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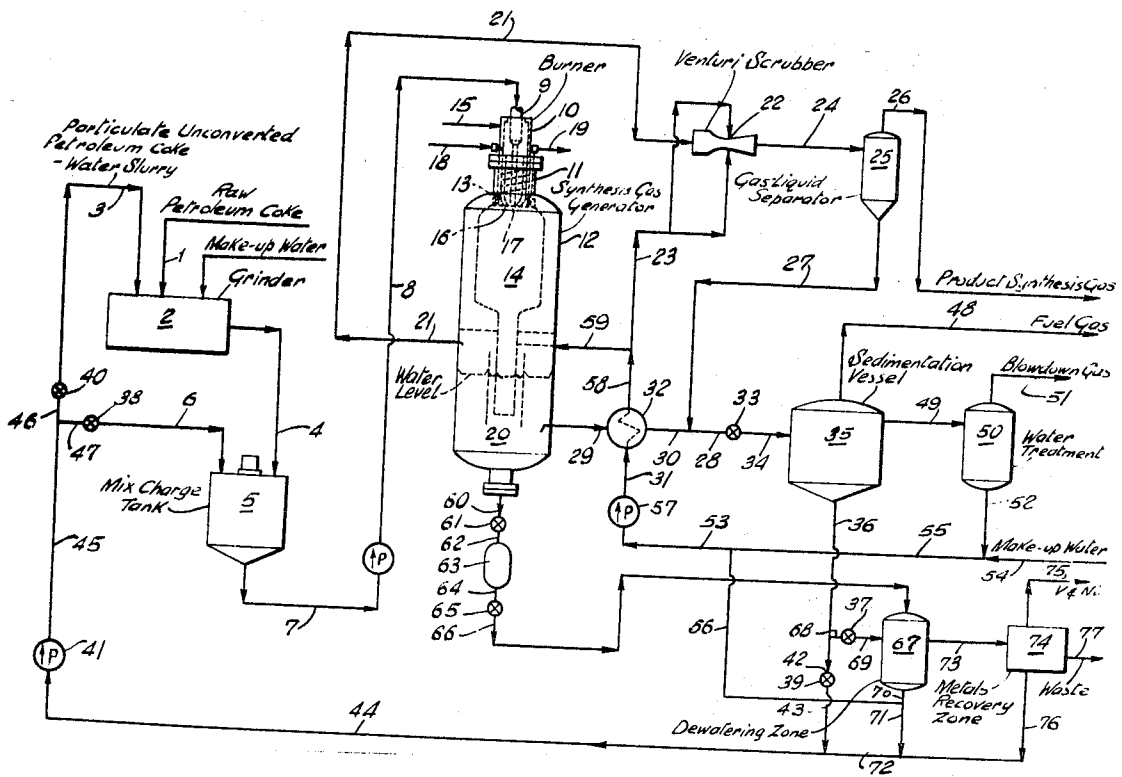
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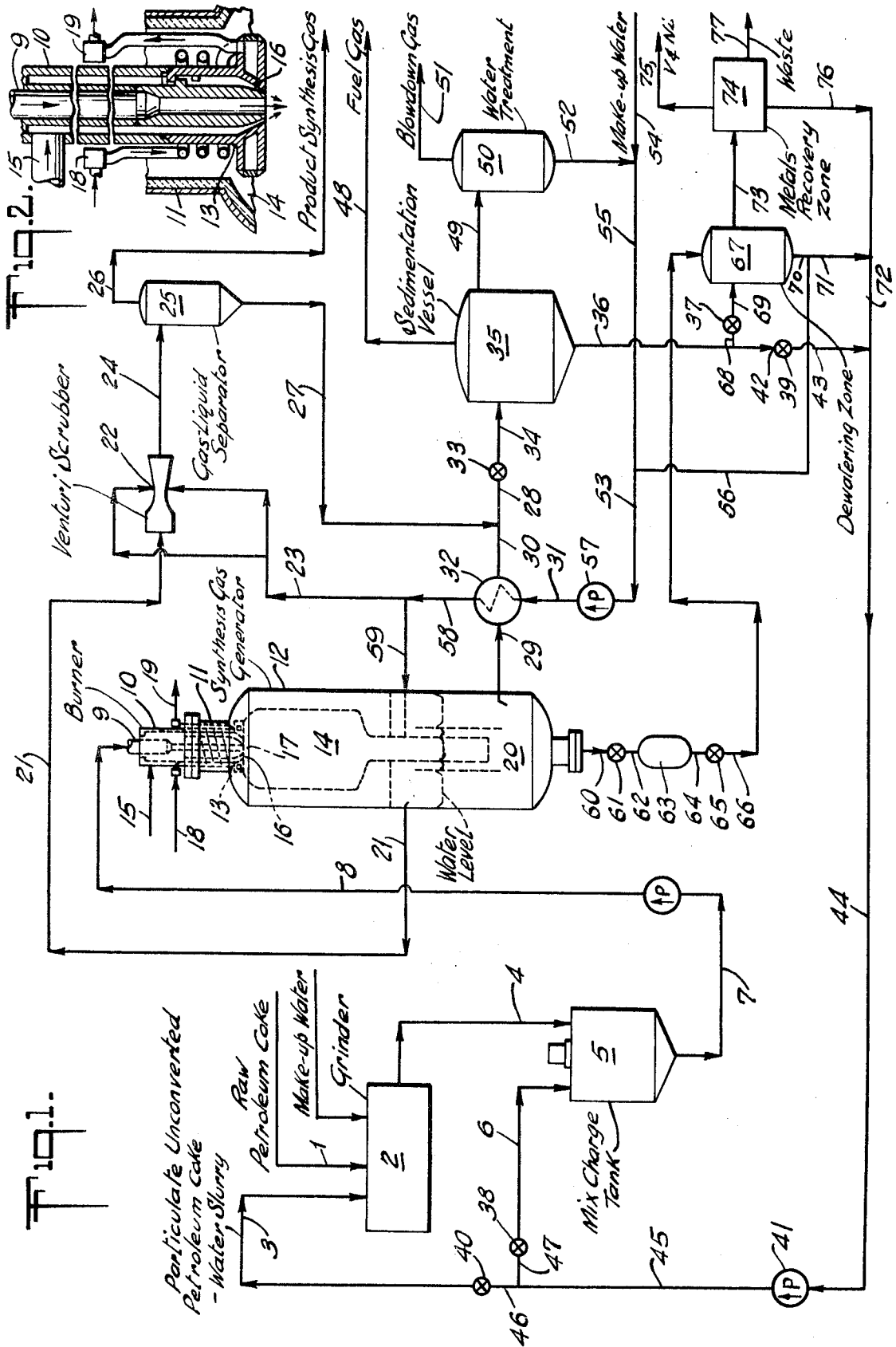
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- [54] **SYNTHESIS GAS FROM PETROLEUM COKE**
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C10j 3/16, C22b 59/00
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ABSTRACT: Production of synthesis gas (mixtures of hydrogen and carbon monoxide) in a refractory lined reaction zone of a partial oxidation free-flow synthesis gas generator by feeding to said reaction zone a stream of particulate petroleum coke containing heavy metal constituents dispersed in H₂O. Attack of said refractory lining by the metals and metal compounds present in said petroleum coke, or their reaction products, is substantially prevented by controlling the feed-streams to the reaction so that entrained in the product gas leaving the reaction zone is an amount of unconverted petroleum coke containing unreacted about 8 weight percent or more of the quantity of carbon originally present in the petroleum coke feedstream.





SYNTHESIS GAS FROM PETROLEUM COKE

This application is a continuation-in-part of our application Ser. No. 787,191, filed on Dec. 26, 1968.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the production of synthesis gas from petroleum coke. More particularly, it relates to improvements in the partial oxidation process for generating hydrogen and carbon monoxide from aqueous dispersions of particulate petroleum coke containing heavy metal constituents which ordinarily attack the refractory lining of the reaction zone.

The parent case, Ser. No. 787,191 pertains to the production of synthesis gas from a slurry of particulate solid carboniferous fuel, e.g., petroleum coke, coke from bituminous coal, coal, oil shale, tar sands, pitch, or mixtures of said solid fuels in water or in a hydrocarbon liquid fuel. A pumpable slurry containing 1 to 60 weight of ground solid carboniferous fuel in petroleum oil or 25 to 55 weight percent of ground solid carboniferous fuel in water at a relatively low discharge velocity in the range of 5 to 50 feet per second is mixed with a stream of oxidizing gas at a relatively high discharge velocity in the range of 200 feet per second to sonic velocity at the burner tip to form an atomized dispersion of water, hydrocarbon liquid fuel, oxidizing gas and particulate solid carboniferous fuel. Under synthesis gas generating conditions the atomized dispersion is reacted to produce a gaseous mixture of hydrogen and carbon monoxide. By said process, slurry feeds of low-cost solid carboniferous fuels may be gasified without being preheated.

2. Description of the Prior Art

The gasification of solid carboniferous fuels is well known in the prior art. However, the gasification of certain petroleum cokes containing heavy metal constituents was found to damage the refractory lining in synthesis gas generation. This occurred when the heavy metal constituents were present in the petroleum coke in concentrations of about 100 to 5,000 parts per million or more. These metal constituents or their reaction products were found to attack the refractory lining, causing equipment failure and shutdown. Now, however, by the process of our invention this difficulty has been substantially overcome.

SUMMARY

By the process of our invention a feedstream of petroleum coke containing about 100 to 5,000 parts per million or more of heavy metal constituents dispersed in H₂O may be reacted with an oxygen-rich gas in a closed, compact, refractory lined reaction zone of a free-flow, noncatalytic synthesis gas generator in such a manner that damage to the refractory lining by said metal constituents in the coke or their reaction products is substantially prevented.

First, particles of the petroleum coke from about 12 to 325 mesh and finer are dispersed in steam or liquid water. The dispersion is atomized and reacted with an oxygen-rich gas in the refractory lined zone of a synthesis gas generator. At an autogenous temperature in the range of about 1,800 to 3,500 F. and a pressure in the range of atmospheric to 3,000 p.s.i.g., and preferably 100 to 3,500 p.s.i.g., a hot product gas stream is produced comprising principally hydrogen and carbon monoxide and containing minor amounts of CH₄, H₂S, N₂, and A.

It was unexpectedly found that by permitting a small amount of the petroleum coke feed to pass through the reaction zone unconverted and entrained in the product gases leaving the reaction zone, damage to the refractory lining is prevented. Thus, by controlling the amount of unconverted petroleum coke in the product gases so that about 8 weight percent and higher of the carbon originally present in the petroleum coke feed is retained by said quantity of unconverted petroleum coke in the product gas as unreacted carbon, then from about 17 to 60 weight percent of any harmful

heavy metal constituent in the petroleum coke or its oxidation product is retained by the unconverted petroleum coke entrained in the product gases leaving the reaction zone and damage to the refractory lining is prevented.

The quantity of unconverted particulate petroleum coke entrained in the product gas for a given period of time and the amount of unreacted carbon contained therein, as compared with the quantity of carbon originally present in the petroleum coke feedstream, are determined by standard sampling procedures and methods of chemical analysis. Responsive to said determination the amount of unconverted petroleum coke in the product stream leaving the reaction zone unreacted is regulated by controlling the feedstreams to the reaction zone, preferably by regulating the oxygen-to-carbon atomic ratio in the feed or to some degree by regulating the H₂O-to-fuel weight ratio in the feed to the reaction zone, or by both methods.

The hot gaseous effluent from the reaction zone is contacted with water in a gas cooling and scrubbing zone where substantially all of the unconverted particulate petroleum coke is extracted from the product gas. Subsequently, in a sedimentation tank, the unconverted petroleum coke forms a petroleum coke-water slurry. The slurry is drawn off at the bottom of the tank and is introduced into a metals recovery zone where it is processed to recover vanadium and nickel. Metal-free particulate petroleum coke may be slurried with water and recycled to the generator as a portion of the feed; thus, no net carbon is produced by the process. Also, clarified water from the sedimentation tank and the metals recovery zone may be recycled back to the quench and scrubbing zone.

It is therefore a principal object of the present invention to produce synthesis gas from petroleum coke containing metal constituents in a refractory lined gas generator without damaging the refractory lining.

Another object of the present invention is to improve the economy and efficiency of the continuous partial oxidation process for producing large volumes of synthesis gas by burning as feed pumpable water slurries containing high concentrations of low-cost particulate petroleum coke.

A further object of the invention is to react water slurries of particulate petroleum coke with an oxidizing gas in a novel manner which avoids preheating the slurry and which produces superior results upon gasification.

A still further object of the process of the invention is to recover as valuable byproducts the vanadium and nickel found in petroleum coke while protecting the refractory walls of the reaction vessel from attack by said metals.

These and other objects and advantages of the invention will be apparent from the following drawings wherein:

FIG. 1 is a general flow diagram of a preferred embodiment of the process; and

FIG. 2 is an enlarged diagrammatic longitudinal cross section of the front end of the annulus-type burner inserted into the top of the synthesis gas generator shown in FIG. 1.

DESCRIPTION OF THE INVENTION

Petroleum coke containing minor amounts of heavy metal constituents is ground to a particle size of about 12 to 325 mesh (U.S. Standard Sieve Size) and then dispersed in either stream or liquid water in preparation for gasification with an oxygen-rich gas in a compact, unpacked, noncatalytic, refractory lined steel gas generator.

The gasification reaction may be carried out at a pressure in the range of atmospheric to 3,000 p.s.i.g., and preferably in the range of 100 to 3,000 p.s.i.g. Gasification is usually effected at a temperature within the range of about 1,800 to 3,500° F., and preferably in the range of about 2,200 to 2,800° F.

The time in the reaction zone is a value in the range of 1 to about 8 seconds. The generator is insulated, and it is optional but usually desirable to preheat the feedstreams.

The hot product gas from the reaction zone comprises principally hydrogen and carbon monoxide and contains small amounts of unconverted petroleum coke. There may also be included minor quantities of carbon dioxide, water vapor, hydrogen sulfide, nitrogen and methane.

The hot gaseous product stream from the reaction zone of the synthesis gas generator is quickly cooled below the reaction temperature to a temperature in the range of 300 to 700°F. by being immediately discharged into a quench tank of the type shown in the drawing and further described in U.S. Pat. No. 2,896,927, issued to R. E. Nagle et al. (which patent is incorporated herein by reference). Further, during cooling most of the unconverted particulate petroleum coke in the hot effluent gaseous stream is simultaneously recovered as an unconverted petroleum coke-water slurry in said quench water. Then, in a scrubbing zone, the cooled effluent product gas stream may be given an additional washing with water to remove any remaining particulate petroleum coke. A gas-liquid contact apparatus such as a venturi scrubber may be used for this operation.

Alternately, the hot product gas stream from the reaction zone may be cooled to a temperature in the range of 300 to 700° F. by indirect heat exchange in a waste heat boiler. The entrained unconverted particulate petroleum coke may be then scrubbed from the carrier gas by contacting the effluent stream of cooled product gas with water in a gas-liquid contact apparatus, for example in a spray tower, venturi scrubber, bubble plate contactor, packed column, or in a combination of said equipment.

Particulate unconverted petroleum coke settles by gravity to the bottom of the quench tank and scrubbing zone, forming an unconverted petroleum coke-water slurry which is then concentrated in a sedimentation vessel. Dissolved gases may be released from the sedimentation vessel by reducing the tank pressure. The gases may be then recovered as potential fuel gas. Clarified water overflow from the sedimentation vessel may be treated to remove soluble solids, mixed with makeup water, deaerated by conventional methods to remove oxygen and prevent corrosion, and recycled to the quench and scrubbing zone. Conventional deaeration procedures are described in "Water Treatment For Industrial and Other Uses" by Eskel Nordell, chapter 9, Reinhold Publishing Co., 1951. Concentrated unconverted petroleum coke-water slurry from the bottom of the sedimentation vessel may be recycled to the front end of the process and mixed with raw ground petroleum coke to prepare fresh slurry feed to the synthesis gas generator.

Although the stream of hot synthesis gas may be analyzed for suspended unconverted petroleum coke, it is easier to determine the quantity of unconverted particulate petroleum coke entrained in the product gas stream from samples of the unconverted petroleum coke-water slurry over a given period of time, i.e., pounds per hour.

Petroleum coke may be analyzed for carbon and metals by standard methods of chemical analysis. For example, the carbon in the petroleum coke may be burned to carbon dioxide, which is collected and weighed; and metals may be determined from the ash by spectrographic analysis.

Based on said determinations, conditions in the reaction zone are regulated so that entrained in the product gas leaving the reaction zone is an amount of unconverted petroleum coke containing 8 weight percent or more of the quantity of carbon originally present in the petroleum coke feedstream, and preferably in the range of 8 to 20 weight percent. Generally, no economic benefit is gained by operating with a quantity of unconverted petroleum coke in the product gas containing more than 20 weight percent of the amount of carbon originally present in the petroleum coke feedstream.

Further, it was unexpectedly found that in this range of 8 to 20, about 17 to 60 weight percent of a metal constituent or its reaction product passes out of the reaction zone combined with the unconverted petroleum coke. Nickel and vanadium and their reaction compounds are primarily responsible for

the deterioration of the refractory lining; and, their elimination from the generator, along with the unconverted petroleum coke, increases the life of the refractory thousands of hours.

Control of the amount of unconverted petroleum coke in the product gas may be accomplished preferably by regulating the oxygen-to-carbon ratio at a level in the range of 0.7 to 1.5 atoms of oxygen per atom of carbon in the fuel. Some control may also be effected by regulating the weight ratio of H₂O to fuel at a level in the range of about 0.3 to 3.0 pounds of H₂O per pound of particulate petroleum coke fuel supplied to the reaction zone. Control may also be effected by regulating at the same time both the oxygen-to-carbon ratio and the H₂O-to-fuel ratio.

The particulate petroleum coke may be introduced into the reaction zone by any suitable method by which the petroleum coke particles are atomized and highly dispersed in a carrier. Although steam and liquid water are the preferred carriers for the particles of petroleum coke, other suitable substances or combinations of materials may be used, i.e., recycle product gas.

For example, the petroleum coke may be admixed with sufficient water to form a pumpable slurry or dispersion containing from 25 to 55 weight percent of solids, or higher. The slurry may be then passed through a tubular heating zone as a confined stream at relatively high velocity. As the dispersion flows through the heating zone in highly turbulent flow, water vaporizes and the petroleum coke is pulverized and is finally discharged into the reaction zone as a stream of fine solids entrained in steam at a temperature in the range of about 100° to 400° F. Oxygen-rich gas, which may be preheated to a temperature in the range of about 100 to 800° F., is introduced into said reaction zone in admixture with the dispersion of steam and petroleum coke. Further information about dispersing petroleum coke in steam is disclosed in U.S. Pat. No. 2,987,387, issued to C. R. Carkeek et al. which is herewith incorporated by reference.

In a preferred embodiment of this invention, the gasification of liquid-solid phase slurries of water and particulate petroleum coke (containing preferably about 25 to 55 weight percent of solids and higher) may be accomplished without being preheated, in accordance with the process of our invention, by using an annulus-type burner.

An annulus-type burner by which a slurry feed of particulate petroleum coke and water may be atomized, mixed together with a stream of oxygen-rich gas, and discharged into the reaction zone is shown in the drawing and will be described later in greater detail. Other suitable burners are described in coassigned U.S. Pat. No. 2,928,460, issued to DuBois Eastman Charles P. Marion and William L. Slater, which patent is incorporated herewith by reference. Such annulus-type burners were previously used only for heavy liquid hydrocarbon fuels.

A suitable annulus-type burner is shown in FIGS. 1 and 2 of the drawing. The discharge end of the annulus burner assembly is inserted into the reaction zone of a compact, unpacked, free-flow, noncatalytic synthesis gas generator of the type described in coassigned U.S. Pat. No. 2,980,523, issued to R. M. Dille et al., which patent is incorporated herewith by reference. The discharge end of the annulus burner, for example as shown enlarged in FIG. 2 of the drawing herein, comprises an inner conduit through which the petroleum coke-water slurry may be passed, surrounded by an annular passage through which an oxygen-rich gas may be passed.

The oxygen-rich gas may be either air, oxygen-enriched air (40 mole percent O₂ and more), substantially pure oxygen (95 mole percent O₂ and more), or mixtures of gases such as steam and one of said oxygen-rich gases.

Near the tip of the burner the annular passage converges inwardly in the shape of a cone. The oxygen-rich gas is thereby accelerated and discharged from the burner as a high velocity conical stream having an apex angle in the range of about 30° to 45° and an apex located from about 0 to 6 inches beyond

the burner face. When the high velocity stream of oxidizing gas hits the relatively low velocity stream of petroleum coke slurry, atomization of the slurry stream takes place and a fine mist comprising minute particles of water and particulate coke highly dispersed in said oxygen-rich gas is formed in the reaction zone. The particles of petroleum coke impinge against one another and are fragmented further. The discharge velocity of the slurry from the burner is in the range of 5 to 50 feet per second and the discharge velocity of the oxygen-rich gas is greater than 100 feet per second and preferably in the range of 200 feet per second to sonic velocity at the burner tip. In another embodiment of our invention, the feed to the burner is reversed and the petroleum coke-water slurry is passed through the annular passage while the oxygen-rich gas is passed through the inner conduit. The relative velocities of the streams remain the same.

In the atomized dispersion, relative proportions of petroleum coke, water and oxygen-rich gas are regulated within the previously stated ranges to ensure an autogenous temperature in the gas generation zone within the range of 1,800 to 3,500° F. In addition to unconverted petroleum coke in the amount as previously specified, the product gas includes in mole percent dry basis: H₂ 25 to 45, CO 20 to 50, CO₂ 5 to 35, CH₄ 0.06 to 8, and COS+H₂S 0.1 to 2.0. Substantially no free carbon soot is produced.

The process of the invention as just described requires no preheat for the reactants. However, if desired, the oxygen-rich gas or an oxygen-rich gas-stream mixture may be preheated to a temperature in the range of about 100° to 800° F.; and to improve pumpability the feed slurry may be heated to a temperature in the range of 100 to 400° F. but below the vaporization temperature of the water in the slurry. Supplying steam to the reaction zone is optional since the slurry feed usually contains sufficient water to satisfy the process requirements.

The heavy metals and their compounds found in petroleum coke are derived from naturally occurring metallic compounds present in the petroleum from which the coke was made. The naturally occurring metallic compounds in petroleum have a variety of forms including oil-soluble materials, colloidal dispersed metallic compounds, and complex organometallic compounds. The most common heavy metals contained in petroleum coke, generally in the form of oxides, sulfides and other salts, include vanadium, nickel, iron and smaller amounts of chromium, and molybdenum. These metals and compounds are referred to herein as heavy metal constituents and are present in petroleum coke in varying amounts ranging from a trace to over 5,000 parts per million by weight.

The reaction zone in which the partial oxidation of the petroleum coke takes place is free from packing and catalyst and has nearly minimum internal surface. It generally comprises a steel pressure vessel provided with a high temperature refractory lining, for example aluminum oxide. It is postulated that during gasification of the petroleum coke, oxides of the aforesaid metal compounds and metals combine with the refractory to form a composite having a lower melting point than that of the original refractory. Nickel and vanadium in concentrations above about 100 p.p.m. are particularly destructive by combining with the alumina refractory to form NiO·Al₂O₃ and V₂O₅·Al₂O₃, whose crystalline structures weaken the alumina refractory. As a result, at a temperature in the range of 1,800 to 3,500° F. and at the preferred operating temperature in the reaction zone of about 2,200 to 2,800° F., the refractory may spall and deteriorate in a relatively short time; for example, in some cases within a few hours. However, by the process of our invention the life of the refractory lining may be extended many thousands of hours.

While the exact mechanism by which the heavy metal constituents or their oxidation products produced in the reaction zone are prevented from attacking the refractory lining is unknown, it may be postulated that as the raw petroleum coke particles pass through the reaction zone carbon is consumed

um coke. The metal constituents or their oxidation products then leave the reaction zone in the product gas along with the entrained unconverted portion of the petroleum coke feed.

It has been found profitable to process the unconverted petroleum coke-water slurry in order to remove the metal values. For example, after dewatering the slurry by filtration, vanadium, nickel and other metals may be recovered by the process comprising the steps of roasting the unconverted petroleum coke in an oxidizing atmosphere at a temperature of about 220° F. but below the ignition temperature, extracting the resulting water-soluble metal salts with a dilute aqueous solution of a strong mineral acid, e.g., 0.1 to 0.5 N HCl, washing the residue with water, and adding phosphoric acid to the solution to precipitate the metals as the phosphates, which are industrially useful as additives in the manufacture of steel. The metals-free particulate petroleum coke is then recycled as a portion of the feed to the synthesis gas generator.

In the preparation of raw petroleum coke-water slurry feedstock to the generator, in order to keep the solid particles of petroleum coke in suspension thereby preventing the settling and plugging of pipes, lines, pumps and valves, it was desirable to grind the raw petroleum coke quite fine. Petroleum coke may be pulverized to a particle or agglomerate size of from about 44 to 420 microns diameter by any suitable standard procedure, e.g., U.S. Pat. 2,846,150, issued to Lincoln T. Work. The small size of the solid fuel particle is important to assure a uniform suspension in the liquid vehicle which will not settle out, to allow sufficient motion relative to the gaseous reactions, and to assure substantially complete gasification.

However, fine grinding will increase the surface area of the petroleum coke and decrease the amount that can be mixed with water to form a pumpable slurry. A water slurry of petroleum coke ground to -325 mesh may be no longer pumpable when the solids content exceeds about 40 to 50 weight percent. Thus, although fine grinding may be desirable to prevent plugging, it is expensive and may result in dilute slurries with excess water being added to the synthesis gas generator. By increasing the particle size of the petroleum coke to as large as -12 mesh (U.S. Standard Sieve Size), the amount of particulate petroleum coke in the slurry may be increased to about 75 weight percent. By adding about 2 to 10 weight percent of a gelling agent, the slurry becomes thixotropic and settling is greatly diminished. Although the slurry may then appear thickened or gelled, the slurry will easily work into a fluid which can be readily pumped. Pectins may be used as gelling agents in the preparation of petroleum coke-water slurries. A pumpable petroleum coke-water slurry is one having a viscosity less than 700 centipoise.

Petroleum coke consists of dehydrogenated and condensed hydrocarbons of high molecular weight in the form of a matrix of considerable physical extent comprising principally carbon and containing dispersed throughout a very minor amount of petroleum-based asphalticlike like compounds. Raw petroleum coke suitable for use as a starting material in the process of this invention may be produced by the "delayed coling" process for converting heavy residual fuel oil into gasoline, gas oil, and coke. Other suitable petroleum coking processes are available that produce a petroleum coke having a similar structure and chemical analysis. A typical delayed coking process is described in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Vol. 15, Inter-Science Publishers 1968, pages 20-23. Typical analysis of petroleum coke in weight percent follows:

	Petroleum Coke
Volatiles	3-7
Fixed Carbon	89-96
Ash*	0.1-1.3
Sulfur	1.0-5
H ₂ O	0
Density, g./ml.	1.28-1.6
Oil Absorption No., cc./g.r	less than 1.0
Size, microns	44-1,680

DESCRIPTION OF THE DRAWING

A more complete understanding of the invention may be had to by reference to the accompanying schematic drawing which shows the previously described process in detail. Although the drawing illustrates a preferred embodiment of the process of this invention, it is not intended to limit the invention to the particular apparatus or materials described.

With reference to the drawing, raw petroleum coke is passed through line 1 into grinder 2 where it is mixed with a recycle stream of water-petroleum coke slurry from line 3 and ground until about 88 weight percent of the petroleum coke passes through a U.S. Standard Sieve of about 200 meshes per square inch. The water slurry of ground petroleum coke is discharged through line 4 into mix-charge tank 5 where a stream of water-petroleum coke slurry from line 6 may be added and the concentration of petroleum coke in the slurry feed may be adjusted to 50 weight percent. With no preheat, the water-petroleum coke slurry feedstream is pumped through lines 7 and 8 and is discharged at a relatively low velocity in the range of 5 to 50 feet per second from the central conduit 9 of an annulus-type burner 10, which is mounted in the top flanged head 11 of vertical, unpacked, free-flow, noncatalytic synthesis gas generator 12. FIG. 2 depicts an enlarged view of the discharge end 13 of burner 10 which extends into the refractory lined reaction zone 14 of the gas generator 12.

A stream of oxygen-rich gas, such as substantially pure oxygen (95 mole percent O_2 or more) or oxygen-enriched air (40 mole percent O_2 or more) is introduced into the burner 10 through line 15. The oxygen-rich gas is discharged through annular passage 15 of burner 10 at a relatively high velocity in the range of about 200 feet per second to sonic velocity. Reactant streams from 9 and 16 make contact at point 17 located about 0 to 6 inches beyond the tip of burner 10. There the streams mix and form an atomized dispersion. Reaction then takes place immediately at an autogenous temperature in the range of 1,800° to 3,000° F., and preferably at a temperature in the range of 2,200 to 2800° F., and at an elevated pressure in the range of about atmospheric to 3,000 p.s.i.g., and preferably in the range of 100 to 3,000 p.s.i.g., to produce synthesis gas comprising principally carbon monoxide and hydrogen and a quantity of entrained unconverted petroleum coke containing unreacted carbon in the amount of 8 weight percent or more of the quantity of carbon originally present in the petroleum coke feedstream to the reaction zone. Cooling water is supplied to the burner through line 18 and is discharged through line 19 to prevent the burner from overheating.

The hot effluent gas from reaction zone 14 is discharged directly into quench water contained in quench chamber 20. Water in the quench zone effects quick cooling of the hot effluent gas to below the reaction temperature, provides a means for removing most of the entrained unconverted particulate petroleum coke from the product gas, and produces steam which is useful in subsequent operations. For example, in the water-gas shift reaction for increasing the hydrogen yield, H_2O and CO in the product gas are reacted over an iron oxide-chromic oxide catalyst to product additional H_2 and CO_2 .

Most of the remaining entrained particulate petroleum coke is removed from the cooled synthesis gas by passing the cooled effluent gas stream from quench zone 20 through line 21 and into venturi scrubber 22 where it is further contacted and scrubbed with water from line 23. The scrubbed synthesis gas is then passed through line 24 into gas-liquid separator 25 where condensed water vapor in the gas stream drops to the bottom carrying with it any remaining petroleum coke particles in the synthesis gas stream. A product stream of solids-free synthesis gas is removed by way of line 26 at the top of

gas-liquid separator 25 for further use in processes which are not shown in the drawing.

The carbon-water mixture from the bottom of gas-liquid separator 25 is passed through line 27 and mixed in line 28 with the particulate unconverted petroleum coke-water slurry which is pumped from the bottom of quench tank 20 by way of lines 29 and 30. The sensible heat in the slurry in line 29 is used to heat the scrub water in line 31 by means of heat exchanger 32. The unconverted particulate petroleum coke-water slurry in line 28 is passed through pressure reducing valve 33 and line 34 in sedimentation vessel 35.

Unconverted particulate petroleum coke settles by gravity to the bottom of sedimentation vessel 35 where it is drawn off through line 36 as a concentrated slurry of unconverted particulate petroleum coke and water. With valves 37 and 38 closed and valves 39 and 40 open, this slurry may be recycled to grinder 2 for use as a vehicle for the raw petroleum coke feed in line 1. By means of pump 41, the slurry is passed through lines 42 to 46, and 3. If desired, a portion of this slurry may be diverted through lines 47 and 6 into mix tank 5 in order to adjust the slurry concentration from line 4. Dissolved gases are discharged through line 48 at the top of sedimentation vessel 35 and recovered as potential fuel gas. Clear water overflow is withdrawn from vessel 35 through line 49 and introduced into a conventional water treatment facility 50, such as ion exchange resins, for removing soluble solids. Dissolved gases may be released and removed through line 51.

Clear water is withdrawn through line 52 at the bottom of water treatment facility 50, and mixed in line 53 with fresh makeup water from lines 54 and 55 and water from line 56. By means of pump 57, a first portion of water from line 53 is recycled to quench vessel 20 by way of line 31, heat exchanger 32, and lines 58 and 59. A second portion of the water from line 53 is pumped through line 31, heat exchanger 32, and lines 58 and 23 to provide sufficient hot water to operate venturi scrubber 22 as previously described.

Periodically, heavy uncombustible solids that settle to the bottom of quench vessel 20 are withdrawn as a water-solids slurry through line 60, valve 51, line 62 and are passed into lock hopper 63. The slurry is then passed through line 64, valve 65, line 66 into the dewatering zone 67. Dewatering may be accomplished by standard methods such as by filtration and centrifuge. By closing valve 39 and opening valve 37, unconverted petroleum coke-water slurry bottoms from sedimentation tank 35 may be passed into dewatering zone 67, by way of lines 36, 68 and 69. A portion of clarified water from the bottom of dewatering zone 67 may be recycled to the quench and scrubbing zones by way of lines 70, 56 and 53 in the manner previously described. Another portion of the clear water may be recycled to grinder 2 or mix-charge tank 5 by way of lines 70, 71, 72, 44, pump 41, and line 45 in the manner previously described.

Substantially water-free unconverted petroleum coke is conveyed from dewatering zone 67 over line 73 and into a metals recovery zone 74. Any suitable process for recovering vanadium and nickel from the unconverted petroleum coke may be used. Vanadium and nickel are discharged from the metals recovery zone 74 through line 75. Vanadium and nickel-free petroleum coke from the bottom of metals recovery zone 74 is passed through line 76 and slurried in line 72 with water from line 71. Then, by means of pump 41, the slurry is distributed to grinder 2 or to mix-charge tank 5 in the manner previously described. Uncombustible solids are discharged from metals recovery zone 74 through line 77 as waste.

EXAMPLE OF THE PREFERRED EMBODIMENT

The following example is offered as a better understanding of the present invention, but the invention is not to be construed as limited thereto.

EXAMPLE I

With reference to FIG. 1 of the drawing, 525 pounds of raw petroleum coke prepared from reduced crude oil by the "delayed coking" process are ground to -200 mesh (U.S. Standard Sieve Size) and mixed with a recycle slurry comprising 27 pounds of unconverted petroleum coke and 523 pounds of water. Analysis of the raw petroleum coke as received and the recycled unconverted petroleum coke are shown below in table I.

1,075 pounds per hour of the resulting slurry containing 51.4 weight percent of petroleum coke are discharged at a rate of 25 feet per second and at a temperature of 124° F. from the central passage of an annulus-type burner as shown in FIG. 2. The burner is mounted through the top head of a compact, unpacked, free-flow, noncatalytic 11.8 cubic feet synthesis gas generator in the manner shown in FIG. 1. 9024 standard cubic feet per hour (SCFH) of oxygen (100 mole percent O₂) at a rate of 350 feet per second and at a temperature of 264° F. are discharged from the annular passage of said burner.

22,631 SCFH of dry synthesis gas are produced in the gas generator from the ensuing partial oxidation reaction of the atomized streams at a temperature of 2,550° F. and at a pressure of 346 p.s.i.g.

An analysis of product gas follows: In mole percent dry basis: H₂ 32.77, CO 45.46, CO₂ 20.58, H₂S 0.24, CH₄ 0.06, N₂ 0.79, and A 0.10. Also entrained in the product gas stream are 27 pounds per hour of unconverted petroleum coke containing 1,995 parts per million of nickel and 1,082 p.p.m. of vanadium. This represents a recovery of 13 weight percent of the nickel present in the feed and 10 weight percent of the vanadium present in the feed.

The hot product gas stream issuing from the reaction zone of the generator is immediately cooled in the quench chamber with water. Substantially all of the unconverted petroleum coke is recovered from the product gas stream by forming a petroleum coke-water slurry comprising 6,030 pounds per hour of water and about 27 pounds per hour of unconverted petroleum coke containing about 5 weight percent of the amount of carbon originally present in the petroleum coke feed. The slurry is cooled, combined with the bottoms from the gas-liquid separator comprising 3,328 pounds per hour of water and a trace of petroleum coke, and introduced into a sedimentation vessel where the particulate unconverted petroleum coke settles to the bottom by gravity.

8,900 pounds per hour of clarified water is removed as overflow from the sedimentation vessel and introduced into a conventional water treatment purification system. About 8,900 pounds per hour of clarified water from the water treatment purification system and 400 pounds per hour of makeup water are recycled to the quench zone and carbon scrubbing operation. The slurry underflow from the sedimentation water comprising 470 pounds per hour of water and 27 pounds per hour of unconverted petroleum coke may be recycled to the grinding operation (ball mill) or to the mix tank as the source of water to produce the feed slurry, and also as a means for disposing of the unconverted carbon.

About 2.9 pounds per hour of uncombustible ash are removed from the bottom of the quench vessel by way of the lock hopper system and are introduced into a conventional de-watering zone, for example, a vacuum filter. 94 pounds per hour of water are removed from the ash and recycled to the grinder or to the mix tank and the uncombustible ash is discarded as waste. Thus, by operating in this manner, there is no net carbon produced by the process. A summary of the performance data for run 1 follows in table II.

Operating the synthesis gas generator in the manner described above for run 1, within a relatively short time (less than 25 hours) the refractory lining in the reaction zone begins to spall and deteriorate.

To prevent this damage to the refractor, samples of the slurry water and unconverted particulate petroleum coke from the quench chamber are dried, analyzed, the amount of unconverted particulate petroleum coke and the carbon therein

that pass unreacted through the reaction zone for a given period of time are determined. Responsive to said determinations, the feedstreams to the reaction zone are regulated in steps by decreasing the oxygen-to-fuel ratio, by increasing the stream-to-fuel ratio, or by both of these techniques, while maintaining all other conditions in the generator substantially the same. This causes the unconverted petroleum coke in the product gas to increase. When the amount of unconverted petroleum coke in the product gas contains 8 weight percent or more of the quantity of carbon originally present in the petroleum coke feedstream, damage to the refractory lining in the generator is substantially stopped.

For example, as a comparison with run 1, run 2 shows that by decreasing the oxygen-to-fuel ratio in run 1 from 16.36 standard cubic feet per hour per pound of particulate petroleum coke feed to a value of 15.83 in run 2, and by increasing the H₂O-to-fuel ratio in run 1 from 0.95 pounds of H₂O per pound of petroleum coke feed to a value of 1.03, while maintaining other conditions substantially the same, the temperature in the reaction zone decreases from 2,550° F. to 2,450° F., and the quantity of unconverted petroleum coke entrained in the product gas increases from an amount containing about 5 weight percent of the quantity of carbon originally present in the petroleum coke feedstream to a quantity of entrained unconverted petroleum coke containing 13 weight percent of the amount of carbon originally present in the petroleum coke feedstream. Further, at this level substantially all attack of the generator lining has stopped.

In run 2, 473 pounds of raw petroleum coke prepared from reduced crude oil by the "delayed coking" process are ground to -200 mesh (U.S. Standard Sieve Size) and mixed with a recycle slurry comprising 71 pounds of unconverted petroleum coke and 563 pounds of water. Analysis of the raw petroleum coke as received and the recycled unconverted petroleum coke are shown below in table I.

1,107 pounds per hour of the resulting slurry containing 49.2 weight percent of petroleum coke are discharged at rate of 25 feet per second and at a temperature of 132° F. from the central passage of an annulus-type burner as shown in FIG. 2. The burner is mounted through the top head of a compact, unpacked, free-flow, noncatalytic 11.8 cubic foot synthesis gas generator in the manner shown in FIG. 1. 8,615 SCFH of oxygen (100 mole percent O₂) at a rate of 350 feet per second and at a temperature of 265° F. are discharged from the annular passage of said burner. 20,298 SCFH of dry synthesis gas are produced in the gas generator from the ensuing partial oxidation reaction of the atomized stream at a temperature of 2,450° F. and at a pressure of 350 p.s.i.g.

An analysis of the product gas follows: In mole percent dry basis: H₂ 33.02, CO 47.22, CO₂ 18.94, H₂S 0.06, CH₄ 0.20, N₂ 0.47, and A 0.09. Substantially no free carbon soot is produced. Also entrained in the product gas stream are 71 pounds per hour of unconverted petroleum coke containing 2,440 p.p.m. of nickel and 2,380 p.p.m. of vanadium. This represents a recovery of 35.1 weight percent for nickel and 40.1 weight percent for vanadium. The remaining nickel and vanadium is intermittently removed along with heavy ash or slag in the lock hopper system at the bottom of the quench vessel and eventually recovered in the vanadium and nickel recovery section. A summary of the performance data for run 2 follows in table II.

TABLE I—ANALYSIS OF PETROLEUM COKE

Element	Units	Raw—line 1		Unconverted—line 36	
		Run 1	Run 2		
C	wt. %	89.28	89.28	83.60	91.34
H	wt. %	2.58	2.58	4.55	0.57
N	wt. %	2.35	2.35	0	0
Ash	wt. %	2.41	2.41	9.95	6.2
S	wt. %	1.6	1.6	1.90	1.89
Ni	p.p.m.	750	710	1,995	2,440
V	p.p.m.	500	590	1,082	2,380

TABLE II—PERFORMANCE DATA

	Run 1	Run 2
Oxygen/Fuel Ratio, SCFH/lb.	16.36	15.83
H ₂ O/Fuel Ratio, lb./lb.	0.95	1.03
Oxygen/Carbon Ratio, atom/atom	1.16	1.12
Residence Time, sec.	5.54	5.79
O ₂ /Fuel, moles per MM B.t.u.	2.85	2.76
Heat of Combustion, B.t.u./lb.	15,122	15,122
Generator Temperature, ° F.	2,550	2,450

The process of the invention has been described generally and by examples with reference to petroleum coke-water 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.

We claim:

1. A partial oxidation process for producing synthesis gas from particulate petroleum coke containing heavy metal constituents comprising mixing together to form a pumpable feed slurry containing about 25 to 75 weight percent of solids said particulate petroleum coke having a particle size of about 12 to 325 mesh and H₂O, introducing a stream of said feed slurry into a refractory lined reaction zone of a free-flow noncatalytic unpacked partial oxidation synthesis gas generator, introducing a stream of oxygen-rich gas into said reaction zone, bringing said streams into contact with one another in said reaction zone to produce a dispersion of said feed slurry and said oxygen-rich gas, and reacting said dispersion in said reaction zone at an autogenous temperature in the range of about 1,800° to 3,500° F. and at a pressure in the range of about 100 to 3,000 p.s.i.g., and controlling the amounts of said feedstreams to said reaction zone so as to produce a hot product gas stream comprising principally hydrogen and carbon monoxide and containing a controlled amount of entrained unconverted particulate petroleum coke containing at least 8 weight percent of the quantity of carbon originally present in said petroleum coke feedstream, so that said entrained unconverted petroleum coke retains a sufficient amount of said heavy metal constituents or the oxidation products of said heavy metal constituents from said reaction zone to prevent damage to said refractory lining.

2. The process of claim 1 with the added steps of preheating said stream of feed slurry to a temperature in the range of 100° to 400° F. and preheating said stream of oxygen rich gas to a temperature in the range of 100° to 800° F. and wherein the entrained unconverted particulate petroleum coke in the product gas stream leaving the reaction zone is in an amount so that about 8 to 20 weight percent of the carbon originally present in the petroleum coke feedstream is retained unreacted by said entrained unconverted petroleum coke in the product gas stream, and wherein about 17 to 60 weight percent of the heavy metal constituents in the petroleum coke feedstream or their oxidation products are retained by the unconverted particulate petroleum coke entrained in said product gas stream, and wherein said heavy metal constituents comprise heavy metals and their oxides, sulfides and salts, and said heavy metals are selected from the group consisting of vanadium, nickel, iron, chromium and molybdenum.

3. The process of claim 1 wherein said petroleum coke-water slurry is atomized and mixed with said oxygen-rich gas by passing said stream of slurry at a discharge velocity of about 5 to 50 feet per second through the inner conduit of an annulus-type burner, passing said stream of oxygen-rich gas at a discharge velocity in the range of about 200 feet per second to sonic velocity through the annular passage of said burner, and contacting said slurry stream with said oxygen-rich gas stream in said reaction zone where combustion of said atomized mixture takes place.

4. The process of claim 1 wherein said petroleum coke-H₂O stream is atomized by passing said stream of oxygen-rich gas at a discharge velocity in the range of about 200 feet per second to sonic velocity through the inner conduit of an annulus-type burner in said reaction zone and contacting said oxygen-rich gas stream with a stream of said petroleum coke-H₂O stream passing at a discharge velocity of about 5 to 50 feet per second through the annular passage of said burner.

5. The process of claim 1 wherein said particulate petroleum coke is dispersed in water to form the pumpable slurry less than 10 weight percent of a gelling agent.

6. The process of claim 1 with the added steps of quenching the hot product gas stream from the reaction zone by discharging it directly into a quench zone, thereby simultaneously cooling it with quench water to a temperature in the range of about 300° to 700° F. and recovering most of said unconverted particulate petroleum coke as an unconverted particulate petroleum coke-water slurry, and scrubbing the cooled product gas stream from the quench zone with water in a scrubbing zone to recover any remaining unconverted particulate petroleum coke as an unconverted petroleum coke-water slurry.

7. The process of claim 6 with the added step of dewatering at least a portion of said unconverted particulate petroleum coke-water slurry in a dewatering zone by sedimentation or filtration, recovering vanadium and nickel from said dewatered petroleum coke in a metals recovery zone, slurring the metals-free unconverted petroleum coke from the metals recovery zone with water from the dewatering zone, and recycling said slurry as a portion of the feed to the reaction zone of said synthesis gas generator.

8. In a partial oxidation process for producing synthesis gas in a high temperature refractory lined reaction zone of a catalytic, free-flow, unpacked synthesis gas generator, the improvement for extending the life of said high temperature refractory lining while reacting in said reaction zone as fuel a H₂O dispersion of petroleum coke containing heavy metal constituents which comprises:

1. feeding to said reaction zone in admixture are atomized dispersion of said petroleum coke having a particle size in the range of about 12 to 325 mesh and a stream of oxygen-rich gas selected from the group consisting of air, substantially pure oxygen, and oxygen-enriched air;
2. reacting the feed mixture of (1) in said reaction zone at an autogenous temperature in the range of from about 1,800° to 3,500° F. and a pressure in the range of about atmospheric to 3,000 p.s.i.g. to produce a hot effluent gas stream comprising principally hydrogen and carbon monoxide and containing entrained a controlled amount of unconverted particulate petroleum coke;
3. cooling the hot effluent gas stream from (2) and recovering the unconverted particulate petroleum coke in water as a slurry;
4. determining the quantity of unconverted petroleum coke in the effluent gas stream of (2) for a given period of time;
5. responsive to the determination in (4), controlling the amount of said unconverted particulate petroleum coke in the hot effluent gas stream leaving (2) by regulating the ratio of free oxygen to carbon in the feed mixture of (1) in the range of 0.7–1.5 atoms of oxygen per atom of carbon and the ratio of H₂O to carbon in the feed mixture of (1) in the range of 0.2–3.0 parts by weight of H₂O per part by weight of carbon so as to produce said hot effluent gas stream leaving (2) comprising in mole percent dry basis: H₂ 25 to 45, CO 20 to 50, CO₂ 5 to 35, CH₄ 0.06 to 8.0, (COS+H₂S) 0.1 to 2.0, and said entrained unconverted petroleum coke containing about 8 to 20 weight percent of the quantity of carbon originally present in the petroleum coke feed in (1), so that said entrained unconverted particulate petroleum coke in the product gas retains from about 17–60 weight percent of the heavy metal constituents as contained in the petroleum coke feed of (1) or the oxidation products of said heavy metal constituents as produced in said reaction zone so that damage to said refractory lining is prevented.

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9. The process of claim 8 with the additional steps of cooling the hot effluent gas steam from (2) in a cooling zone and recovering said unconverted particulate petroleum coke from said effluent gas by contacting it with water forming an unconverted particulate petroleum coke-water slurry; dewatering said unconverted particulate petroleum coke-water slurry in a dewatering zone producing clear water and unconverted particulate petroleum coke; recovering heavy metals from said

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dewatered unconverted particulate petroleum coke in a metals recovery zone, leaving metals-free unconverted particulate petroleum coke; forming a slurry of metals-free unconverted particulate petroleum coke with the water from said dewatering zone and recycling said slurry as a portion of the feed to the reaction zone of said synthesis gas generator.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,607,157 Dated September 21, 1971

Inventor(s) WARREN G. SCHLINGER, WILLIAM L. SLATER, ROGER M. DILLE
and JOSEPH P. TASSONEY

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

- Col. 1, line 42 "hover" should be --however--
- Col. 3, line 26 "colled" should be --cooled--
- Col. 3, line 54 "unconnverted" should be --unconverted--
- Col. 4, line 31 "stream" should be --steam--
- Col. 5, line 75 Add the following after "consumed": --by
oxidation leaving behind the heavy metal
constituents or their oxidation products
attached to the unconverted petrole--
- Col. 6, line 55 "asphalticlike like" should be
--asphaltic-like--
- Col. 6, line 57 "coling" should be --coking--
- Col. 6, line 75 Insert --*non-volatile inorganic compounds
including the oxides of naturally occurring
organo-metallic compounds--
- Col. 9, line 72 "refractor" should be --refractory--
- Col. 9, line 73 Before "water" insert --of--
- Col. 10, line 68 Table I heading for column 5 should be
--Run 1-- and heading for column 6 should
be --Run 2--
- Col. 12, line 40 "are" should be --an--
- Col. 12, line 63 "weigh" should be --weight--

Signed and sealed this 12th day of September 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents