of California Reduced Crude make-up (as previously described) which enters the system through line 58 and a dispersion from line 59 comprising particulate carbon and California Reduced Crude. This dispersion consists of about 0.4 wt. % solids and is pumped by means of pump 60 from the bottom of oil knockout pot 61 through lines 65, 66, and 59. A portion of this dispersion is introduced into grinding system 31 by way of line 33 as previously described. The process gas stream and scrubbing oil mixture leaving orifice scrubber 56 by way of line 62 is passed into oil knockout pot 61 where the normally liquid dispersion separates and is drawn off near the bottom as previously described. The clean process gas stream leaves through line 68 near the top of oil knockout pot 61. Optionally, to remove any remaining particulate carbon, the gas stream is passed through conventional orifice scrubber 69 and scrubbed with water from line 70. This water may include fresh make-up water. The process gas stream is then introduced into knockout pot 75 where clean product gas is removed through line 76 near the top of knockout pot 75. The composition of this product gas stream is similar to that in line 49 with the exception that the water content is less than 10

ator) is less than 6 parts per million. Optionally, H₂O and one or more gaseous impurities from the group CO₂, H₂S, COS, A, and N₂ may be removed from the product gas stream in line 70 in a conventional gas purification zone not shown in the drawing. A water dispersion containing 0.1 wt. % solids substantially comprising particulate carbon and optionally some ash is removed through line 77 at the bottom of pot 75.

The dispersion of water and solid particles in line 77 is mixed in line 78 with the dispersion of water and solid particles containing 1.0 wt. % solids e.g. particulate carbon and any ash leaving water quench tank 48 by way of line 79. The mixture is passed into a conventional settler unit 80. Clarified water is removed by way of line 81 and by means of pump 82 is recycled to water quench tank 48 through line 83. A water slurry of particulate carbon and any fine ash is removed from settler unit 80 and is passed through line 84 into a conventional froth flotation unit 85. Any coarse ash may be removed from settler 80 through 86. In flotation unit 85, any fine ash may be removed by way of line 87 and water may be removed by way of line 88. Some of this water may be treated and discharged from the system for disposal while other portions of this water may be recycled to quench tank 48 or to orifice scrubber 70 or to both. A concentrated dispersion of particulate carbon and water is removed by way of line 26 and is passed into mix and hold up tank 24, as previously described. 245 lbs. of ash or other solids may be removed from the system by way of lines 86 and 87.

To show the advantages of the subject process over systems employing a single slurry feed stream, runs 2 and 3 which do not represent the subject invention are shown below in Table III in comparison with the process of the subject invention (Run No. 1). The operating conditions, and the amount of synthesis gas produced in all three runs are about the same. In Run No. 2 the feed to the burner comprises: a coal-particulate carbon-emulsion of liquid hydrocarbon fuel and water pumpable slurry; and a separate stream of free-oxygen containing gas. In Run No. 3 the feed to the burner comprises: a coal-particulate carbon-water pumpable slurry; and a separate stream of free-oxygen containing gas.

TABLE III

| Feed | Run No. 1 | Run No. 2 | Run No. 3 |
|---|--------------|--------------|--------------|
| Coal-particulate carbon-oil slurry, lbs. | 4125 | — | — |
| Coal-particulate carbon-water slurry, lbs. | 2750 | — | 11000 |
| Coal-particulate carbon-oil and water emulsion, lbs. slurry | — | 7857 | — |
| Free-Oxygen containing Gas (99.7 mole % O ₂), SCF | 64200 | 64200 | 65500 |
| Effluent Gas Stream Leaving Gas Generator (line 42), Vol. % | | | |
| Hydrogen | 33.49 | 30.88 | 24.64 |
| Carbon Monoxide | 53.08 | 47.05 | 32.39 |
| Carbon Dioxide | 3.40 | 5.86 | 10.55 |
| Water | 9.25 | 15.50 | 31.87 |
| Methane | .09 | .08 | .06 |
| Carbonyl Sulfide | .02 | .01 | .01 |
| Hydrogen Sulfide | .26 | .22 | .19 |
| Nitrogen | .33 | .32 | .49 |
| Argon | .08 | .08 | .06 |
| Performance | | | |
| Oxygen Consumption, SCF/MSCF H ₂ +CO net | 306 | 323 | 375 |
| Water/Fuel ratio, lb/lb | .25 | .43 | 1.00 |
| Total Solid Fuel/liquid hydrocarbon fuel, lb/lb | 1.67 | 3.5 | — |
| H ₂ +CO, SCFH | 209,000 | 198,300 | 174,100 |
| SCF H ₂ +CO/lb. fuel | 38.0 | 36.1 | 31.7 |
| SCF H ₂ +CO/lb. solid fuel | 60.8 | 50.5 | 31.7 |
| Unconverted Carbon, wt. percent | 4.0 | 4.0 | 4.0 |

mole percent and the wt. % of particulate carbon (basis weight of total carbon in the feedstock to the gas gener-

From Table III it is readily apparent that the performance characteristics for Run Number 1 which repre-

sents the subject invention, are superior to that of the other Runs. Significant economic savings are effected and a more stable operation is attainable by the subject invention. This is evident by the increased production of H_2+CO per lb. of fuel charged; the higher ratio of total solid fuel/liquid hydrocarbon fuel; the lower oxygen consumption per MSCF H_2+CO ; and the reduced water to fuel ratio.

The process of the invention has been described generally and by examples with reference to liquid-solid carboniferous fuel slurries and synthesis gas of particular compositions for purposes of clarity and illustration only. It will be apparent to those skilled in the art from the foregoing that various modifications of the process and materials disclosed herein can be made without departure from the spirit of the invention.

I claim:

1. In the continuous manufacture of gaseous mixtures principally comprising H_2 and CO , and optionally containing at least one member of the group CO_2 , H_2O , CH_4 , N_2 , A , COS , and H_2S by the partial oxidation of a hydrocarbonaceous fuel with a free-oxygen containing gas in the presence of a temperature moderator in a reaction zone free from packing and catalyst of a free-flow gas generator, the improvement which comprises introducing into said reaction zone a continuous first slurry feedstream comprising a ground solid carbonaceous fuel and a liquid hydrocarbon fuel at a velocity in the range of about 1 to 500 feet per second; simultaneously introducing into said reaction zone so as to contact said first slurry feedstream a continuous separate second slurry feedstream comprising a ground solid carbonaceous fuel and water at a velocity in the range of about 1 to 500 feet per second; simultaneously introducing into said reaction zone a continuous separate third stream comprising a free-oxygen containing gas interposed between said first and second slurry feedstreams; and contacting and mixing said three streams together to form an atomized dispersion in which the ratio of atoms of oxygen to atoms of carbon in the total fuel is in the range of about 0.6 to 1.6, the weight ratio of H_2O to fuel is in the range of about 0.10 to 1.3, and the weight ratio of total solid carbonaceous fuel to liquid hydrocarbon fuel is in the range of about 0.8 to 12, and reacting said atomized dispersion in said reaction zone at a temperature in the range of about $1,500^\circ$ to $3,500^\circ F.$, and a pressure in the range of about 1 to 250 atmospheres.

2. The process of claim 1 wherein said first slurry stream comprises 0.30 to 0.65 parts by weight of a ground solid carbonaceous fuel selected from the group consisting of petroleum coke, coal, particulate carbon, coal char, coke from coal, oil shale, tar sands, pitch and mixtures thereof for each part by weight of liquid hydrocarbon fuel selected from the group consisting of fuel oil, residual fuel oil, reduced crude oil, whole crude oil, coal oil, shale oil, gasoline, kerosene, naphtha, gas oil fractions of petroleum distillate, benzene, toluene, hexane, heptane, cyclohexane, tetralin, decalin and mixtures thereof; and wherein said second slurry stream comprises 0.30 to 0.65 parts by weight of said solid carbonaceous fuel for each part by weight of water.

3. The process of claim 1 provided with the additional steps of (1) splitting the effluent gas stream from said reaction zone into first and second process gas streams; (2) cooling said first process gas stream from (1) by indirect heat exchange with water to produce

steam in a waste heat boiler; (3) simultaneously cooling and scrubbing said second process gas stream from (1) to remove entrained solids by immersion in water in a quench tank; (4) scrubbing the effluent gas stream from the waste-heat boiler in (2) with scrubbing oil to remove entrained solids and to produce a product gas stream principally comprising H_2 and CO and containing less than 10 mole % H_2O ; and (5) removing the effluent gas stream from the quench tank in (3) to produce a product gas stream saturated with water and principally comprising H_2 and CO .

4. A process for the production of fuel gas or synthesis gas comprising introducing into the reaction zone free from packing and catalyst of a free-flow gas generator a continuous first slurry feedstream comprising a solid carbonaceous fuel and a liquid hydrocarbon fuel at a velocity in the range of about 1 to 500 feet per second, wherein said first slurry stream comprises 0.30 to 0.65 parts by weight of a ground solid carbonaceous fuel selected from the group consisting of petroleum coke, coal, particulate carbon, coal char, coke from coal, oil shale, tar sands, pitch, and mixtures thereof for each part by weight of liquid hydrocarbon fuel selected from the group consisting of fuel oil, residual fuel oil, reduced crude oil, whole crude oil, coal oil, shale oil, gasoline, kerosene, naphtha, gas oil fractions of petroleum distillate, benzene, toluene, hexane, heptane, cyclohexane, tetralin, decalin and mixtures thereof; simultaneously introducing into said reaction zone so as to contact said first slurry feedstream a continuous separate second slurry feedstream comprising a solid carbonaceous fuel and water at a velocity in the range of about 1 to 500 feet per second, and wherein said second slurry stream comprises 0.3 to 0.65 parts by weight of said ground solid carboniferous fuel for each part by weight of water; simultaneously introducing into said reaction zone a continuous separate third feedstream comprising a free-oxygen containing gas interposed between said first and second slurry feedstreams, and contacting and mixing said three feedstreams together to form an atomized dispersion in which the ratio of atoms of oxygen to atoms of carbon in the total fuel is in the range of about 0.6 to 1.6, the weight ratio of H_2O to fuel is in the range of about 0.10 to 1.3, and the weight ratio of total solid carbonaceous fuel to liquid hydrocarbon fuel is in the range of about 0.8 to 12, and reacting said atomized dispersion in said reaction zone at a temperature in the range of about $1,500^\circ$ to $3,500^\circ F.$, a pressure in the range of about 1 to 250 atmospheres, and for a residence time of 1 to 10 seconds; splitting the effluent gaseous stream from said reaction zone into first and second split process gas streams; cooling said first split process gas stream by indirect heat exchange with water in a waste heat boiler to produce steam; scrubbing with liquid hydrocarbon fuel or a dispersion of particulate carbon and liquid hydrocarbon fuel the effluent gas stream from said waste heat boiler to remove entrained solid particles, separating a dispersion of particulate carbon and liquid hydrocarbon fuel, and separating a first product gas stream principally comprising H_2 and CO and containing at least one member of the group CO_2 , H_2O , CH_4 , N_2 , A , COS , and H_2S ; mixing a portion of said dispersion of particulate carbon and liquid hydrocarbon fuel with make-up solid carboniferous fuel to produce said first slurry feedstream to the gas generator; separating at least one member of the group CO_2 , H_2O , CH_4 , N_2 , A , COS , and H_2S from said first product gas stream in

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a gas purification zone; and simultaneously cooling and scrubbing to remove entrained solid particles from said second split process gas stream by immersion in water in a quench zone, removing a second product gas stream from said quench zone similar to said first product gas stream but saturated with H₂O and substantially free from entrained solid particles; removing a dispersion of solid particles and water from said quench zone and separating therefrom a concentrated particulate carbon-water dispersion, and mixing said ground solid carbonaceous fuel with said concentrated dispersion of particulate carbon-water to produce said second slurry feedstream to the gas generator.

5. The process of claim 4 provided with the additional steps prior to said gas purification zone of scrubbing said first product gas stream with water to remove any remaining entrained solids; separating a clean first

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product gas stream, separating a dispersion of entrained solids and water and mixing said dispersion with said dispersion of solid particles and water from said quench zone.

6. The process of claim 5 provided with the additional steps of introducing said mixed dispersion of solid particles and water into a settling zone; withdrawing from said settling zone a separate stream of clear water and recycling same to said quench zone, and a separate stream of coarse ash, and a separate stream of particulate carbon and fine ash dispersed in water; introducing said water dispersion of particulate carbon and fine ash into a froth flotation zone and removing therefrom three separate streams comprising water, ash, and said concentrated dispersion of particulate carbon-water.

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