

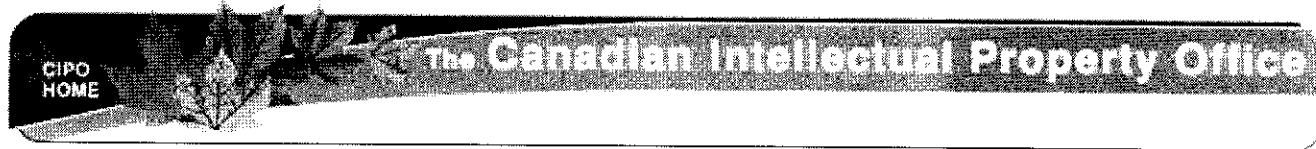


Industry Canada / Industrie Canada

Canada

strategis.gc.ca

Strategis Index:



Canadian Patents Database

12/20/2001 - 08:04:51

(11) CA 951900

(12) Patent:

(54) HYDROGEN AND CARBON MONOXIDE FROM SLURRIES OF SOLID CARBONIFEROUS FUELS

(54)

(72) (Country): **SCHLINGER, WARREN G.** (Not Available)
TASSONEY, JOSEPH P. (Not Available)
SLATER, WILLIAM L. (Not Available)
DILLE, ROGER M. (Not Available)

(73) (Country): **Texaco Development Corporation** (United States)

(71) (Country):

(74)

(45) **July 30, 1974**

(22)

(43)

(52) **44/23 44/26 48/26 44/28 44/9**

(51) **N/A**

No

(30) **None**

N/A

Unknown

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
-

BACKGROUND OF THE INVENTION

Field of the Invention: This invention relates to the production of synthesis gas. More particularly, it relates to improvements in the partial oxidation process for generating hydrogen and carbon monoxide by utilizing as feed-stock atomized dispersions of liquid slurries of solid carboniferous fuels.

DESCRIPTION OF THE PRIOR ART

10 Synthesis gas, a mixture of carbon monoxide and hydrogen, is usually made by the partial oxidation of gaseous or liquid hydrocarbons by means of an oxidizing gas such as air, oxygen (95 mole % or more) or oxygen-enriched air (40 mole % O_2 or more). The raw synthesis gas leaving the unpacked noncatalytic reaction zone of the synthesis gas generator at a temperature in the range of about 1800 to 3200°F. comprises principally CO and H_2 , together with minor amounts of H_2O , CO_2 , CH_4 , H_2S , and free particulate carbon or soot. For a more complete description of the synthesis gas process, refer to U.S. Patent 2,809,104 issued to Dale M. Strasser et al.

20

Synthesis gas mixtures are important commercially as a source of hydrogen for hydrogenation reactions, and as a source of feed gas for the synthesis of hydrocarbons, oxygen-containing organic compounds, or ammonia.

The gaseous and liquid hydrocarbon fuels used in conventional processes for manufacturing synthesis gas include methane, propane, naphtha, crude oil, and vacuum residuum. Heavy oils are usually atomized and mixed with superheated steam in a tubular furnace, and the resulting fuel-steam mixture is then mixed with an oxidizing gas in

30



a burner. Previous to our invention many processing problems made impractical the gasification of slurries of solid carboniferous fuels. For example, preheating the slurry feed in a tubular furnace was troublesome as solids would plug the furnace tubing during vaporization of the slurry. Plugging the tubing might occur even with dilute slurries having a solids content of 1 to 4 wt. %. Although by diluting slurries one might improve their pumpability, this is undesirable since dilution adds excessive amounts of water to the generator. Further, it was found that the surface area of the particulate carbon formed in the synthesis gas process is related to the H₂O to fuel ratio, and excess H₂O caused problems in the carbon-recovery system. Since our invention requires substantially no preheating, the aforesaid plugging difficulties are eliminated and pumpable slurries with greater solids contents may be used as feed, thereby reducing considerably the quantity of H₂O fed to the synthesis gas generator.

10

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 5000 parts per million or more. These metal constituents or their reaction products were found to attack the refractory lining, causing equipment failure and shut-down. Now, however, by the process of our invention this difficulty has been substantially overcome.

20

SUMMARY

By the process of our invention a slurry of particulate carboniferous fuel, e.g., petroleum coke, coke from bituminous coal, coal, oil shale, tar sands, pitch, or mixtures of these materials in a liquid vehicle selected from the group comprising water, a hydrocarbon liquid fuel, or a mixture of these liquids is passed through the inner conduit of an annulus type burner at a relatively low velocity of 5 to 50 feet per second. Simultaneously, at a relatively high velocity in the range of from 200 feet per second to sonic velocity at the burner tip, a converging atomizing stream of oxidizing gas is passed through a concentric annular passage in the burner. The two streams meet in front of the burner face which is located inside of the reaction zone of an unpacked noncatalytic synthesis gas generator. There they mix and form an atomized dispersion of water, hydrocarbon liquid fuel, oxidizing gas, and particulate solid carboniferous fuel. If desired the water may be introduced into the burner as steam mixed with the oxidizing gas or as a liquid vehicle for the solid fuel. Under synthesis gas generating conditions, the atomized dispersion is reacted to produce a gaseous mixture of hydrogen and carbon monoxide. By the process of our invention, low cost solid carboniferous fuels may be gasified in a synthesis gas generator without being preheated.

The amount of particulate solid carboniferous fuel in a pumpable slurry may be increased to 75 wt. % and the particle size of the solid fuel may be increased to pass through a standard 12 mesh screen by the addition of 2 to 10 wt. % of free carbon soot as produced for

example by the partial oxidation of crude oil in a synthesis gas generator.

In one embodiment of our invention a feedstream of petroleum coke containing about 100 to 5000 parts per million or more of heavy metal constituents dispersed in H_2O may be reacted with an oxygen-rich gas in the closed, compact refractory lined reaction zone of the 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.

10

First, particles of the petroleum coke from about U.S. Standard No. 12 to 350 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 1800 to 3500°F. and a pressure in the range of atmospheric to 3000 psig, and preferably 100 to 3000 psig, a hot product gas stream is produced comprising principally hydrogen and carbon monoxide and containing minor amounts of CH_4 , H_2S , N_2 and A.

20

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 % 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 % of any harmful heavy metal

30

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.

It is therefore a principal object of the present invention to improve the economy and efficiency of the continuous partial oxidation process for producing large volumes of synthesis gas comprising principally hydrogen and carbon monoxide and containing controlled amounts of particulate carbon.

10

Another object of the invention is to utilize directly as feedstock in the partial oxidation process for producing synthesis gas liquid slurries of low cost solid carboniferous fuels containing a high solids content.

A still further object of the invention is to react liquid slurries of solid carboniferous fuels with an oxidizing gas in a novel manner which avoids preheating the slurry and which produces superior results upon gasification.

20

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

DESCRIPTION OF THE INVENTION

The gasification of liquid slurries of solid carboniferous fuels (containing about 1 to 75 wt. % of solids) may be accomplished in accordance with the process of our invention using an annulus type burner, for example as shown in the drawing of coassigned U.S. Patent No.

30

2,928,460 issued to DuBois Eastman, Charles P. Marion, and

William L. Slater. The front end of the annulus type burner assembly, as shown in Figure 2 of said drawing, is inserted into the compact, unpacked, noncatalytic reaction zone of a synthesis gas generator of the type described in United States Patent 2,980,523 issued to R. M. Dille et al. The front end of said burner comprises an inner conduit 10, through which the liquid-solid slurry may be passed, surrounded by an annular passage 15 through which an oxidizing gas or an oxidizing gas-steam mixture may be passed. In preparing the liquid-solid slurry, the liquid vehicle for the solid carboni-
ferous fuel may be water or a hydrocarbon liquid or a mixture of both. Pumpable slurries containing 1-60 wt. % of ground solid carboniferous fuel in petroleum oil and 25-55 wt. % of ground solid carboniferous fuel in water are preferred. When the liquid vehicle is water, steam need not be mixed with the oxidizing gas. The oxidizing gas may be air, oxygen enriched air (more than 40 mole % O_2), or pure oxygen (more than 95 mol % O_2).

Near the tip of the burner said annular passage converges inwardly in the shape of a hollow, right cone, as shown in Figure 2 of United States Patent 2,928,460. The oxidizing gas or oxidizing gas-steam mixture 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° . The streams from the burner converge at a point located about 0 - 6 inches beyond the burner face. The high velocity stream of oxidizing gas hits the relatively low velocity stream of liquid-solid slurry, atomizing it and forming a fine mist comprising minute particles of water, hydrocarbon liquid fuel, and particulate solid carboniferous fuel highly dispersed in said oxidizing gas. The particles of

solid carboniferous matter impinge against one another and are fragmented further. The velocity of the slurry is in the range of 5 to 50 feet per second and the velocity of the oxidizing gas is greater than 100 feet per second and preferably at a velocity in the range of 200 feet per second to sonic velocity at the burner tip.

While this discussion was based on a burner and feed stream arrangement as previously described, it is understood that the feed to the burner may be reversed.

10 That is in another embodiment of our invention, the liquid-solid slurry may be passed through the annular passage 15 while the oxidizing gas or oxidizing gas-steam mixture is passed through the inner conduit 10.

Partial oxidation of the feed takes place in the reaction zone of the synthesis gas generator at a temperature in the range of about 1800 to 3500°F, and at a pressure in the range of atmospheric to 3000 psig, and preferably in the range of about 100 to 3000 psig. The atomic ratio of free oxygen to carbon in the feed is a value in the range of 0.70 to 1.2 and the weight ratio of water to fuel present in the reaction zone is a value in the range of 0.2 to 3.0. The composition of the effluent stream of synthesis gas leaving the generator expressed as mole % dry basis is as follows: H₂ 30 to 49, CO 35 to 68, CO₂ 7 to 25, CH₄ 0.1 to 8.0, COS + H₂S 0.1 to 2.0, and soot + unconverted coke 1 to 20.

20 In the preparation of slurries of coke and other solid carboniferous fuels, in order to keep the solid particles in suspension thereby preventing the settling and plugging of pipes, lines, pumps, and valves, it was found

30

desirable to pulverize the material to a particle size so that 60-95% passes through a 325 mesh screen. However, fine grinding increases surface area and decreases the amount of solids that can be mixed with the liquid vehicle before the slurry becomes too thick to be pumped. Thus, although fine grinding may be desirable in certain respects, it is expensive and may result in dilute slurries with excess water being added to the synthesis gas generator.

10 It was unexpectedly found that by adding to an unpumpable slurry of particulate solid carboniferous fuel about 2-10 wt.% of particulate free carbon soot of the type produced by the partial oxidation of crude oil in a synthesis gas generator, the amount of particulate solid carboniferous fuel in the slurry may be increased to 75 wt.%, the slurry may be readily pumped or otherwise conveyed, and settling is greatly diminished. Although the slurry may appear thickened or gelled, the mixture is thixotropic and will easily work into a fluid which can be readily pumped. The term pumped includes other suitable means for conveying
20 the slurry. Further, the particle size of the solid carboniferous fuel may be increased from -325 to -12 mesh. Now by our invention -12 mesh particles of solid carboniferous fuel are fine enough to stay in suspension and are easily reacted in the synthesis gas generator. Also, the larger particle size results in reduced grinding costs and the solids content of the slurries may be increased. With water and distillate hydrocarbon liquid fuels, such as water, naphtha, and gas oils, about 2-4 wt.% of free carbon soot will thicken the mixture enough to prevent settling; however,
30 with non-distillate hydrocarbon liquid fuels such as fuel oil,

about 4-10 wt. % of soot may be required. Soot is based on amount of liquid vehicle.

B Electron micrographs of the soot particles suitable for use as a slurry gelling agent in the process of our invention resemble hollow spheres of "sponge like" texture of about .01 to .5 microns ~~millimeters~~ in diameter. Because of this structure the carbon has a tremendously high surface area, about 300 to 1000 square meters per gram. The carbon varies in surface area depending on the generator conditions and the ash content of the fuel. Generally the surface area is related to the oil absorption number, which is determined by ASTM Method D-281 and may be expressed by cubic centimeters of oil required to make a single coherent ball of paste from a 1 gram sample of dry particulate carbon. The oil absorption number of typical free carbon blacks or soot made by the partial oxidation process is greater than 1 and usually varies from 2 to 4 cc of oil per gram of C. The surface area of the carbon limits the loading of carbon in fuel oil. Because of the high adsorption number, i.e. greater than 1, slurries of the free carbon soot in water or in a hydrocarbon liquid fuel tend to become gels at low carbon concentrations. Particulate carbon - soot is both oleophilic and hydrophilic. Whereas, a gram of soot will absorb 2-3 cc. of oil, it will also absorb large amounts of water. It is postulated that this property of the free carbon soot makes it a good gelling or thixotropic agent when added in small amounts to slurries water and hydrocarbon liquid fuels with petroleum coke, which has an oil absorption number of less than 1. An analysis follows of soot made by the partial oxidation of residual fuel oil in a synthesis gas

generator as described in U.S. Patent 2,809,104 issued to D. Strasser and F. Guptill. In weight percent the soot comprises: carbon 92.3 to 93.4, hydrogen 0.35 to 1.05, sulfur 0.27 to 0.59, and ash 3.36 to 4.64.

10 Atomizable liquid vehicles which are suitable for the preparation of the suspension include water, coal oil, shale oil, gasoline, kerosene, naphtha, gas oil fractions of petroleum distillate, benzene, toluene, hexane, heptane, cyclohexane, tetralin, decalin, fuel oil, residual fuel oil, reduced crude oil, whole crude oil, and mixtures of these various liquids. Also, water and hydrocarbon liquid fuel mixtures, suitably in the form of emulsions with an emulsifying agent or with a gelling agent such as pectins may be used in preparing the liquid-solid carboniferous fuel slurry.

In accordance with the aforesaid description the following new composition of matter suitable for use as a fuel and for feed to a free-flow noncatalytic synthesis gas generator may be produced.

20 A new composition of matter comprising in admixture about 10 to 75 wt.% of solid carboniferous fuel in a liquid vehicle selected from the group consisting of water, gasoline, naphtha, residual fuel oil, reduced crude oil, whole crude oil, coal oil, shale oil, tar sand oil, and mixtures of said liquid vehicles, and containing about 2 to 10 wt. % of free carbon soot (basis weight of said liquid vehicle). In one embodiment, a new fuel composition may consist of about 10 to 75 wt. % of petroleum coke in admixture with about 25 to 88 wt. % of a liquid vehicle selected from the
30 aforesaid group, and about 2 to 10 wt. % of free carbon soot (basis weight of said liquid vehicle).

The process of the invention, as just described, requires no preheat for the reactants. However, if desired the oxidizing gas or the oxidizing gas-steam mixture may be heated to a temperature in the range of about 100 to 600°F. to reduce oxygen consumption. Similarly, the slurry may be heated to a temperature in the range of about 100 to 300°F., but below the vaporization temperature of the liquid vehicle, to reduce the viscosity of the slurry and to improve its pumpability.

10

Although our invention is described hereinafter in particular with reference to petroleum coke, as previously stated it is applicable to other solid carboniferous fuels including coal, coke from bituminous coal, oil shale, tar sands, pitch, and like.

20

Petroleum coke is comprised in general of minute graphite-like crystals imbedded in an organic matrix of highly condensed aromatic compounds such as anthracene, phenanthracene, chrysene, picene and crackene. Petroleum coke suitable for use as a starting material in the process of this invention may be produced by the "delayed coking" process - a process for converting heavy residual fuel oil into gasoline, gas oil, and coke or by other petroleum coking processes that produce a petroleum coke having a similar structure and chemical analysis. For example, see Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Vol. 15, Inter-Science Publishers 1968, pages 20-23. The solid carboniferous residue remaining after the high temperature distillation of moisture and volatile matter from bituminous coal is also known by the name coke and may be also gasified in the manner taught by the process

30

of our invention. Typical analysis of petroleum coke and coke from bituminous coal in wt. % follow:

	Petroleum Coke	Bituminous Coal Coke
Volatiles	3-7	0.5-4.6
Fixed Carbon	89-96	76-95
*Ash	0.1-1.3	0.5-20
Sulfur	0.5-5.0	0.5-5.0
H ₂ O	0	0.5-5.0
Density, g/ml	1.28-1.6	1.3-1.8
10 Oil Absorption No. cc/gr	less than 1.0	1.0
Size, microns	40 to 1680	-

*non-volatile inorganic compounds including the oxides of naturally occurring organo-metallic compounds.

In one embodiment of the invention by which aqueous slurries of petroleum coke are gasified, 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. 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.

10

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 make-up 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.

20

30

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.

10 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 % or more of the quantity of carbon originally present in the petroleum coke feedstream, and preferably in the range of 8 to 20 weight %. Generally, no economic benefit is gained by operating with a quantity of unconverted petroleum coke in the product gas containing more than 20 weight % of the amount of carbon originally present in the petroleum coke feedstream.

20 Further, it was unexpectedly found that in this range of 8 to 20, about 17 to 60 weight % 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.

30 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 H_2O to fuel at a level in the range of about 0.3 to 3.0 pounds of H_2O 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 H_2O -to-fuel ratio.

10 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 wt. % of solids, or higher.

20 While in a preferred embodiment of the invention, the gasification of liquid-solid phase slurries of water and particulate petroleum coke may be accomplished without being preheated using an annulus-type burner, the slurry may be 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 1400°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
30 of steam and petroleum coke. Further information about

dispersing petroleum coke in steam is disclosed in U.S. Patent No. 2,987,387, issued to C. R. Carkeek et al, which is herewith incorporated by reference.

In the atomized dispersion, relative proportions of petroleum coke, water and oxygen-rich gas are regulated within the previously stated ranges to ensure an auto-genous temperature in the gas generation zone within the range of about 1800 to 3500°F. In addition to unconverted petroleum coke in the amount as previously specified, the product gas includes in mole % dry basis: H₂ 25 to 45, CO 20 to 50, CO₂ 5 to 35, CH₄ 0.06 to 8, and COS+H₂S .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, colloidally-dispersed metallic compounds, and complex organo-metallic 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 5000 parts per million by weight.

10 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 ppm are particularly destructive by combining with the alumina refractory to form $\text{NiO} \cdot \text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5 \cdot \text{Al}_2\text{O}_3$, whose crystalline structures weaken the alumina refractory. As
20 a result, at a temperature in the range of 1800 to 3500°F. and at the preferred operating temperature in the reaction zone of about 2200 to 2800°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.

30 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 by oxidation leaving behind the heavy metal constituents or their oxidation products attached to the unconverted petroleum 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.

10 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 20 the feed to the synthesis gas generator.

EXAMPLES OF THE PREFERRED EMBODIMENTS

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

EXAMPLE I

30 1,186.5 pounds of petroleum coke prepared from reduced crude oil by the "delayed coking" process is ground to -325 mesh and mixed with 1,186.5 pounds of 12°API gravity

crude oil. An analysis of the coke and crude oil is shown below in Table I. 2,373 lbs./hr. of the resulting slurry containing 50% by wt. of solids is pumped at a rate of 25 ft./sec. and at a temperature of 100°F. through the central passage of an annulus type burner as shown in Figure 2 of the aforesaid U.S. Patent 2,928,460. The burner is mounted in the top head of a compact, unpacked, noncatalytic 16.0 CF synthesis gas generator in the manner shown in Figure 1 of U.S. Patent 2,980,523. 1,186 lbs/hr of steam and 2,524 lbs/hr. of oxygen (100 mole %) are combined and at a rate of 350 ft./sec. and at a temperature of 425°F. are introduced into the annular passage of said burner. 109,277 SCFH (Standard Cubic Feet per Hour) of synthesis gas is produced in the gas generator from the ensuing partial oxidation reaction at a temperature of 2490°F. and at a pressure of 550 psig. An analysis of the product gas follows: In mole % dry basis: H₂ 40.3, CO 51.1, CO₂ 7.8, H₂S 0.2, and soot + unconverted coke 3.8.

10

20

TABLE I - FEED TO GENERATOR

<u>Element</u>	<u>Oil</u>	<u>Petroleum Coke</u>	<u>Slurry Feed</u>
C	87.43 wt. %	91.47 wt. %	89.45 wt. %
H	10.41 wt. %	3.75 wt. %	7.08 wt. %
N	0.77 wt. %	2.75 wt. %	1.76 wt. %
Ash	0.11 wt. %	0.43 wt. %	0.27 wt. %
S	1.28 wt. %	1.60 wt. %	1.44 wt. %
Ni	67 ppm	553 ppm	300 ppm
V	60 ppm	640 ppm	350 ppm

30

A summary of the performance data follows:

Oxygen/Fuel Ratio, SCF/lb.	12.62
Water/Fuel Ratio, lb/lb	0.50
Oxygen/Carbon Ratio, atom/atom	0.893
Oxygen Consumption, SCF/MSCF H ₂ +CO	299.71
Gas Velocity, ft./sec., gen. exit	46.52
Residence Time, sec.	3.22
O ₂ /Fuel, moles per MM Btu	2.00
Heat of Combustion, Btu/lb.	16,615
Cold Gas Efficiency	81.6

10

EXAMPLE II

20

30

1,424 lbs. of petroleum coke are prepared from reduced crude oil by the "delayed coking" process and crushed to a particle size so that 100 wt. % passes through a U.S. Standard 12 mesh sieve. The oil absorption number of the petroleum coke is less than 1. The petroleum coke is mixed with 854 lbs. of 12° API gravity crude oil. The resulting slurry containing 62.3% by wt. of solid fuel could not be readily pumped at a uniform rate and composition because of settling in the lines and plugging of valves. 95 lbs of soot produced by the partial oxidation of a hydrocarbon fuel oil and having a particle size of less than 10 microns and an oil absorption number greater than 1 were then added to the petroleum coke-oil slurry to increase the solids content of the slurry to 64 wt. %. The slurry became thicker and gel-like. Settling was greatly diminished. Although the slurry appeared semi-solid it could be easily worked into a pumpable fluid without increasing the temperature.

EXAMPLE III

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) are 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.

10 1,075 pounds per hour of the resulting slurry containing 5.4 weight % 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. The burner is mounted through the top head of a compact, unpacked, free-flow, non-catalytic 11.8 cubic feet synthesis gas generator lined with refractory. 9024 standard cubic feet per hour (SCFH) of oxygen (100 mole % 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.

20 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 2550°F. and at a pressure of 346 psig.

An analysis of the product gas follows: In mole % 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 1995 parts per million (ppm) of nickel and 1082 ppm of vanadium. This represents a recovery of 13 weight % of the nickel present in the feed and 10 weight %
30 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 6030 pounds per hour of water and about 27 pounds per hour of unconverted petroleum coke containing about 5 weight % 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 3328 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.

8900 pounds per hour of clarified water is removed as overflow from the sedimentation vessel and introduced into a conventional water treatment purification system. About 8900 pounds per hour of clarified water from the water treatment purification system and 400 pounds per hour of make-up water are recycled to the quench zone and carbon scrubbing operation. The slurry underflow from the sedimentation vessel 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 in a slurry are removed from the bottom of the quench vessel by way of the lock hopper system and are introduced

into a conventional dewatering 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.

10 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 refractory, samples of the slurry of water and unconverted particulate petroleum coke from the quench chamber are dried, analyzed, and 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 steam-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 % 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.

20

 For example, as a comparison with run 1, run 2 shows that by decreasing the oxygen-to-fuel ratio in run 1

30

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 2550°F. to 2450°F., and the quantity of unconverted petroleum coke entrained in the product gas increases from an amount containing about 5 weight % of the quantity of carbon originally present in the petroleum coke feedstream to a quantity of entrained unconverted petroleum coke containing 13 weight % 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 653 pounds of water. Analysis of the raw petroleum coke as received and the recycled unconverted petroleum coke are shown below in Table 1.

1,107 pounds per hour of the resulting slurry containing 49.2 weight % of petroleum coke are discharged at a rate of 25 feet per second and at a temperature of 132°F. from the central passage of an annulus-type burner. The burner is mounted through the top head of a compact, unpacked, free-flow, non-catalytic 11.8 cubic foot synthesis gas generator. 8,615 SCFH of oxygen

(100 mole % O_2) 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 2450°F. and at a pressure of 350 psig.

An analysis of the product gas follows:

In mole % dry basis: H_2 33.02, CO 47.22, CO_2 18.94, H_2S 0.06, CH_4 0.20, N_2 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 2440 parts per million (ppm) of nickel and 2380 ppm of vanadium. This represents a recovery of 35.1 weight % for nickel and 40.1 weight % 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 Pet. Coke		Unconverted Pet. Coke	
		Run 1	Run 2	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. %	1.16	1.16	1.90	1.89
Ni	ppm	750	710	1,995	2,440
V	ppm	500	590	1,082	2,380

TABLE II - PERFORMANCE DATA

	<u>Run 1</u>	<u>Run 2</u>
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 Btu	2.85	2.76
Heat of Combustion, Btu/lb.	15,122	15,122
Generator Temperature, °F.	2,550	2,450

10

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.

20

30

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A partial oxidation process for producing synthesis gas which comprises:
 - (1) mixing particulate solid carboniferous fuel with a liquid vehicle selected from the group consisting of water, hydrocarbon liquid fuel, and mixtures thereof to form a pumpable slurry comprising 1-60 weight percent of solids when said liquid vehicle is hydrocarbon liquid fuel and 25-55 weight percent of solids when said liquid vehicle is water;
 - (2) atomizing the slurry of (1) within the reaction zone of a synthesis gas generator by contacting therein a stream of said slurry at a relatively low velocity in the range of 5 to 50 feet per second with a stream of oxidizing gas at a relatively high velocity in the range of 100 feet per second to sonic velocity and selected from the group consisting of air, oxygen, oxygen-enriched air, and mixtures of steam and one of said oxidizing gases to form an atomized dispersion in which the ratio of atoms of oxygen to atoms of carbon is in the range of 0.7 to 1.2 and the weight ratio of H_2O to fuel is in the range of 0.2 to 3.0; and
 - (3) reacting the atomized dispersion of (2) in said reaction zone at a temperature in the range of 1,800° to 3,500°F. and a pressure in the range of 100 to 3,000 psig.

2. The process of Claim 1 wherein said hydrocarbon liquid fuel is selected from the group consisting of gasoline, naphtha, residual fuel oil, reduced crude oil, whole crude oil, shale oil, coal oil, and tar sand oil.

3. The process of Claim 1 wherein said solid carboniferous fuel is selected from the group consisting of petroleum coke, coal, coke made from bituminous coal, oil shale, tar sands, pitch, and mixtures of said materials.

4. The process of Claim 1 wherein the atomizing of (2) is effected by passing said stream of slurry at a velocity of 5 to 50 feet per second through the inner conduit of an annulus-type burner in said reaction zone and contacting said stream with said stream of oxidizing gas passing at a velocity in the range of 200 feet per second to sonic velocity at the burner tip through the annular passage of said burner.

5. The process of Claim 1 wherein the atomizing of (2) is effected by passing said stream of oxidizing gas at a velocity in the range of 200 feet per second to sonic velocity at the burner tip through the inner conduit of an annulus-type burner in said reaction zone and contacting said stream with a stream of said slurry passing at a velocity of 5 to 50 feet per second through the annular passage of said burner.

6. The process of Claim 1 wherein said solid carboniferous fuel is petroleum coke in which 60-95 weight percent passes through 325 mesh screen and said hydrocarbon liquid fuel is residual fuel oil.

7. A process for the gasification of solid carboniferous fuel which comprises:

- (1) pulverizing a solid carboniferous fuel selected from the group consisting of petroleum coke, oil shale, coal, coke produced from bituminous coal, pitch, and mixtures of said materials;
- (2) mixing the particulate solid carboniferous fuel of (1) with a liquid vehicle selected from the group consisting of water, gasoline, naphtha, residual fuel oil, reduced crude oil, whole crude oil, coal oil, shale oil, tar sand oil, and mixtures of said liquid vehicles to form a pumpable slurry comprising 1-60 weight percent of solids;
- (3) passing a stream of the slurry of (2) at a temperature in the range of about 100 to 300°F. and at a relatively low velocity in the range of 5 to 50 feet per second through the inner conduit of a burner discharging into the reaction zone of a synthesis gas generator and having an annular passage and passing a stream of oxidizing gas at a temperature in the range of about 100 to 600°F. selected from the group consisting of air, oxygen-enriched air, oxygen, and mixtures of steam and one of said oxidizing gases through the annular passage of said burner at a relatively high velocity in the range of 100 feet per second to sonic velocity.
- (4) contacting said streams in said reaction zone to produce an atomized dispersion of said liquid vehicle, oxidizing gas, particulate solid carboniferous fuel, and steam in which the ratio of atoms of oxygen to atoms of carbon is in the range of 0.7 to 1.2 and the weight ratio of H₂O to fuel present is in the range of 0.2 to 3.0; and

(5) reacting the atomized dispersion of (4) in said reaction zone at a temperature in the range of 1800° to 3500°F. and a pressure in the range of 100 to 3000 psig to produce a stream of synthesis gas.

8. The process of Claim 1 wherein the slurry in step (1) comprises in admixture about 10 to 75 wt. % of particulate solid carboniferous fuel having a particulate size which passes through a U.S. Standard No. 12 mesh sieve, in said liquid vehicle and about 2 to 10 wt. % (basis wt. of liquid vehicle) of free carbon soot having an oil absorption number greater than one.

9. The process of Claim 1 wherein the slurry in step (1) comprises about 10 to 75 wt. of petroleum coke in admixture with a liquid vehicle selected from the group consisting of water, gasoline, naphtha, residual fuel oil, reduced crude oil, whole crude oil, shale oil, coal oil, and tar sand oil, and about 2 to 10 wt. % (basis weight of said liquid vehicle) of free carbon soot having an oil absorption number greater than one.

10. The process of Claim 1 where in step (1) the solid carboniferous fuel is particulate petroleum coke containing heavy metal constituents, the liquid vehicle is water, and the product gas stream from step (3) comprises on a dry basis principally hydrogen and carbon monoxide and a controlled amount of entrained unconverted particulate petroleum coke containing at least 8 weight % of the quantity of carbon originally present in said petroleum coke slurry 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.

11. The process of Claim 10 provided with the additional steps of preheating said stream of feed slurry from step (1) to a temperature in the range of 100° to 400°F. and preheating the stream of oxidizing gas used in step (2) 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 in step (3) is in an amount so that about 8 to 20 weight % of the carbon originally present in the petroleum coke feedstream to step (2) 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.

12. The process of Claim 11 provided with the additional steps for reclaiming heavy metal constituents in said particulate petroleum coke by cooling the hot product gas stream from the reaction zone by quenching in water forming an unconverted petroleum coke-water slurry, dewatering said slurry, roasting the unconverted petroleum coke in an oxidizing atmosphere at a temperature of about 220°F., extracting the metal salts with a dilute aqueous solution of a strong mineral acid, washing the residue with water, and adding phosphoric acid to the solution to precipitate the metals as the phosphates.

13. A solid fuel slurry composition consisting of carboniferous solids in the range of about 40-75 weight percent in a liquid vehicle selected from the group consisting of water, gasoline, naphtha, residual fuel oil reduced crude oil, whole crude oil, coal oil, shale oil, tar sand oil, and mixtures thereof; said carboniferous solids consisting essentially of petroleum coke and containing about 2-10 weight percent based on the liquid vehicle of free-carbon soot as produced by the partial oxidation of hydrocarbon fuel oil and having an Oil Absorption Number of at least 1 and a particle size of at less than 10 microns.

14. A new composition of matter comprising in admixture about 10 to 75 wt. % of solid carboniferous fuel in a liquid vehicle selected from the group consisting of water, gasoline, naphtha, residual fuel oil, reduced crude oil, whole crude oil, coal oil, shale oil, tar sand oil, and mixtures of said liquid vehicles, and containing about 2 to 10 wt. % (basis weight of said liquid vehicle) of free carbon soot having an oil absorption number greater than one.

15. A new fuel composition comprising about 10-75 wt. % of petroleum coke in admixture with a liquid hydrocarbon fuel and about 2 to 10 wt. % (basis weight of said liquid vehicle) of free carbon soot having an oil absorption number greater than one.

