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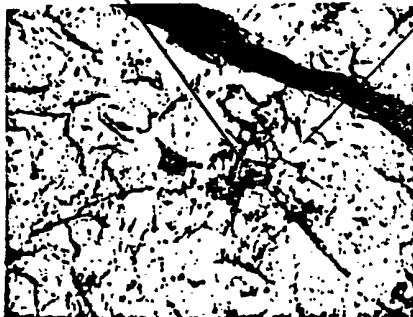
**Partial oxidation process.**

Synthesis gas is produced by the partial oxidation of a feedstock comprising petroleum coke and/or heavy liquid hydrocarbonaceous fuel and/or solid carbonaceous fuels containing sulfur and having an ash that contains nickel, vanadium and silicon. An iron-containing additive is introduced into the reaction zone along with the feed. A first portion of the additive combines with at least a portion of the nickel, iron and sulfur constituents found in the feedstock to produce a first liquid phase washing agent. A second portion of the additive combines with at least a portion of the silicon, aluminum, calcium, sodium, and/or potassium and iron constituents found in the feedstock to produce a second liquid phase washing agent. The first and second liquid phase washing agents collect and transport at least a portion of the vanadium-containing oxide laths and spinels and other ash components out of the reaction zone.

**FIG. 1**

SLAG FROM FIRST LIQUID PHASE WASHING AGENT  
(FIELD OF VISION = 0.55mm)

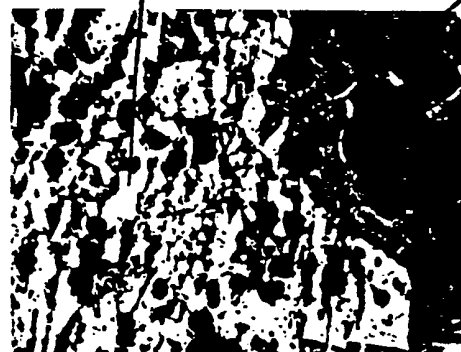
VANADIUM-CONTAINING SPINEL      FIRST LIQUID PHASE WASHING AGENT



**FIG. 2**

SLAG FROM SECOND LIQUID PHASE WASHING AGENT  
(FIELD OF VISION = 1.1mm)

VANADIUM-CONTAINING SPINEL      SECOND LIQUID PHASE WASHING AGENT



EP 0 386 352 A1

## PARTIAL OXIDATION PROCESS

This invention relates to the partial oxidation ash-containing heavy liquid hydrocarbonaceous fuels, ash-containing petroleum coke, or mixtures thereof to produce gaseous mixture comprising  $H_2 + CO$  and of sulfur and ash-containing heavy liquid hydrocarbonaceous fuels, solid carbonaceous fuels, or mixtures thereof to produce gaseous mixtures comprising  $H_2 + CO$  which are substantially free from molten slag and sulfur-containing gases.

More particularly it pertains to an additive system or an additive-refractory combination for removing nickel and vanadium-containing contaminants along with other molten ash components which are produced during the partial oxidation of a heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash, or a low-silicon heavy liquid hydrocarbonaceous fuel, and/or petroleum coke having a nickel and vanadium-containing ash to produce synthesis gas, reducing gas, or fuel gas.

It also pertains, more particularly to an additive system for in-situ desulfurization and simultaneous removal of nickel and vanadium-containing contaminants along with other molten ash components which are produced during the partial oxidation of heavy liquid hydrocarbonaceous fuel and/or solid carbonaceous fuel. Synthesis gas, reducing gas, or fuel gas may be thereby produced which are substantially free from molten ash and sulfur-containing gases.

The partial oxidation of liquid hydrocarbonaceous fuels such as petroleum products and slurries of solid carbonaceous fuels such as coal and petroleum coke are well known processes. However, troublesome molten slags are produced along with the product gas in the free-flow unobstructed vertical reaction zone of the partial oxidation gas generator. At the high temperatures e.g. about  $2100^\circ F$  to  $3000^\circ F$  prevailing the reaction zone, the highly corrosive molten slag attacks the refractory which lines the reaction zone. Lining failures have sometimes occurred within a few hundred hours. A compatible additive-refractory system is required wherein the molten slag is modified by contact with the refractory so that it runs more freely from the gasifier. The refractory lining should resist substantial corrosion, erosion, and chemical attack by the additive modified molten slag. Costly down-times for replacement of the refractory lining would thereby be avoided.

The Texaco partial oxidation gasification process offers an alternative processing route for the coke or the ash-containing heavy liquid hydrocarbonaceous fuel. For example, water slurries of petroleum coke are reacted by partial oxidation in coassigned U.S. Patent No. 3,607,157. Gasification is often cited as a convenient means of coke disposition. The decision to use gasification as a coke disposal means is generally based on economics. The expected rise in energy costs and the total use of feed crude should shortly bring about a great utilization of petroleum coke feeds to the partial oxidation gas generator.

Previous gasification runs with delayed coke and/or ash-containing heavy liquid hydrocarbonaceous fuel gave rise to some unexpected operating problems. The ash, which normally melts and is discharged from the gasifier as a slag, was not melting completely and being discharged but was building up on the ash in said materials collected on the gasifier walls and formed oxides during shut-down. Upon subsequent exposure of the gasifier walls to air these deposits involving vanadium can catch fire with vanadium converting to the lower melting  $V_2O_5$  or metal vanadate states. The strong solvent action of vanadium oxide on the refractory lining contributed to the clogging of the outlet in the bottom of the gasifier. Nickel impurities may under certain conditions form troublesome nickel oxide and nickel sulfide downstream in the system. Fluxing as used in coal operations and in U.S. Patent Numbers 1,799,885 and 2,644,745 does not provide a solution to Applicant's problem involving troublesome vanadium and nickel. The subject invention is an improvement in the art since it permits long time operation of the partial oxidation gas generator without shut-down due to failure of the refractory lining in the reaction zone that was brought about by the presence of vanadium. Further, the product gas containing mixtures of  $H_2O + CO$  is produced containing substantially no corrosive sulfur-containing gases.

The foreseeable trend for petroleum reserves is that the produced crude will be increasingly heavier and of poorer quality. To compensate for this trend, refiners must employ more "bottom of the barrel" upgrading to provide the desired light products. The current industry workhouse to provide this upgrading is some type of coking operation (either delayed or fluid). A good deal of current refinery expansion includes the installation or expansion of coker units, and thus, coking will be process of general use for some time to come. Since the crudes more contaminants, i.e. sulfur, metals (predominately vanadium, nickel, and iron), and ash and these contaminants are concentrated in the product coke, this coke is of a much poorer quality and is excluded from its normal product applications. Because the crudes are heavier, i.e., contain more coke precursors, more of this poorer quality coke is produced from each barrel of ash-containing heavy liquid hydrocarbonaceous fuel. The manufacturers of petroleum coke pellets by a delayed coking process is

described in coassigned U.S. Patent No. 3,673,080. A fluid coking process is described in U.S. Patent No. 2,709,676.

5 A major drawback for coking is the disposal of the product coke. With a reasonably clean coker feed, the product coke has been substituted for applications requiring only relatively pure carbon, such as electrode manufacture. However, with the feed crudes becoming poorer, there are compounding factors affecting coker operations. First, since the crudes contain more contaminants, i.e. sulfur, metals (predominately vanadium, nickel, and iron), and ash, and these contaminants are concentrated in the product coke, this coke is of a much poorer quality and is excluded from its normal product applications. Second, because the crudes are heavier, i.e., contain more coke precursors, more of this poorer quality  
10 coke is produced from each barrel of ash-containing heavy liquid hydrocarbonaceous fuel. The manufacture of petroleum coke pellets by a delayed coking process is described in coassigned U. S. Patent No. 3,673,080. A fluid coking process is described in U. S. Patent No. 2,709,676.

The Texaco partial oxidation gasification process offers an alternative processing route for the coke or the ash-containing heavy liquid hydrocarbonaceous fuel. For example, water slurries of petroleum coke are  
15 reacted by partial oxidation in coassigned U. S. Patent No. 3,607,157. Gasification is often cited as a convenient means of coke disposition. The Flexicoking Process is an integrated coker/gasifier operation but is often criticized because of the gasifier design. Further, no molten petroleum coke ash having a reduced ash fusion temperature is produced. The decision to use gasification as a coke disposal means is generally based on economics. The expected rise in energy costs and legislation (primarily Canadian) requiring total  
20 use of feed crude should shortly bring about a great utilization of petroleum coke feeds to the partial oxidation gas generator.

Previous gasification runs with delayed coke and ash-containing heavy liquid hydrocarbonaceous fuel gave rise to some unexpected operating problems. The ash, which normally melts and is discharged from the gasifier as a slag, was not melting completely and being discharged but was building up on the walls of  
25 the refractory. Vanadium and nickel constituents of the ash in said materials collected on the gasifier walls and formed oxides during shut-down. Upon subsequent exposure of the gasifier walls to air these deposits involving vanadium can catch fire with vanadium converting to the lower melting  $V_2O_5$  or metal vanadate states. The strong solvent action of vanadium oxide on the refractory lining contributed to the clogging of the outlet in the bottom of the gasifier. Nickel impurities may under certain conditions form troublesome  
30 nickel carbonyl deposits downstream in the system. Fluxing as used in coal operations and in U.S. Patent Numbers 1,799,885 and 2,644,745 do not provide a solution to Applicant's problem involving troublesome vanadium and nickel. The subject invention is an improvement in the art since it permits long time operation of the partial oxidation gas generator without shut-down due to failure of the refractory lining in the reaction zone that was brought about by the presence of vanadium.

35 Furthermore the expected rise in energy costs and the economic necessity for the total use of feed crude should shortly bring about a greater utilization of comparatively low cost sulfur and ash-containing heavy liquid hydrocarbonaceous fuel and solid carbonaceous fuel as feeds in the partial oxidation process for producing gaseous mixtures comprising  $H_2 + CO$ . By the subject process, build-up of slag on the inside walls of the gasifier is substantially eliminated. Further, in-situ desulfurization is provided for by the process.

40 The invention provides a process for the production of gaseous mixtures comprising  $H_2 + CO$  by the partial oxidation of a feedstock comprising a heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash or petroleum coke having a nickel and vanadium-containing ash, or mixtures thereof. Further, said feedstock includes a minimum of 0.1 wt. % of sulfur and greater than about 7 ppm such as about 10 parts per million (ppm) to about 70,000 ppm of silicon, such as in the range of greater  
45 than about 350 ppm to about 10,000 ppm of silicon; and said ash includes a minimum of 2.0 wt. % of vanadium, and a minimum of 1.0 wt. % of nickel, such as about 2.0 to 5.0 wt. %. The process includes the steps of (1) mixing together an iron-containing additive with said feedstock; wherein the weight ration of iron-containing additive to ash in the reaction zone in (2) is in the range of about 0.1-10.0 to 1.0, and there is at least 2 parts by weight of iron for each part by weight of vanadium; (2) reacting said mixture from (1)  
50 at a temperature in the range of 1700° F to 3000° F and a pressure in the range of about 2 to 250 atmospheres in a free-flow refractory lined partial oxidation reaction zone with a free-oxygen containing gas in the presence of a temperature moderator and in a reducing atmosphere to produce a hot raw effluent gas stream comprising  $H_2 + CO$  and molten slag; and where in said reaction zone a first portion of said iron-containing additive combines with at least a portion of the nickel, iron, and sulfur constituents found in the  
55 feedstock to produce a first liquid phase washing agent; a second portion of said iron-containing additive combines with at least a portion of the silicon, aluminum, calcium, sodium and/or potassium, and iron constituents found in the feedstock to produce a second liquid phase washing agent; and wherein the first and second liquid phase washing agents collect and transport at least a portion of the vanadium containing

oxide laths and spinels and other ash components and refractory out of the reaction zone; and (3) separating non-gaseous materials from said hot raw effluent gas stream. Silicon-containing addition agents, including coal, will increase the ratio of second liquid phase washing agent to first liquid phase washing agent thereby more effectively washing the vanadium-bearing spinels from the gasifier.

5 In one embodiment, a mixture of heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash and said iron-containing additive is fed to a coker to produce petroleum coke with a nickel and vanadium-containing ash, and with said additive being uniformly dispersed throughout. This petroleum coke is then reacted in the partial oxidation gas generator to produce synthesis gas, reducing gas, or fuel gas.

10 In another embodiment, a small amount of additional additive selected from the group of elements consisting of magnesium, chromium, and mixtures thereof in the form of compounds, such as oxides is introduced into the reaction zone. The magnesium and chromium further increase the life of the refractory lining.

In still another embodiment, formation of elemental iron in the reaction zone is prevented by introducing 15 sufficient supplemental oxygen and/or sulfur into the reaction zone at a specified temperature in the reaction zone so as to keep the partial pressure of the oxygen and/or S<sub>2</sub> gas in the reaction zone slightly above that calculated by Formulae I and/or II, to be described later.

The invention also provides a process for the production of gaseous mixtures comprising H<sub>2</sub> + CO by 20 the partial oxidation of a feedstock comprising a heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash, or a low silicon-containing petroleum coke having a nickel and vanadium-containing ash, or mixtures thereof. Further, said feedstock includes a minimum of 0.1 wt. % of sulfur and less than about 350 parts per million (ppm) of silicon; such as in the range of about 1.0 parts per million (ppm) to about 350 ppm of silicon; and said ash includes a minimum of 1.0 wt. % of vanadium, such as about 2.0 to 20 wt. % and a minimum of 1.0 wt. % of nickel, such as about 2.0 to 20 wt. %, and a minimum 25 of 1.0 wt. % of nickel, such as about 2.0 to 5.0 wt. %. The process includes the steps of (1) mixing together an iron-containing additive with said feedstock; wherein the weight ratio of iron-containing additive to ash in the reaction zone in (2) is in the range of about 0.1-10.0 to 1.0, and there is at least 2 parts by weight of iron for each part by weight of vanadium; (2) reacting said mixture from (1) at a temperature in the range of 2100° F to 3000° F and about 100° F to 200° F above the fluid temperature of the slag, and a pressure in 30 the range of about 2 to 250 atmospheres in a free-flow vertical refractory lined partial oxidation reaction zone of a gasifier with a free-oxygen containing gas in the presence of a temperature moderator and in a reducing atmosphere to produce a hot raw effluent gas stream comprising H<sub>2</sub> + CO molten slag; wherein said refractory lining comprises in weight percent: MgO 85 to 98, Fe<sub>2</sub>O<sub>3</sub> 0.03 to 3.0; Al<sub>2</sub>O<sub>3</sub> 0.02 to 2.0, CaO 0.1 to 10 and SiO<sub>2</sub> 0.02 to 2.0; and where in said reaction zone a first portion of said iron-containing 35 additive combines with a least portion of said nickel, iron, and sulfur constituents found in the feedstock and refractory components to produce a first liquid phase washing agent substantially comprising in wt. % iron about 40 to 80; nickel about 0.1 to 5; and sulfur about 10 to 32; and optionally a minor amount of at least one element selected from the group consisting of Al, Ca, V, Si, Ti, Mg, Mn, Na, K, and mixtures thereof, a second portion of said iron-containing additive combines with a least a portion of the silicon, aluminum, 40 calcium, sodium, and/or potassium, and iron constituents found in the feedstock and refractory components to produce a second liquid phase washing agent substantially comprising in wt. % iron about 5 to 40; magnesium about 0.01 to 2.0; aluminum about 5 to 20; silicon about 20 to 50; calcium about 1.0 to 35; and sodium and/or potassium about 0.01 to 5; and wherein the first and second liquid phase washing agents collect and transport at least a portion of the vanadium-containing oxide laths and spinels and other ash and refractory components out of the reaction zone as said molten slag, and said molten slag combines with 45 a portion of said refractory in the iron-containing additives to produce localized vanadium-containing spinels and contain substantially no interlocking laths; and (3) separating non-gaseous materials from said hot raw effluent gas stream.

In one embodiment, a mixture of heavy liquid hydrocarbonaceous fuel containing less than 350 ppm of 50 silicon and having a nickel and vanadium-containing ash and said iron-containing additive is fed to a coker unit to produce petroleum coke with a nickel and vanadium-containing ash, and with said additive being uniformly dispersed throughout. This petroleum coke is then reacted in the partial oxidation gas generator to produce synthesis gas, reducing gas, or fuel gas.

In another embodiment, a small amount of an additional material selected from the group of oxides 55 consisting of manganese, magnesium, and mixtures thereof is introduced into the reaction zone. These additional elements further increase life of the magnesia refractory by forming a spinel before the vanadium interacts with the refractory. Manganese oxide further increases the fluidity of the slag. These additional materials are provided in the total amount of about 1.0 to 10.0 wt. % of the iron-containing additive. There is

no formation of elemental iron.

The invention further provides a process for the production of gaseous mixtures comprising  $H_2 + CO$  by the partial oxidation of a feedstock comprising a heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash or petroleum coke having a nickel and vanadium-containing ash, or mixtures thereof. Further, said feedstock includes a minimum of 0.1 wt. % of sulfur and greater than about 7 ppm, such as about 10 parts per million (ppm) to about 70,000 ppm of silicon; say in the range of greater than about 350 ppm to about 10,000 ppm of silicon; and said ash includes a minimum of 2.0 wt. % of vanadium, and a minimum of 1.0 wt. % of nickel, such as 2.0 to 5.0 wt. %. The process includes the steps of (1) mixing together an iron-containing additive with said feedstock; wherein the weight ratio of iron-containing additive to ash in the reaction zone in (2) is in the range of about 0.1-10.0 to 1.0, and there is at least 2 parts by weight of iron for each part by weight of vanadium; (2) reacting said mixture from (1) at a pressure in the range of about 2 to 250 atmospheres in a down-flowing free-flow unobstructed refractory lined vertical partial oxidation reaction zone of a gasifier with a free-oxygen containing gas in a reducing atmosphere and in the presence of a gaseous slag fluidizing agent which is introduced at the top of the reaction zone in a sufficient amount so as to maintain a uniform temperature throughout the reaction zone in the range of about 2100° F to 3000° F and said gaseous slag fluidizing agent is selected from the group consisting of superheated steam,  $CO_2$ , and mixtures thereof, to produce a hot raw effluent gas stream comprising  $H_2 + CO$  and entrained molten slag; wherein an equilibrium oxygen concentration is provided in the gas phase in the reaction zone with a partial pressure in the range of about  $1.18 \times 10^{-13}$  to  $5.64 \times 10^{-9}$  atmospheres, an equilibrium sulfur concentration is provided in the gas phase in the reaction zone with a partial pressure in the range of about  $2 \times 10^{-6}$  to  $2.12 \times 10^{-4}$  atmospheres, the free O/C atomic ratio is in the range of about 0.6 to 1.6, the  $H_2O$ /liquid hydrocarbonaceous and/or solid carbonaceous fuel weight ratio is in the range of about 0.1 to 5.0, and about 90 to 99.9 wt. % of the carbon in said liquid hydrocarbonaceous fuel and/or solid carbonaceous fuel is converted into carbon oxides; and where in said reaction zone a first portion of said iron-containing additive combines with at least portion of said nickel, iron, and sulfur constituents found in the feedstock to produce a first liquid phase washing agent, a second portion of said iron-containing additive combines with at least a portion of the silicon, aluminum, calcium, sodium and/or potassium and iron constituents found in the feedstock to produce a second liquid phase washing agent; and wherein the first and second liquid phase washing agents collect and transport substantially all of the vanadium-containing oxide laths and spinels and other ash components and refractory out of the reaction zone, and there is substantially no build-up of slag on the inside walls of the reaction zone; and (3) separating nongaseous materials from said hot raw effluent gas stream. In a preferred embodiment, gaseous mixtures of  $H_2O$  and substantially all of the sulfur-containing gases produced in the process are recycled to the gas generator for use as at least a portion of the slag fluidizing agent.

In still another embodiment, a mixture of heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash and said iron-containing additive is fed to a coker unit to produce petroleum coke with a nickel and vanadium-containing ash, and with said additive being uniformly dispersed throughout. This petroleum coke is then reacted in the partial oxidation gas generator to produce synthesis gas, reducing gas, or fuel gas.

The problem associated with slag-buildup on refractory walls of the partial oxidation gas generator, and others are minimized by the subject process in which the amount of slag containing vanadium constituents which remains in the reaction zone is substantially reduced or eliminated. Advantageously, the subject invention provides a gaseous slag fluidizing agent and an improved method of operation so that the molten slag flows freely by gravity out of the gasifier. Further, a means of introducing this addition agent into the system to give maximum effectiveness is provided. In addition, substantially all of the sulfur in the fuel is simultaneously removed along with the molten slag. In-situ desulfurization of the feedstock takes place in the gasifier so that the raw effluent gas may leave the gasifier containing less than about 1.00 mole %, such as less than about 0.6 mole %, of  $H_2S$  and  $COS$ .

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#### Disclosure of the Invention

The following description relates to a first embodiment of the invention.

The partial oxidation of heavy liquid hydrocarbonaceous fuel and petroleum coke are described respectively in coassigned U.S. Patent Numbers 4,411,670 and 3,607,156, which are incorporated herein by reference. Further, suitable free-flow refractory lined gas generators and burners that may be used in the production of synthesis gas, reducing gas, or fuel gas from these materials are also described in the aforesaid references. Advantageously, the subject process uses relatively inexpensive feedstocks compris-

ing heavy liquid hydrocarbonaceous fuel and/or petroleum coke feedstocks having nickel and vanadium-containing ashes. Further, said feedstock includes a minimum of 0.1 wt. % of sulfur, such as at least 2.0 wt. % sulfur; and greater than about 7 ppm, such as about 10 parts per million (ppm) to about 70,000 ppm of silicon, such as in the range of greater than about 350 ppm to about 10,000 ppm of silicon; and said ash includes a minimum of 2.0 wt. % of vanadium and, a minimum of 1.0 wt. % of nickel, such as about 2.0 to 5.0 wt. %.

By definition, the term heavy liquid hydrocarbonaceous material or fuel having a nickel and vanadium-containing ash is a petroleum or coal derived fuel selected from the group consisting of virgin crude, residua from petroleum distillation and cracking, petroleum distillate, reduced crude, whole crude, asphalt, coal tar, coal derived oil, shale oil, tar sand oil, and mixtures thereof.

By definition, the term petroleum coke having a nickel and vanadium-containing ash is petroleum coke made from ash containing heavy liquid hydrocarbonaceous fuel by conventional coking methods such as by the delayed or fluid coking process, such as described in coassigned U.S. Patent No. 3,673,080, which is incorporated herein by reference.

Closer study of the ashes derived from the partial oxidation, without an additive, of a feedstock comprising heavy liquid hydrocarbonaceous fuels and/or petroleum coke having nickel and vanadium-containing ashes shows that they are largely composed of oxide and sulfide compounds of vanadium, nickel, iron, along with some normally occurring mineral matter species. Vanadium-containing oxide laths are present including V, V+Ca, V+Fe, V+Al, and mixtures thereof. Vanadium-containing spinels are present of the spinel-type aluminate phases and may include metals selected from the group consisting of V, Fe, Cr, Al, Mg and mixtures thereof. The presence of abundant interlocking needle to lath-like crystals is the cause of the high viscosity of the slag.

The metals present in the ash provide a system that is significantly different from that occurring in coal. A further factor is that the total ash content of the petroleum coke or heavy liquid hydrocarbonaceous fuel may be only about one-half to 5 weight percent (wt.%), whereas coal typically contains 10-20 wt.% ash. The comparatively low ash concentration in petroleum coke and heavy liquid carbonaceous fuel may be the reason why the ash removal problem is only noticed after prolonged gasifier runs. The chance for effective ash and additive mixing that is necessary to wash the vanadium constituents out of the reaction zone or for effective fluxing is therefore greatly reduced.

It is theorized that in the heavy liquid hydrocarbonaceous material and petroleum coke systems, a good deal of the ash material is liberated as individual molecular species. This is because upon vacuum distillation or coking, the metallic species in the crude, which are generally presented as porphyrin type structures (metal atoms, oxides or ions thereof confined in an organic framework), are entrapped within the collapsed carbon matrix.

Problems arise when the heavy metal constituents build-up in the system. In particular, vanadium and nickel are known to accumulate on the walls of the refractory lined reaction zone of the partial oxidation gas generator and not flow smoothly from the gasifier under normal gasifier conditions. During shut down and subsequent exposure of the gasifier walls to air, these deposits involving vanadium can catch fire with the vanadium converting to the lower melting  $V_2O_5$  or metal vanadate states. These materials prove to be very corrosive to refractory thereby decreasing the life of the refractory lining of the reaction zone. These problems and others are minimized by the subject process in which the amount of vanadium constituents remaining in the reaction zone are substantially reduced or eliminated.

This invention provides an improved iron-containing additive. Further, a means of introducing this addition agent into the system to give maximum effectiveness is provided.

The iron-containing additive comprises an iron compound, preferably iron oxide. In the reaction zone of the partial oxidation gas generator, a first portion of the additive combines with at least a portion, such as substantially all or a large fraction e.g. about 90 to 97 wt. of the nickel and about 30 to 90 wt. %, say about 50 to 70 wt. % of the iron and sulfur constituents found in the feedstock to produce a first low viscosity liquid phase washing agent or carrier. Minor amounts e.g. less than about 5 wt. % of the amount present in the feedstock, of other elements from the feedstock may be picked up by the first liquid phase washing agent and dissolved therein. Accordingly, a minor amount of at least one extraneous element selected from the group consisting of Al, Ca, V, Si, Ti, Mg, Mn, Na, K, and mixtures thereof may be present in the first liquid phase washing agent. A second portion of the iron-containing additive combines with at least a portion, such as substantially all or a large fraction e.g. about 40 to 100 wt. %, say about 70 to 90 wt. % of the silicon, aluminum, calcium, sodium and/or potassium, and a portion e.g. 5 to 70 wt. %, of the remainder of the iron constituents found in the feedstock to produce a second liquid phase washing agent. Any remaining iron may go to the vanadium-containing spinel phase. Minor amounts e.g. less than about 5 wt. % of the amount present in the feedstocks, of other elements from the feedstock may be picked up by the

second liquid phase washing agent and dissolved therein. Accordingly, a minor amount of at least one extraneous element selected from the group consisting of Ni, V, S, Mg, Cr, and mixtures thereof may be present in the second liquid phase washing agent. Advantageously, by the subject process the S<sub>2</sub> potential in the gas and downstream gas cleaning costs are substantially reduced or possibly eliminated.

5 The relative proportion of first and second liquid phase washing agents present in the reaction zone depends on the temperature prevailing in the reaction zone and the materials present. An elemental analysis of the first liquid phase washing agent substantially comprises in wt. %: iron about 40 to 80, such as about 60 to 70; nickel about 0.1 to 5, such as about 1 to 10; and sulfur about 10 to 32, such as about 15 to 30. The extraneous elements which may be present in the first liquid phase washing agent in the reaction  
10 zone include in wt. % vanadium about 0.1 to 3, such as about 0.2 to 1.0; silicon about 0.01 to 3, such as about 0.5 to 1.5; and aluminum about 0.01 to 3, such as about 0.4 to 1.2. It was unexpectedly found that most of the nickel e.g. 99 wt. % or more goes into the first liquid phase washing agent. Accordingly, in one embodiment to insure the elimination of harmful nickel subsulfide, the amount of first liquid phase washing agent comprises at least about 5.0 wt. % (basis total amount of first and second washing agents). An  
15 elemental analysis of the second washing agent substantially comprises in wt. %: iron about 5 to 40, such as about 10 to 30; aluminum about 5 to 20, such as about 8 to 12; silicon about 20 to 50, such as about 30 to 40; calcium about 1.0 to 35, such as about 5 to 15; and sodium and/or potassium about 0.01 to 5, such as about 0.5 to 2. The extraneous elements which may be present in the second liquid phase washing agent in the reaction zone include in wt. % vanadium about 0.2 to 5, such as about 0.5 to 2; and sulfur  
20 about 0.01 to 1.5, such as about 0.1 to 1.0.

It was unexpectedly found that these liquid phase washing agents have strong wetting capabilities for the high temperature non-flowing vanadium-containing oxide laths and spinels. These washing agents function in a completely different manner than that of a fluxing additive which may be used for example to solubilize slag constituents in coal. For example, these washing agents do not solubilize the troublesome  
25 vanadium-containing oxide laths and spinels. Rather, they serve as carriers and wash them out of the reaction zone. These washing agents wash at least a portion, such as from about 40 to 100 wt. %, say about 60 to 80 wt. %, and preferably all of the vanadium-containing contaminants out of the reaction zone of the partial oxidation gas generator. The mixtures of the first and second liquid phase washing agent and vanadium oxide laths and spinels are referred to herein as slag. The vanadium-containing oxide laths and  
30 spinels contain (i) substantially all e.g. 80 to 99 wt. % or a large fraction e.g. 85 to 95 wt. % of the vanadium present in the feed; (ii) the remainder of the Fe, Al, Mg, Ti, and other minor impurities from the iron-containing additive and/or feedstock; and (iii) refractory components. The vanadium-containing oxide laths and spinels comprise about 1 to 10 wt. %, such as about 4 to 8 wt. % of vanadium oxide.

The first liquid phase washing agent is present in the amount of about 5 to 99.5 wt. %, (basis total  
35 weight of first and second washing agents), such as about 30 to 70 wt. %. The second liquid phase washing agent is present in the amount of about 0.5 to 95.0 wt. % such as about 30 to 70 wt. %. The two liquid phase washing agents are substantially immiscible in each other. For example, the solubility of the first liquid phase washing agent in the second liquid phase washing agent is only about 0.05 to 2.0 wt. %, such as about 0.1 to 2.0 wt. %. Actually, with the exception of the vanadium-containing laths and spinels, the first  
40 liquid phase washing agent does a better job than the second liquid phase washing agent in washing out of the reaction zone the particulate matter entrained in the hot raw effluent gas stream from the reaction zone. In general, the vanadium-bearing spinels tend to concentrate in the second liquid phase washing agent rather than in the first liquid phase washing agent. In some cases when the amount of the second liquid phase washing agent is less than 10 wt. %, the vanadium-bearing spinels have been so abundant that they  
45 actually constitute a more or less continuous mass with the second liquid phase washing agent. It is apparent that the vanadium-bearing spinels form very early in the crystallization sequence. Further, they have very high melting points and the grains composed of major proportions of them are rigid to very viscous at very high temperatures. The first liquid phase washing agent in contrast with the second liquid phase washing agent, have much lower melting points, and much lower viscosities. However, they also  
50 contain very much less of the vanadium-containing spinels. For example, the melting point and viscosity of the first liquid phase washing agent are in the range of about 1900 °F to 2200 °F, and about 5 to 120 poises respectively; whereas, the melting point and viscosity of the second liquid phase washing agent are in the range of about 2150 °F to 2475 °F, and about 100 to 1200 poises, respectively.

In one embodiment, it was unexpectedly found that the proportion of second liquid phase washing  
55 agent may be increased from a value in the range of about 0.5 to 9.5 wt. % (basis total wt. of first and second liquid phase washing agents) to a value in the range of about 30 to 95 wt. % by the addition of a supplemental silicon-containing material to the feed mixture to the reaction zone. The concentration of vanadium-bearing spinels is thereby diluted so that their contribution to the viscosity is decreased. The

spinel are thereby more effectively washed from the gasifier. The atomic ratio of Si/V in the feed to the gasifier may be increased from a normal value in the range of about 0.1 to 10, such as about 0.5 to 2.0, to an increased value in the range of about 5.0 to 100, such as about 20 to 50.

Suitable silicon-containing addition agents include materials selected from the group consisting of oxides and sulfides of silicon, coal, coal ash, tar sand, sand, rock, soil, earth, and mixtures thereof. For example, in one embodiment where the silicon containing addition agent is coal and petroleum coke is the fuel feed, sufficient coal is introduced into the reaction zone along with the petroleum coke to provide a weight ratio of coal ash in the range of about 0.1 to 100 for each part by wt. of petroleum coke ash, such as about 0.5 to 20 parts by weight of coal ash per part by wt. of petroleum coke ash. The coal and petroleum coke may be ground together and introduced into the reaction zone entrained in a liquid carrier e.g. water, CO<sub>2</sub>, liquid hydrocarbonaceous fuel; or entrained in a gaseous carrier e.g. steam, CO<sub>2</sub>, air, recycle synthesis gas and mixtures thereof. The coal serves as a carbonaceous fuel and as a source for supplemental silicon.

The distribution of iron between the first and second liquid phase washing agents is influenced by the partial pressures of the oxygen and/or S<sub>2</sub> gas in the reaction zone. The lower the partial pressure of oxygen and/or S<sub>2</sub> gas at a given temperature, the more iron is driven into the first liquid phase washing agent in preference to the second liquid phase washing agent. The formation of elemental iron in the reaction zone leads to difficulties with slag removal. In order to prevent elemental iron from forming, the partial pressure of the oxygen and/or S<sub>2</sub> gas in the reaction zone of the gasifier at a specific temperature is kept slightly above that calculated by Formulae I and/or II below.

The relationship between temperature in the reaction zone (T° Fahrenheit), and the common logarithm of the equilibrium partial pressure of oxygen log P<sub>(O<sub>2</sub>)</sub> in the reaction zone is shown by Formula I. When the equilibrium partial pressure of oxygen in the reaction zone drops below that calculated in Formula I for the design temperature in the reaction zone, then sufficient supplemental free-oxygen containing gas is introduced into the reaction zone to restore the equilibrium partial pressure of the oxygen in the reaction zone to a value which is slightly above that calculated in Formula I. Additions of supplemental free-oxygen containing gas in excess of that required to do the job are economically unattractive. Further, they will reduce the efficiency of the process and should be avoided.

$$\log P_{(O_2)} = -38.9691 + 0.01744 T^\circ F - 0.0000024 T^2 F \quad I$$
 wherein: T is a value in the range of about 1700° F to 3000° F, such as about 2000° F to 2600° F.

For example, when the temperature in the reaction zone is 2500° F, a first value for the equilibrium partial pressure of oxygen in the reaction zone, as determined from Formula I, is 10<sup>-12.39</sup> atmosphere. This value for the partial pressure of the oxygen in reaction zone is compared with a second value for the partial pressure of oxygen which is determined by conventional calculations for the reactions going on in the reaction zone of the gasifier. When the second value for the partial pressure of oxygen is less than the value calculated from Formula I then sufficient supplemental free-oxygen containing gas e.g. air, oxygen, oxygen-enriched air is introduced into the reaction zone to bring the partial pressure of oxygen to a value which is slightly above 10<sup>-12.39</sup> atmospheres, such as to about 10<sup>-12</sup> atmospheres or above. The term "slightly above" means an increase of about 3%. Over the reaction temperature range of 1700 to 3000° F and an atomic O/C ratio in the range of about 0.6 to 1.6, the equilibrium partial pressure of oxygen in the reaction zone will increase in the range of about 10<sup>-16.36</sup> to 10<sup>-8.25</sup>.

As previously mentioned, elemental iron may be prevented from forming in the reaction zone of the partial oxidation gas generator by maintaining the partial pressure of S<sub>2</sub> gas in the reaction zone above the value calculated from Formula II for the specified reaction zone temperature. The relationship between the temperature in the reaction zone (T° Fahrenheit), and the common logarithm of the equilibrium partial pressure of S<sub>2</sub> gas "log P<sub>(S<sub>2</sub>)</sub>" is shown in Formula II.

When the equilibrium partial pressure of the S<sub>2</sub> gas in the reaction zone drops below that calculated in Formula II for the design temperature in the reaction zone, then sufficient supplemental elemental sulfur or a sulfur-containing material is introduced into the reaction zone to bring the equilibrium partial pressure of the S<sub>2</sub> gas in the reaction zone to a value which is slightly above that calculated in Formula II. Additions of supplemental elemental sulfur or sulfur-containing materials in excess of that required to do the job are economically unattractive and should be avoided. Further, costly downstream purification steps for the S<sub>2</sub> gas may be then avoided.

$$\log P_{(S_2)} = -17.3454 + 0.007857 T^\circ F - 0.0000011 T^2 F \quad II$$
 wherein: T is a value in the range of about 1700° F to 3000° F, such as about 2000° F to 2600° F.

For example, when the temperature in the reaction zone is 2200° F, the equilibrium partial pressure of S<sub>2</sub> gas in the reaction zone when calculated from Formula II is 10<sup>-5.28</sup> atmosphere. This value for the partial pressure of S<sub>2</sub> gas in the reaction zone is compared with a second value for the partial pressure of S<sub>2</sub> gas



which is determined by conventional calculations for the reactions going on in the reaction zone of the gasifier. When the second value for the partial pressure of S<sub>2</sub> gas is less than the value calculated from Formula II, then sufficient supplemental elemental sulfur or sulfur-containing material e.g. metal sulfides, H<sub>2</sub>S, COS, SO<sub>2</sub> are introduced into the reaction zone to restore the equilibrium partial pressure of S<sub>2</sub> gas to a value which is slightly above 10<sup>-5.28</sup> atmospheres, such as about 10<sup>-5</sup>. The term "slightly above" means an increase of about 3%.

In another embodiment, it was unexpectedly found that other benefits could be achieved by including in the iron-containing additive, an additional material selected from the group of elements consisting of magnesium, chromium, and mixtures thereof. The elements are provided as suitable compounds selected from the groups consisting of oxides, hydroxides, carbonates, bicarbonates, sulfates, nitrates and mixtures thereof. The total amount of the compounds of magnesium, chromium, and mixtures thereof in the additive may be in the range of about 1.0 to 10.0 wt. %, such as about 2.0 to 8.0 wt. % of the additive. The addition of the aforesaid supplemental amount of magnesium and/or chromium compound saturates the slag with respect to these constituents thereby preventing their dissolution from the refractory. The life of the refractory lining is thereby extended.

A suitable amount of iron-containing additive is introduced into the reaction zone along with the fuel feedstock in order to satisfy the following two ratios: (i) a wt. ratio of iron-containing additive to ash (noncombustible material) in the reaction zone in the range of about 0.1 - 10.0 to 1.0, such as in the range of about 1-6 to 1; and (ii) at least 2 parts by weight, such as about 10-30, say 20 parts by weight of iron for each part by weight of vanadium.

Advantageously by the subject process, the two washing phases of the molten slag which are produced in the reaction zone have low viscosities, e.g. less than 100 poise at 2500 °F, in comparison with prior art high viscosity slag. This facilitates slag removal. Further, at shut-down of the gasifier, the refractory walls of the reaction zone are provided clean with substantially no net accumulation of vanadium contaminants.

The partial oxidation reaction takes place in a reducing atmosphere under the following conditions: temperature - 1700 °F to 3000 °F, such as about 2200 °F to 2600 °F; say about 2725 °F to 2825 °F; pressure - about 5 to 250 atmospheres, such as about 15 to 200 atmospheres; when steam or water is used as a temperature moderator, the H<sub>2</sub>O/fuel weight ratio is in the range of about 0.1 to 5.0, such as about 0.2 to 0.9; and atomic ratio of free oxygen to carbon in the fuel (O/C ratio) is in the range of about 0.6 to 1.6, such as about 0.8 to 1.4.

The composition of the hot, raw effluent gas stream directly leaving the reaction zone of the free-flow partial oxidation gas generator is about as follows, in mole percent: H<sub>2</sub> 10 to 70, CO 15 to 57, CO<sub>2</sub> 0.1 to 25, H<sub>2</sub>O 0.1 to 20, CH<sub>4</sub> nil to 60, H<sub>2</sub>S nil to 2, COS nil to 0.1, N<sub>2</sub> nil to 60, and Ar nil to 2.0. Particulate carbon is present in the range of about 0.2 to 20 weight % (basis carbon content in the feed). Ash is present in the range of about 0.5 to 5.0 wt. %, such as about 1.0 to 3.0 wt. % (basis total weight of fuel feed). Depending on the composition after removal of the entrained particulate carbon and ash by quench cooling and/or scrubbing with water and with or without dewatering the gas stream may be employed as synthesis gas, reducing gas or fuel gas.

Another aspect of this invention is that the iron-containing additive may be selected on the basis of serendipitous catalytic properties in addition to its use in the generation of the washing agent, as previously described. For example, it may act to produce more and/or a better quality of light products from the coker operation. It may also aid in the gasification reactions either by increasing the reaction rate and thus the throughput capacity of the gasifier or by increasing the conversion of the soot and thus the overall efficiency of the process. Again, however, this invention does not depend on the catalytic properties of the iron-containing additive.

It was unexpectedly found that a preferred iron-containing additive for mixing with the heavy liquid hydrocarbonaceous material having a nickel and vanadium-containing ash or petroleum coke having a nickel and vanadium-containing ash is selected from the group consisting of elemental iron; iron compounds including oxides, sulfides, sulfates, carbonates, cyanides, chlorides, nitrates; and mixtures thereof. In another embodiment, the iron compound is a water soluble iron salt. In still another embodiment the iron compound is a ferro or ferri organic compound selected from the group consisting of naphthenates, oxalates, acetates, citrates, benzoates, oleates, tartrates, and mixtures thereof.

In one embodiment of the subject invention the aforesaid mixture of fuel feedstock comprising heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash and/or the petroleum coke having a nickel and vanadium-containing ash, and the iron-containing additive are introduced into the partial oxidation gasifier. In another embodiment, the iron-containing additive is mixed with the heavy liquid hydrocarbonaceous material having a nickel and vanadium-containing ash and the mixture is then fed into a conventional coking unit to produce petroleum coke. By this means, the finely ground iron-containing

additive may be intimately mixed throughout the petroleum coke product. The preferable particle size of the comminuted iron-containing additive and the comminuted petroleum coke is in the range of ASTM E-11 Standard Sieve Designation about 210 microns to 37 microns, or below. The ingredients of the aforesaid mixtures may be separately ground and then mixed together. Alternatively, the ingredients may be wet or  
5 dry ground together. Intimate mixing of the solid materials is thereby achieved, and the particle sizes of each of the solid materials in the mixture may be substantially the same. The dry ground mixture may be mixed with water or a liquid hydrocarbonaceous material or both to produce a pumpable slurry having a solids content in the range of about 50-65 wt.%. Alternatively, the solid materials may be wet ground with  
10 the liquid slurry medium. Alternatively, the mixture of particulate solids may be entrained in a gaseous medium and then introduced into the gas generator. The gaseous transport medium may be selected from the group consisting of steam, CO<sub>2</sub>, N<sub>2</sub>, free-oxygen containing gas, recycle synthesis gas, and mixtures thereof.

In the embodiment wherein ground iron-containing additive is mixed with the heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash and fed into a coker, the iron-containing  
15 washing additive may be introduced directly into the ash-containing petroleum liquid feed to the vacuum distillation tower, which normally precedes the coker unit. In either unit operation (coking or distillation), substantially all of the iron-containing additive should stay behind in the desired bottoms stream. In other words, there should be little, if any, carry over of the additive with the lighter products. A possible advantage for mixing the additive with the vacuum tower feedstream in preference to the bottoms stream  
20 (i.e. coker feed) is that the feed to the vacuum tower is significantly less viscous than the bottoms from the vacuum tower. A more thorough mixing may be thereby effected.

For example, a mixture comprising a high boiling liquid petroleum i.e. heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash and the comminuted iron-containing additive at a  
25 temperature in the range of about 650 °F to 930 °F is introduced into a delayed coking zone, for example by way of line 33, such as shown and described in coassigned U. S. Patent No. 3,673,080, which is incorporated herein by reference. At a temperature in the range of about 800 °F to 895 °F and a pressure in the range of about 20 to 60 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and petroleum coke in admixture with iron-containing additive is removed from the bottom of said  
30 delayed coking zone.

In one embodiment, the petroleum coke in admixture with iron-containing additive is ground with coal which is introduced as a silicon-containing addition agent. The ground mixture is introduced into the partial  
oxidation reaction zone as the fuel feed. Sufficient coal is mixed with the petroleum coke to provide in the reaction zone a weight ratio of coal ash in the range of about 0.1 to 100 for each part by weight of  
35 petroleum coke ash.

In another embodiment, a mixture comprising a high boiling liquid petroleum having a nickel and vanadium-containing ash and the comminuted iron-containing additive at a temperature in the range of  
40 about 550 °F to 750 °F is introduced into a fluidized bed coking zone for example by way of line 31, such as shown and described in U. S. Patent No. 2,709,676, which is incorporated herein by reference. At a temperature in the range of about 1000 °F to 1200 °F and a pressure in the range of about 10 to 20 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and said petroleum coke is removed from the bottom of said coking zone.

In other embodiments, this invention may be applied to other similar petroleum processes that produce a stream suitable for gasification. Any "bottom of the barrel" process that does not upgrade the bottoms or  
45 residue stream to extinction must ultimately produce such a stream. These streams, either liquid or normally solid but pumpable at elevated temperatures, will produce the same gasification problems as discussed for coke. Thus, the invention of introducing an iron-containing additive as part of the petroleum processing prior to gasification should, depending on the specific process, produce a feedstock that will be free of the gasification problems mentioned above. Most of these processes employ vacuum distillation as a pretreatment. Accordingly, as described above, the iron-containing addition agent may be mixed with the  
50 vacuum distillation feed having a nickel and vanadium-containing ash. The additive will then emerge from the distillation column in the bottoms stream. In turn, the bottoms stream is the feed stream for the upgrading process. This incorporation of the iron-containing additive should not adversely affect these processes, and the iron-containing addition agent should ultimately emerge with the vanadium-rich residue stream from each respective process. In all of these processes, this residue stream should be suitable for  
55 gasification by partial oxidation.

In still another embodiment of the invention, it was unexpectedly found that the softening temperature of the iron-containing addition agent could be reduced about 100-300 °F, such as about 200 °F by mixing a calcium compound with the previously described feedstock e.g. petroleum coke, liquid hydrocarbonaceous

fuel, or mixtures thereof. The calcium compound may be selected from the group consisting of calcium oxide, calcium carbonate, calcium hydroxide, by adding calcium in this manner, the partial oxidation gas generator may be started up at a lower temperature e.g. about 200 to 300° F lower. The calcium compound is temporarily introduced into the partial oxidation reaction zone at start-up in admixture with the feedstock  
5 and/or iron-containing addition agent in the critical amount of about 2.0 to 8.0 wt. % or below of the iron-containing addition agent. The calcium compound will lower the softening temperature of the iron-containing addition agent, thus enhancing the rate of sulfur pick-up in the slag. It was found that when the addition of calcium compound exceeded 8.0 wt. % of the iron-containing addition agent then calcium sulfide and calcium carbonate would clog up the central passage of the dip tube thereby blocking the discharge of the  
10 hot effluent gas stream from the reaction zone into the quench water.

Shortly after start-up when the sulfur begins to transfer into the molten slag, the liquid sulfide slag of iron and nickel will lower the softening temperature of the iron-containing agent thus eliminating thereafter the need of introducing calcium. Excess calcium will pick up the sulfur to form an undesirable viscous sulfide phase. Keeping the amount of calcium to 8.0 wt. % and below of the iron-containing addition agent  
15 will ensure the washing of the high melting calcium sulfide phase with the high melting vanadium laths and spinels. The use of calcium in this manner in admixture with the iron-containing additive is substantially different from its use as an ash fluxant, as described in coassigned U.S. Patent No. 4,277,365.

20

### EXAMPLE

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

25

### EXAMPLE I

30 Synthesis gas substantially comprising in mole % dry basis H<sub>2</sub> 25 to 45, CO 20 to 50, CO<sub>2</sub> 5 to 35, CH<sub>4</sub> 0.06 to 8.0, and COS + H<sub>2</sub>S 0.1 to 2.0 is produced in a free-flow refractory lined partial oxidation reaction zone, such as that shown and described in coassigned U. S. Patent No. 3,607,157, which is incorporated herein by reference. The feedstock comprises an atomized aqueous dispersion or a dispersion of substantially dry petroleum coke having a nickel and vanadium-containing ash and being entrained in a  
35 gaseous transport medium comprising a mixture of free-oxygen containing gas and/or steam. The petroleum coke feedstock contains about 3.2 wt. % of sulfur and about 1000 ppm of silicon. The ash in the petroleum coke comprises about 12.0 wt. % of vanadium, and about 5.0 wt. % of nickel. The petroleum coke also has uniformly dispersed therein an iron-containing additive comprising about 100 wt.% of iron oxide. The wt. ratio of iron-containing additive to ash is about 5 to 1. The weight ratio of iron to vanadium in  
40 the reaction zone is about 16 to 1. In another run the petroleum coke having a nickel and vanadium-containing ash and being in admixture with an iron oxide additive is introduced into the free-flow partial oxidation zone as a pumpable slurry of petroleum coke in water. The solids content of the slurry is about 60 weight percent.

The petroleum coke is reacted with a free-oxygen containing gas e.g. air, oxygen-enriched air,  
45 substantially pure oxygen, in the presence of a temperature moderator e.g. H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>, in the refractory lined partial oxidation reaction zone at an autogenous temperature of about 2750° F and a pressure of about 6 atmospheres. The molten slag droplets are readily separated from the hot effluent gas stream leaving the reaction zone by gravity or by quenching and/or scrubbing the gas stream with water or other gas scrubbing medium. The ash fusion temperature for the first liquid phase washing agent and associated ash  
50 is below 2100° F. The ash fusion temperature for the second liquid phase washing agent and associated ash is below 2550° F. In comparison, the ash fusion of the coarse slag with no iron-containing additive is greater than 2750° F.

An elemental analysis of the components in a typical slag is shown in Table I below. Photomicrographs of cross-sections of typical slags produced from the first and second liquid phase washing agents and  
55 illustrating the undissolved vanadium-containing oxide spinels in a matrix of liquid phase washing agents are shown in the drawings for Figures 1 to 3.

Table I - Elemental Analysis of Slag Components

5

(weight %)	Fe	Ni	Al	Si	S	V	Ca	Na+K	Cr	Others (1)
<u>Liquid Phase</u>										
<u>Washing Agents</u>										
First	69.3	0.92	1.31	1.63	25.52	0.51	0.2	0.1	0	0.51
Second	30.86	0	8.02	34.74	1.76	3.09	19.1	1.49	0	0.94
<u>Spinel Phase</u>	37.58	0	4.05	0.73	0.09	30.66	0.1	0	23.86	2.91

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(1) minor ash components and refractory pick-up

EXAMPLE II

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The process described in Example I was repeated in substantially all respects but with the addition of supplemental amount of silicon to the petroleum coke feedstock. SiO<sub>2</sub> was added in the amount of 1.6 times the amount of ash in the petroleum coke feedstock. There was substantially no effect on the composition and the ash fusion temperature by the addition of this supplementary amount of silica. The elemental analysis of the second liquid phase washing agent was as follows in weight % Fe 31.89, Ni 0, Al 10.45, Si 45.65, S 1.34, V 0.95, Ca 5.57, Na+K 2.66, minor ash components and refractory pick-up 1.49. The proportion of second liquid phase washing agent to first liquid phase washing agent is increased. There was a dilution in concentration of vanadium-rich spinels in the slag. The ash fusion temperature of the second liquid phase washing agent slag was reduced to below 2225° F; and, the slag viscosity in comparison with that of the second liquid phase washing agent in Example I decreased.

40

Another embodiment of a process according to the invention uses relatively inexpensive feedstocks comprising heavy liquid hydrocarbonaceous fuel and/or petroleum coke feedstocks having nickel and vanadium-containing ashes. Further, said feedstock includes a minimum of 0.1 wt. % of sulfur, such as at least 2.0 wt. % sulfur; and less than about 350 ppm, such as about 1.0 ppm to about 350 ppm of silicon; and said ash includes a minimum 1.0 wt. % of vanadium, such as about 2.0 to 10.0 wt. %; and a minimum of 1.0 wt. % of nickel, such as about 2.0 to 5.0 wt. %. The present embodiment is generally in accordance with the first embodiment. Specific differences will be described below. The present embodiment makes use of a unique magnesia refractory lining whereby the reaction zone withstands attack from the corrosive molten slag.

45

This embodiment pertains to the partial oxidation of a low silicon-containing heavy liquid hydrocarbonaceous fuel and/or petroleum coke, and provides an improved combination of iron-containing additive and refractory lining in the material oxidation reaction zone. Further, a means of introducing this additive agent into the system to give maximum effectiveness is provided.

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The high magnesium oxide (e.g. greater than 85 wt. % MgO) refractory lining the partial oxidation reaction zone has the following composition in wt. %: MgO 85 to 98, Fe<sub>2</sub>O 0.03 to 3.0, Al<sub>2</sub>O<sub>3</sub> 0.02 to 2.0, CaO 0.01 to 10, and SiO<sub>2</sub> 0.02 to 2.0. The price of this magnesia refractory is comparable to alumina rich refractories (e.g. ruby bricks). Further, it is much cheaper than chromomagnesite refractories. A fused cast refractory is preferred. While fused casts are more expensive and less resistant to thermal cracking, they offer reduced tendency for slag penetration.

55

The iron-containing additive comprises an iron compound, preferably iron oxide. The iron-containing additive may comprise about 30.0 to 100.0 wt. % of an iron compound. In the reaction zone of the partial oxidation gas generator, a first portion e.g. 10 to 99 wt. % of the additive combines with at least a portion, such as substantially all or a large fraction e.g. about 90 to 97 wt. of the nickel and about 30 to 90 wt. %, of the iron.

say about 50 to 70 wt. % of the iron, and sulfur constituents found in the feedstock to produce a first low viscosity liquid phase washing agent or carrier. Minor amounts e.g. less than about 5 wt. % of the amount present in the feedstock, of other elements from the feedstock may be picked up by the first liquid phase washing agent and dissolved therein. Accordingly, a minor amount of at least one extraneous element selected from the group consisting of Al, Ca, V, Si, Ti, Mg, Mn, Na, K, and mixtures thereof may be optionally present in the first liquid phase washing agent. A second portion of the iron-containing additive combines with at least a portion, such as substantially all or a large fraction e.g. about 40 to 100 wt. %, say about 70 to 90 wt. % of the silicon, aluminum, calcium, sodium and/or potassium, and a portion e.g. 5 to 70 wt. %, of the remainder of the iron constituents found in the feedstock to produce a second liquid phase washing agent. Any remaining iron may go to the vanadium-containing spinel phase. Minor amounts e.g. less than about 5 wt. % of the amount present in the feedstocks, of other elements from the feedstock may be picked up by the second liquid phase washing agent and dissolved therein. Accordingly, a minor amount of at least one extraneous element selected from the group consisting of Ni, V, S, Mg, Cr, and mixtures thereof may be present in the second liquid phase washing agent. Advantageously, by the present process the sulfur content in the gas, and the downstream gas cleaning costs are substantially reduced or possibly eliminated. Further, in one embodiment substantially all of the sulfur in the feedstock is converted into the sulfide of iron and nickel and leaves the reaction zone in the slag.

The relative proportion of first and second liquid phase washing agents present in the reaction zone depends on the temperature prevailing in the reaction zone and the materials present. An elemental analysis of the first liquid phase washing agent substantially comprises in wt. % iron about 40 to 80, such as about 60 to 70; nickel about 0.1 to 5, such as about 1 to 10; and sulfur about 10 to 32, such as about 15 to 30. A minor amount of at least one of the following extraneous elements may be optionally present in the first liquid phase washing agent in the reaction zone in wt. %: vanadium about 0.05 to 5.0, such as about 0.2 to 2.0; silicon about 0.1 to 5.0, such as about 0.3 to 1.0; magnesium about 0.1 to 6.0; and aluminum about 0.01 to 1.0, such as about 0.1 to 0.3. It was unexpectedly found that most of the nickel e.g. 99 wt. % or more goes into the first liquid phase washing agent. Accordingly, in one embodiment to insure the elimination of harmful nickel subsulfide, the amount of the first liquid phase washing agent comprises at least about 5.0 wt. % (basis total amount of first and second washing agents). An elemental analysis of the second washing agent substantially comprises in wt. %: iron about 5 to 40, such as about 10 to 30; magnesium about 0.01 to 2.0; aluminum about 5 to 20, such as about 8 to 12; silicon about 20 to 50, such as about 30 to 40; calcium about 1.0 to 35, such as about 5 to 15; and sodium and/or potassium about 0.01 to 5, such as about 0.5 to 1.0. The extraneous elements which may be present in the second liquid phase washing agent in the reaction zone include in wt. % vanadium about 0.2 to 5.0, such as about 0.5 to 2.0; and sulfur about 0.01 to 1.5, such as about 0.1 to 1.0.

It was unexpectedly found that these liquid phase washing agents have strong wetting capabilities for the magnesia refractory lining and the high temperature non-flowing vanadium-containing oxide laths and spinels in the reaction zone. These washing agents function in a completely different manner than that of a fluxing additive which may be used for example to solubilize slag constituents in coal. For example, these washing agents do not solubilize the troublesome vanadium-containing oxide laths and spinels. Rather, they serve as carriers and wash them out of the reaction zone. These washing agents wash at least a portion, such as from about 60 to 100 wt. %, say about 70 to 90 wt. %, and preferably all of the vanadium-containing contaminants out of the reaction zone of the partial oxidation gas generator. The mixtures of the first and second liquid phase washing agent and vanadium oxide laths and spinels are referred to herein as slag. Combined with the molten slag in the amount of about 1.0 wt. % is a small portion of the magnesia lining from the reaction zone. The vanadium-containing oxide laths and spinels contain (i) substantially all e.g. 80 to 99 wt. % or a large fraction e.g. 85 to 95 wt. % of the vanadium present in the feed; (ii) the remainder of the Fe, Al, Mg, Ti and other minor impurities from the iron-containing additive and/or feedstock; and (iii) refractory components. The vanadium-containing oxide laths and spinels comprise about 1 to 10 wt. %, such as about 1 to 8 wt. % of vanadium oxide.

The first liquid phase washing agent is present in the amount of about 90 to 99.5 wt. %, (basis total weight of first and second washing agents), such as about 92 to 96 wt. %. The second liquid phase washing agent is present in the amount of about 0.5 to 10.0 wt. % such as about 1 to 2 wt. %. The two liquid phase washing agents are substantially immiscible in each other. For example, the solubility of the first liquid phase washing agent in the second liquid phase washing agent is only about 0.05 to 2.0 wt. %. Actually, with the exception of the vanadium-containing laths and spinels, the first liquid phase washing agent does a better job than the second liquid phase washing agent in washing out of the reaction zone the particulate matter entrained in the hot raw effluent gas stream from the reaction zone. In general, the vanadium-bearing spinels tend to concentrate in the second liquid phase washing agent rather than in the first liquid phase

washing agent. In some cases when the amount of the second liquid phase washing agent is less than 1.0 wt. %, the vanadium-bearing spinels have been so abundant that they actually constitute a more or less continuous mass with the second liquid phase washing agent. It is apparent that the vanadium-bearing spinels form very early in the crystallization sequence. Further, they have very high melting points and the grains composed of major proportions of them are rigid to very viscous at very high temperatures. The first liquid phase washing agent, in contrast with the second liquid phase washing agent, has a much lower melting point, and a much lower viscosity. However, it also contains very much less of the vanadium-containing spinels. For example, the melting point and viscosity of the first liquid phase washing agent are in the range of about 1900 to 2200 ° F, and about 5 to 120 poises respectively; whereas, the melting point and viscosity of the second liquid phase washing agent are in the range of about 2150 to 2475 ° F, and about 100 to 1200 poises, respectively.

The distribution of iron between the first and second liquid phase washing agents is influenced by the partial pressures of the oxygen and/or S<sub>2</sub> gas in the reaction zone. The lower the partial pressure of oxygen and/or S<sub>2</sub> gas at given temperature, the more iron is driven into the first liquid phase washing agent in preference to the second liquid phase washing agent. The formation of elemental iron in the reaction zone leads to difficulties with slag removal. In order to prevent elemental iron from forming, the partial pressure in atmospheres of the oxygen and/or S<sub>2</sub> gas in the reaction zone of the gasifier at a specific temperature is kept slightly above that calculated by Formulae I and/or II below.

The relationship between temperature in the reaction zone (T ° Fahrenheit), and the common logarithm of the equilibrium partial pressure of oxygen log P<sub>(O<sub>2</sub>)</sub> in atmospheres in the reaction zone is shown by Formula I. When the equilibrium partial pressure of oxygen in the reaction zone drops below that calculated in Formula I for the design temperature in the reaction zone, then sufficient supplemental free-oxygen containing gas is introduced into the reaction zone to restore the equilibrium partial pressure of the oxygen in the reaction zone to a value which is slightly above that calculated in Formula I. Additions of supplemental free-oxygen containing gas in excess of that required to do the job are economically unattractive. Further, they will reduce the efficiency of the process and should be avoided.

$$\log P_{(O_2)} = -38.9691 + 0.01744 T^{\circ} F - 0.0000024 T^2 \text{ }^{\circ} F \quad \text{I}$$

wherein: T is a value in the range of about 2100 ° F to 3000 ° F.

For example, when the temperature in the reaction zone is 2100 ° F, a first value for the equilibrium partial pressure of oxygen in the reaction zone, as determined from Formula I, is  $1.18 \times 10^{-13}$  atmospheres. This value for the partial pressure of the oxygen in reaction zone is compared with a second value of the partial pressure of oxygen which is determined by conventional calculations of the reactions going on in the reaction zone of the gasifier. When the second value for the partial pressure of oxygen is less than the value calculated from Formula I then sufficient supplemental free-oxygen containing gas e.g. air, oxygen, oxygen-enriched air is introduced into the reaction zone to bring the partial pressure of oxygen to a value which is slightly above  $1.18 \times 10^{-13}$  atmospheres, such as to about  $10^{-12}$  atmospheres or above. The term "slightly above" means an increase of about 3%. Over the reaction temperature range of 2100 to 3000 ° F and an atomic O/C ratio in the range of about 0.6 to 1.6, the equilibrium partial pressure of oxygen in the reaction zone will increase in the range of about  $1.18 \times 10^{-13}$  to  $5.64 \times 10^{-9}$  atmospheres.

As previously mentioned, elemental iron may be prevented from forming in the reaction zone of the partial oxidation gas generator by maintaining the partial pressure of S<sub>2</sub> gas in the reaction zone above the value calculated from Formula II below for the specified reaction zone temperature. The relationship between the temperature in the reaction zone (T ° Fahrenheit), and the common logarithm of the equilibrium partial pressure of S<sub>2</sub> gas "log P<sub>(S<sub>2</sub>)</sub>" in atmospheres is shown in Formula II. When the equilibrium partial pressure of the S<sub>2</sub> gas in the reaction zone drops below that calculated in Formula II for the design temperature in the reaction zone, then sufficient supplemental elemental sulfur or a sulfur-containing material is introduced into the reaction zone to bring the equilibrium partial pressure of the S<sub>2</sub> gas in the reaction zone to a value which is slightly above that calculated in Formula II. Additions of supplemental elemental sulfur or sulfur-containing materials in excess of that required to do the job are economically unattractive and should be avoided. Further, costly downstream purification steps for the S<sub>2</sub> gas may be then avoided.

$$\log P_{(S_2)} = -17.3454 + 0.007857 T^{\circ} F - 0.0000011 T^2 \text{ }^{\circ} F \quad \text{II}$$

wherein: T is a value in the range of about 2100 ° F to 3000 ° F.

For example, when the temperature in the reaction zone is 2100 ° F, the equilibrium partial pressure of S<sub>2</sub> gas in the reaction zone when calculated from Formula II is  $2 \times 10^{-6}$  atmospheres. This value for the partial pressure of S<sub>2</sub> gas in the reaction zone is compared with a second value for the partial pressure of S<sub>2</sub> gas which is determined by conventional calculations for the reactions going on in the reaction zone of the gasifier. When the second value for the partial pressure of S<sub>2</sub> gas is less than the value calculated from

Formula II, then sufficient supplemental elemental sulfur or sulfur-containing material e.g. metal sulfides, H<sub>2</sub>S, COS, SO<sub>2</sub> are introduced into the reaction zone to restore the equilibrium partial pressure of S<sub>2</sub> gas to a value which is slightly above  $2 \times 10^{-6}$  atmospheres, such as about  $10^{-5}$  atmospheres. The term "slightly above" means an increase of about 3%. Over the reaction temperature range of 2100 to 3000 °F, the equilibrium partial pressure of sulfur in the reaction zone will increase in the range of about  $2 \times 10^{-6}$  to  $2.12 \times 10^{-4}$  atmospheres.

In another embodiment, it was unexpectedly found that other benefits could be achieved by including in the iron-containing additive, an additional material selected from the group of elements consisting of magnesium, manganese, and mixtures thereof. The elements are provided as suitable compounds selected from the groups consisting of oxides, hydroxides, carbonates, bicarbonates, sulfates, nitrates and mixtures thereof. The total amount of said additional materials may be in the range of about 1.0 to 10.0 wt. %, such as about 2.0 to 8.0 wt. % of the iron-containing additive. The addition of the aforesaid supplemental amount of materials saturates the slag with respect to these constituents thereby preventing their dissolution from the refractory. The life of the refractory lining is thereby extended.

A suitable amount of iron-containing additive is introduced into the reaction zone along with the fuel feedstock in order to satisfy the following two ratios: (i) a wt. ratio of iron-containing additive to ash (noncombustible material) in the reaction zone in the range of about 0.1 - 10.0 to 1.0, such as in the range of about 1-6 to 1; and (ii) at least 2 parts by weight, such as about 10-30, say 20 parts by weight of iron for each part by weight of vanadium.

Advantageously by the subject process, the two washing phases of the molten slag which are produced in the reaction zone have low viscosities, in comparison with prior art high viscosity slag. This facilitates slag removal. Further, at shut-down of the gasifier, the inside surfaces of the top dome and refractory walls of the reaction zone may be provided clean and with substantially no accumulation of vanadium contaminants.

The partial oxidation reaction takes place in a reducing atmosphere under the following conditions: temperature about 2200 °F to 3000 °F, such as about 2300 °F to 2600 °F; say about 2725 °F to 2825 °F. Further, the temperature in the reaction zone is 100 °F to 200 °F above the fluid temperature of the slag; pressure is about 2 to 250 atmospheres; H<sub>2</sub>O/fuel weight ratio is in the range of about 0.1 to 5.0, such as about 0.2 to 0.9; and atomic ratio of free oxygen to carbon in the fuel (O/C ratio) is in the range of about 0.6 to 1.6, such as about 0.8 to 1.4.

The composition of the hot, raw effluent gas stream directly leaving the reaction zone of the free-flow partial oxidation gas generator is about as follows, in mole percent: H<sub>2</sub> 10 to 70, CO 15 to 57, CO<sub>2</sub> 0.1 to 30, H<sub>2</sub>O 0.1 to 20, CH<sub>4</sub> nil to 60, H<sub>2</sub>S nil to 0.5, COS nil to 0.05, N<sub>2</sub> nil to 60, and A<sub>r</sub> nil to 2.0. Particulate carbon is present in the range of about 0.2 to 20 weight % (basis carbon content in the feed). Ash is present in the range of about 0.5 to 5.0 wt. %, such as about 1.0 to 3.0 wt. % (basis total weight of fuel feed). Depending on the composition after removal of the entrained particulate carbon and ash by quench cooling and/or scrubbing with water and with or without dewatering, the gas stream may be employed as synthesis gas, reducing gas or fuel gas.

Another aspect of this invention is that the iron-containing additive may be selected on the basis of serendipitous catalytic properties during coking in addition to its use in the generation of the washing agent during gasification, as previously described. For example, it may act to produce more and/or a better quality of light products from the coker operation. It may also aid in the gasification reactions either by increasing the reaction rate and thus the throughput capacity of the gasifier or by increasing the conversion of the soot and thus the overall efficiency of the process. Again, however, this invention does not depend on the catalytic properties of the iron-containing additive.

It was unexpectedly found that a preferred iron-containing additive for mixing with the heavy liquid hydrocarbonaceous material containing low silicon and having a nickel and vanadium-containing ash or petroleum coke containing low silicon and having a nickel and vanadium-containing ash is selected from the group consisting of elemental iron; iron compounds including oxides, sulfides, carbonates, cyanides, nitrates; and mixtures thereof. In another embodiment, the iron compound is a water soluble iron salt. In still another embodiment, the iron compound is a ferro or ferri organic compound selected from the group consisting of naphthenates, oxalates, acetates, citrates, benzoates, oleates, tartrates, and mixtures thereof.

In one embodiment of the subject invention the aforesaid mixture of fuel feedstock and the iron-containing additive are introduced into the partial oxidation gasifier. In another embodiment, the iron-containing additive is mixed with the heavy liquid hydrocarbonaceous material containing low silicon and having a nickel and vanadium-containing ash and the mixture is then fed into a conventional coking unit to produce petroleum coke. By this means, the finely ground iron-containing additive may be intimately mixed throughout the petroleum coke product. The preferable particle size of the comminuted iron-containing

additive and the comminuted petroleum coke is in the range of ASTM E-11 Standard Sieve Designation about 210 microns to 37 microns, or below. The ingredients of the aforesaid mixtures may be separately ground and then mixed together. Alternatively, the ingredients may be wet or dry ground together. Intimate mixing of the solid materials is thereby achieved, and the particle sizes of each of the solid materials in the mixture may be substantially the same. The dry ground mixture may be mixed with water or a liquid hydrocarbonaceous materials or both to produce a pumpable slurry having a solids content in the range of about 50-65 wt. %. The slurry is then gasified by partial oxidation in the manner previously described. Alternatively, the solid materials may be wet ground with the liquid slurry medium. Alternatively, the mixture of particulate solids may be entrained in a gaseous medium and then introduced into the partial oxidation gas generator. The gaseous transport medium may be selected from the group consisting of steam, CO<sub>2</sub>, N<sub>2</sub> free-oxygen containing gas, recycle synthesis gas, and mixtures thereof.

For example, a mixture comprising a high boiling liquid petroleum containing low silicon e.g. heavy liquid hydrocarbonaceous fuel containing low silicon and having a nickel and vanadium-containing ash and the comminuted iron-containing additive at a temperature in the range of about 650 °F to 930 °F is introduced into a delayed coking zone, for example, by way of line 33, such as shown and described in coassigned U.S. Patent No. 3,673,080, which is incorporated herein by reference. At a temperature in the range of about 800 °F to 895 °F and a pressure in the range of about 20 to 60 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and petroleum coke in admixture with iron-containing additive is removed from the bottom of said delayed coking zone.

In one embodiment, a mixture comprising a high boiling liquid petroleum containing low silicon and having a nickel and vanadium-containing ash, and the comminuted iron-containing additive at a temperature in the range of about 550 °F to 750 °F is introduced into a fluidized bed coking zone for example by way of line 31, such as shown and described in U.S. Patent No. 2,709,676, which is incorporated herein by reference. At a temperature in the range of about 1000 °F to 1200 °F and a pressure in the range of about 10 to 20 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and said petroleum coke is removed from the bottom of said coking zone.

In other embodiments, this invention may be applied to other similar petroleum processes that produce a stream suitable for gasification. Any "bottom of the barrel" process that does not upgrade the bottoms or residue stream to extinction must ultimately produce such a stream. These streams, either liquid or normally solid but pumpable at elevated temperatures, will produce the same gasification problems discussed for coke. Thus, the invention of introducing an iron-containing additive as part of the petroleum processing prior to gasification should, depend on the specific process, produce a feedstock that will be free of the gasification problems mentioned above. Most of these processes employ vacuum distillation as a pretreatment. Accordingly, as described above, the iron-containing addition agent may be mixed with the vacuum distillation feed having a nickel and vanadium-containing ash. The additive will then emerge from the distillation column in the bottoms stream. In turn, the bottoms stream is the feed stream for the upgrading process. This incorporation of the iron-containing additive should not adversely affect these processes, and the iron-containing addition agent should ultimately emerge with the vanadium-rich residue stream from each respective process. In all of these processes, this residue stream should be suitable for gasification by partial oxidation.

#### EXAMPLES

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

Synthesis gas is produced in a vertical free-flow unobstructed refractory lined partial oxidation reaction zone, such as that shown and described in coassigned U.S. Patent No. 3,607,157, which is incorporated herein by reference. The feedstock comprises an atomized aqueous dispersion of petroleum coke having a nickel and vanadium-containing ash. The petroleum feedstock contains about 3.2 wt % of sulfur and less than 350 ppm of silicon. The ash in the petroleum coke comprises about 12.0 wt. % of vanadium, and about 5.0 wt. % of nickel. The petroleum coke also has uniformly dispersed therein an iron-containing additive comprising about 100 wt. % of iron oxide. The wt. ratio of iron-containing additive to ash is about 5 to 1. The weight ratio of iron to vanadium in the reaction zone is about 16 to 1. The solids content of the slurry is about 60 wt. %.

The petroleum coke is reacted with a free-oxygen containing gas e.g. air, oxygen-enriched air, substantially pure oxygen, in the presence of a temperature moderator e.g. H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub> in the refractory



lined partial oxidation reaction zone at an autogenous temperature of about 2450° F and a pressure of about 6 atmospheres. The molten slag droplets are readily separated from the hot effluent gas stream leaving the reaction zone by gravity or by quenching and/or scrubbing the gas stream with water or other gas scrubbing medium. The ash fusion temperature for the first liquid phase washing agent and associated ash is below 2100° F. The ash fusion temperature for the second liquid phase washing agent and associated ash is below 2250° F. In comparison with tests run with commercially available refractories, including alumina base refractory, the slag generated from the aforesaid gasification shows the least attack on high MgO refractory comprising in wt. %: 92% MgO, 0.3% Fe<sub>2</sub>O<sub>3</sub>, 0.2% Al<sub>2</sub>O<sub>3</sub>, 1% CaO, and 0.2% SiO<sub>2</sub>.

Photomicrographs of cross-sections of typical slags produced from the first and second liquid phase washing agents and illustrating the undissolved vanadium-containing oxide spinels in a matrix of liquid phase washing agents are shown in the drawings for Figures 4 to 6.

The following examples are offered to better understand the present invention. Briefly, Example No. 1 illustrates the problem with removing slag produced by the gasification of low silicon-containing petroleum coke as previously described but without an additive or with an ineffective additive. Example No. 2 illustrates the potential refractory slag problems that might result from the use of the additive with an unsuitable refractory liner. Example No. 3 illustrates Applicant's invention and shows the success of the additive when used with a compatible hot face high MgO refractory liner.

#### Example No. 1

Slag produced from partial oxidation of low silicon-containing petroleum coke and without an additive. The drawing for Figure 4 shows abundant laths comprising the oxides of V, Ca and Fe, with spinels selected from the groups consisting of V, Fe, Ni, Al, and mixtures thereof. The slag is very viscous and there is very little melting, which is necessary to remove the slag from the gasifier.

#### Example No. 2

Slag produced from the partial oxidation of low silicon-containing petroleum coke and with an effective calcium moderated iron oxide additive, but with a chromia-alumina refractory. The drawing for Figure 5 shows interlocking laths of Al, Ca, V-oxide phase in a matrix of Al, Ca, Si, Fe-oxide. The high viscosity of the slag, as evident by the presence of interlocking needles, is a result of the severe interaction of the additive with the alumina based refractory.

#### Example No. 3

Illustrates Applicant's invention. Slag produced from partial oxidation of low silicon-containing petroleum coke and with iron oxide rich additive and the high MgO refractory as previously described. The drawing for Figure 6 shows the presence of a fluid oxy-sulfide melt with localized spinels rich in Mg, Fe, V. The localized occurrence of the spinels that are formed by the interaction of vanadium and iron with the high MgO refractory (as compared to the interlocking nature of the laths with the alumina rich refractory) will cause no slag removal problems.

The following is a description of a further embodiment of a process according to the invention.

The partial oxidation of heavy liquid hydrocarbonaceous fuel and solid carbonaceous fuel e.g. petroleum coke are described respectively in coassigned U.S. Patent Numbers 4,411,670 and 3,607,156, which are incorporated herein by reference. Further, suitable free-flow unobstructed vertical refractory lined gas generators and burners that may be used in the production of synthesis gas, reducing gas, or fuel gas from these materials are also described in the aforesaid references. Preferably, the vertical cylindrical shaped reaction zone has two coaxial inlet and outlet orifices or passages. These are centrally located in the top and bottom of the reaction zone. Advantageously, the subject process uses relatively inexpensive feedstocks comprising heavy liquid hydrocarbonaceous fuel and/or solid carbonaceous fuel feedstocks having nickel and vanadium-containing ashes. Further, said feedstock includes a minimum of 0.1 wt.% of sulfur, such as at least 2.0 wt.% sulfur; and greater than about 7, such as about 10 parts per million (ppm) to about 70,000 ppm of silicon; say in the range of greater than about 350 ppm to about 10,000 ppm of silicon; and said ash includes a minimum of 2.0 wt.% of vanadium and, a minimum of 1.0 wt.% of nickel, such as 2.0 to 5.0 wt. %.

By definition, the term sulfur-containing heavy liquid hydrocarbonaceous material or fuel having a nickel and vanadium-containing ash is a petroleum or coal derived fuel selected from the group consisting of virgin crude, residua from petroleum distillation and cracking, petroleum distillate, reduced crude, whole crude, asphalt, coal tar, coal derived oil, shale oil, tar sand oil, and mixtures thereof.

5 By definition, the term sulfur-containing solid carbonaceous fuel having a nickel and vanadium-containing ash is a solid fuel selected from the group consisting of coal, coke from coal, lignite; residue derived from coal liquefaction; oil shale; tar sands; petroleum coke; asphalt; pitch; particulate carbon (soot); and mixtures thereof. The petroleum coke is made from ash-containing heavy liquid hydrocarbonaceous fuel by conventional coking methods such as by the delayed or fluid coking process, such as described in  
10 coassigned U.S. Patent No. 3,673,080, which is incorporated herein by reference.

Closer study of the ashes derived from the partial oxidation, without an additive, of a feedstock comprising heavy liquid hydrocarbonaceous fuels and/or solid carbonaceous fuel having nickel and vanadium-containing ashes shows that they are largely composed of oxide and sulfide compounds of vanadium, nickel, iron, silicon, aluminum, and magnesium, along with some normally occurring mineral  
15 matter species. Vanadium-containing oxide laths are present and may be selected from the group consisting of V, V+Ca, V+Fe, V+Al, and mixtures thereof. Vanadium-containing spinels are present of the spinel-type aluminate phases and may include any metals selected from the group consisting of V, Fe, Cr, Al, Mg and mixtures thereof. The presence of abundant interlocking needle to lath-like crystals is the cause of the high viscosity of the slag.

20 Petroleum coke is the preferred solid carbonaceous fuel in the subject process. The amount of vanadium and nickel is significantly greater in petroleum coke than in coal. Accordingly, the metals present in the ash provide a system that is significantly different from that occurring in coal. A further factor is that the total ash content of the petroleum coke or heavy liquid hydrocarbonaceous fuel may be only about one-half to 5 weight percent (wt.%) whereas coal typically contains 10-20 wt.% ash. The comparatively low ash  
25 concentration in petroleum coke and heavy liquid carbonaceous fuel may be the reason why the ash removal problem is only noticed after prolonged gasifier runs. The chance for effective ash and additive mixing that is necessary to wash the vanadium constituents out of the reaction zone or for effective fluxing is therefore greatly reduced. It is theorized that in the heavy liquid hydrocarbonaceous material and petroleum coke systems, a good deal of the ash material is liberated as individual molecular species. This  
30 is because upon vacuum distillation or coking, the metallic species in the crude, which are generally presented as porphyrin type structures (metal atoms, oxides or ions thereof confined in an organic framework) are entrapped within the collapsed carbon matrix.

Problems arise when the heavy metal constituents build-up in the partial oxidation gasification system. In particular, vanadium and nickel are known to accumulate on the ceiling and walls of the refractory lined  
35 reaction zone of the partial oxidation gas generator and not flow smoothly from the gasifier under normal gasifier conditions. This is especially prevalent in the area where the burner discharges through the top dome of the gasifier at the entrance to the down-flowing vertical free-flow unobstructed refractory lined gasification chamber. During shut down and subsequent exposure of the gasifier walls to air, these deposits involving vanadium can catch fire with the vanadium converting to the lower melting  $V_2O_5$  or metal  
40 vanadate states. These materials prove to be very corrosive to refractory thereby decreasing the life of the refractory lining of the reaction zone.

The vertical refractory lined free-flow unobstructed gas generator used in the subject process is shown and described in coassigned U.S. Patent No. 4,472,171, which is incorporated herein by reference. It was found that the temperature in the upper region near the top of the vertical, cylindrical-shaped reaction zone  
45 when operating in the normal manner was about  $100^\circ\text{F}$  to  $300^\circ\text{F}$ . greater than the temperature of  $1700^\circ\text{F}$  to  $2800^\circ\text{F}$ . which prevailed in the rest of the gasifier. This temperature differential contributed to slag sticking and build-up on the walls of the gasifier in the upper region.  $H_2O$  is regularly introduced into the reaction zone in the amount so that the weight ratio of  $H_2O$ /liquid hydrocarbonaceous fuel and/or solid carbonaceous fuel weight ratio is in the range of about 0.1 to 5.0, such as about 0.2 to 0.9. The  $H_2O$  may  
50 be introduced as the liquid or gaseous carrier for the solid carbonaceous fuel or the liquid hydrocarbonaceous fuel. It also moderates the exothermic reactions going on in the reaction zone. In the subject process, in addition to the aforesaid amount of  $H_2O$ , a supplemental amount of a gaseous slag fluidizing agent is introduced into the reaction zone. By the subject process, a uniform temperature prevails over the entire gasifier. Further, throughout the reaction zone of the gasifier, the temperature does not vary more  
55 than  $\pm 150^\circ\text{F}$ . Unexpectedly, by means of applicants' invention, a greater amount of sulfur is removed from the reaction zone as a portion of the molten slag, the fluidity of the molten slag is increased, and the inside walls of the entire gasifier are clean and free-from build-up of slag.

The gaseous slag fluidizing agent is selected from the group consisting superheated steam,  $CO_2$  and

mixtures thereof. For example, high pressure superheated steam about 20 to 1000 psi may be used. Sufficient gaseous slag fluidizing agent is introduced to the gasifier so as to reduce the temperature in the upper region of the reaction zone near the top of the gas generator about 100° F to 300° F. so as to maintain a uniform temperature throughout the reaction zone in the range of about 2100° F to 3000° F ± 150° F. For example, the amount of said gaseous slag fluidizing agent that is introduced into the reaction zone may be in the amount of about 1 to 20% of the amount of H<sub>2</sub>O introduced into the reaction zone without the introduction of said gaseous slag fluidizing agent. The gaseous slag fluidizing agent is introduced into the reaction zone in at least one of the following ways:

(1) In admixture with said free-oxygen containing gas and/or in admixture with liquid hydrocarbonaceous or solid carbonaceous fuel.

(2) By way of a separate passage in a partial oxidation annular type burner.

(3) By way of at least one injection port which passes through the top dome or the side walls near the top of the vertical refractory lined steel gasifier.

In other embodiments of the subject invention to be further described, an additional amount of supplemental gaseous material selected from the group consisting of free-oxygen containing gas, H<sub>2</sub>S, COS, SO<sub>2</sub> and mixtures thereof is introduced into the reaction zone along with, said gaseous slag fluidizing agent. For example, the supplemental gaseous material may be introduced into the reaction zone as a separate stream or in admixture with one of the other feed streams, such as in admixture with the gaseous slag fluidizing agent.

An iron-containing additive comprising an iron compound, preferably iron oxide, in admixture with the fuel feedstock is introduced into the partial oxidation gas generator. In the reaction zone of the gas generator, a first portion of the iron-containing additive combines with at least a portion, such as substantially all or a large fraction e.g. about 90 to 97 wt. of the nickel and about 30 to 90 wt%, say about 50 to 70 wt. % of the iron and sulfur constituents found in the feedstock to produce a first low viscosity liquid phase washing agent or carrier. Minor amounts e.g. less than about 5 wt. % of the amount present in the feedstock, of other elements from the feedstock may be picked up by the first liquid phase washing agent and dissolved therein. Accordingly, a minor amount of at least one extraneous element selected from the group consisting of Al, Ca, V, Si, Ti, Mg, Mn, Na, K, and mixtures thereof may be present in the first liquid phase washing agent. A second portion of the iron-containing additive combines with at least a portion, such as substantially all or a large fraction e.g. about 40 to 100 wt. %, say about 70 to 90 wt. % of the silicon, aluminum, calcium, sodium and/or potassium, and a portion e.g. 5 to 70 wt. %, of the remainder of the iron constituents found in the feedstock to produce a second liquid phase washing agent. Any remaining iron may go to the vanadium-containing spinel phase. Minor amounts e.g. less than about 5 wt. % of the amount present in the feedstocks, of other elements from the feedstock may be picked up by the second liquid phase washing agent and dissolved therein. Accordingly, a minor amount of at least one extraneous element selected from the group consisting of Ni, V, S, Mg, Cr, and mixtures thereof may be present in the second liquid phase washing agent. Advantageously, by the subject process the S<sub>2</sub> potential in the process gas stream and downstream gas cleaning costs are substantially reduced or possibly eliminated.

The relative proportion of first and second liquid phase washing agents present in the reaction zone depends on the temperature prevailing in the reaction zone and the materials present. An elemental analysis of the first liquid phase washing agent substantially comprises in wt. %: iron about 40 to 80, such as about 60 to 70; nickel about 0.1 to 5, such as about 1 to 10; and sulfur about 10 to 32, such as about 15 to 30. The extraneous elements which may be present in the first liquid phase washing agent in the reaction zone include in wt. % vanadium about 0.1 to 3, such as about 0.2 to 1.0; silicon about 0.01 to 3, such as about 0.5 to 1.5; and aluminum about 0.01 to 3, such as about 0.4 to 1.2. It was unexpectedly found that most of the nickel e.g. 99 wt. % or more goes into the first liquid phase washing agent. An elemental analysis of the second washing agent substantially comprises in wt. %: iron about 5 to 40, such as about 10 to 30; aluminum about 5 to 20, such as about 8 to 12; silicon about 20 to 50, such as about 30 to 40; calcium about 1.0 to 35, such as about 5 to 15; and sodium and/or potassium about 0.01 to 5, such as about 0.5 to 2. The extraneous elements which may be present in the second liquid phase washing agent in the reaction zone include in wt. % vanadium about 0.2 to 5, such as about 0.5 to 2; and sulfur about 0.01 to 1.5, such as about 0.1 to 1.0.

It was unexpectedly found that these liquid phase washing agents have strong wetting capabilities for the high temperature non-flowing vanadium-containing oxide laths and spinels. These washing agents function in a completely different manner than that of a fluxing additive which may be used for example to solubilize slag constituents in coal. For example, these washing agents do not solubilize the troublesome vanadium-containing oxide laths and spinels. Rather, they serve as carriers and wash them out of the

reaction zone. These washing agents wash at least a portion, such as from about 80 to 100 wt. %, say about 85 to 95 wt. %, and preferably all of the vanadium-containing contaminants out of the reaction zone of the partial oxidation gas generator. The mixtures of the first and second liquid phase washing agent and vanadium oxide laths and spinels are referred to herein as slag. The vanadium-containing oxide laths and spinels contain (i) substantially all e.g. about 80 to 99 wt. % or a large fraction e.g. about 85 to 95 wt. % of the vanadium present in the feed; (ii) the remainder of the Fe, Al, Mg, Ti, and other minor impurities from the iron-containing additive and/or feedstock; and (iii) refractory components. The vanadium-containing oxide laths and spinels comprise about 1 to 10 wt. %, such as about 4 to 8 wt. % of vanadium oxide.

The first liquid phase washing agent is present in the amount of about 90 to 99.5 wt. %, (basis total weight of first and second washing agents), such as about 92 to 96 wt. %. The second liquid phase washing agent is present in the amount of about 0.5 to 10 wt. % such as about 1 to 2 wt. %. The two liquid phase washing agents are substantially immiscible in each other. For example, the solubility of the first liquid phase washing agent in the second liquid phase washing agent is only about 0.05 to 2.0 wt. %. Actually, with the exception of the vanadium-containing laths and spinels, the first liquid phase washing agent does a better job than the second liquid phase washing agent in washing out of the reaction zone the particulate matter entrained in the hot raw effluent gas stream from the reaction zone. In general, the vanadium-bearing spinels tend to concentrate in the second liquid phase washing agent rather than in the first liquid phase washing agent. In some cases when the amount of the second liquid phase washing agent is less than 10 wt. %, the vanadium-bearing spinels have been so abundant that they actually constitute a more or less continuous mass with the second liquid phase washing agent. It is apparent that the vanadium-bearing spinels form very early in the crystallization sequence. Further, they have very high melting points and the grains composed of major proportions of them are rigid to very viscous at very high temperatures. The first liquid phase washing agent in contrast with the second liquid phase washing agent, have much lower melting points, and much lower viscosities. However, they also contain very much less of the vanadium-containing spinels. For example, the melting point and viscosity of the first liquid phase washing agent are in the range of about 1900 to 2200° F, and about 5 to 120 poises respectively; whereas, the melting point and viscosity of the second liquid phase washing agent are in the range of about 2150 to 2475F, and about 100 to 1200 poises, respectively.

The distribution of iron between the first and second liquid phase washing agents is influenced by the equilibrium oxygen and sulfur concentrations in the gas phase in the reaction zone. This is specified by the partial pressures of the oxygen and/or S<sub>2</sub> gas in the reaction zone. The lower the partial pressure of oxygen and/or S<sub>2</sub> gas at a given temperature, the more iron is driven into the first liquid phase washing agent in preference to the second liquid phase washing agent. The formation of elemental iron in the reaction zone leads to difficulties with slag removal. In order to prevent elemental iron from forming, the partial pressure in atmospheres of the oxygen and/or S<sub>2</sub> gas in the reaction zone of the gasifier at a specific temperature is kept slightly above that calculated by Formula I and/or II below.

The relationship between the temperature in the reaction zone (T° Fahrenheit), and the common logarithm of the equilibrium partial pressure of free-oxygen gas "log P<sub>(O<sub>2</sub>)"</sub> in atmospheres in the reaction zone is shown by Formula I. When the equilibrium partial pressure of oxygen gas in the reaction zone drops below that calculated in Formula I, then sufficient supplemental free-oxygen containing gas is introduced into the reaction zone to restore the equilibrium partial pressure of the oxygen gas in the reaction zone to a value which is slightly above that calculated in Formula I. Additions of supplemental free-oxygen containing gas in excess of that required to do the job are economically unattractive. Further, they will reduce the efficiency of the process and should be avoided.

$$\log P_{(O_2)} = -38.9691 + 0.01744 T^\circ F - 0.0000024T^2 \quad I$$

wherein: T is the temperature in the reaction zone and is in the range of about 2100° F to 3000° F.

For example, when the temperature in the reaction zone is 2100° F, a first value for the equilibrium partial pressure of oxygen in the reaction zone, as determined by Formula I, is about 1.18 x 10<sup>-13</sup> atmospheres. This value for the partial pressure of oxygen gas in the reaction zone is compared with a second value of the partial pressure of oxygen which is determined by conventional calculations for the reactions going on in the reaction zone of the gasifier. When the second value for the partial pressure of oxygen is less than the value calculated from Formula I then sufficient supplemental free-oxygen containing gas e.g. air, oxygen, oxygen-enriched air is introduced into the reaction zone to bring the partial pressure of oxygen to a value which is slightly above 1.18 x 10<sup>-13</sup> atmospheres, such as to about 10<sup>-12</sup> atmospheres or above. The term "slightly above" means an increase of about 3%. Over the reaction temperature range of 2100 to 3000° F and an atomic O/C ratio in the range of about 0.6 to 1.6, the equilibrium partial pressure of oxygen in the reaction zone will increase in the range of about 1.18 x 10<sup>-13</sup> to 5.64 x 10<sup>-9</sup> atmospheres.

As previously mentioned, elemental iron may be prevented from forming in the reaction zone of the

partial oxidation gas generator by maintaining the partial pressure of S<sub>2</sub> gas in the reaction zone above the value calculated from Formula II below for the specified reaction zone temperature. The relationship between the temperature in the reaction zone (T ° Fahrenheit) and the common logarithm of the equilibrium partial pressure of S<sub>2</sub> gas "log P<sub>(S<sub>2</sub>)</sub>" in atmospheres in the reaction zone is shown in Formula II. When the equilibrium partial pressure of the S<sub>2</sub> gas in the reaction zone drops below that calculated in Formula II, then sufficient supplemental elemental sulfur or a sulfur-containing material is introduced into the reaction zone to bring the equilibrium partial pressure of the S<sub>2</sub> gas in the reaction zone to a value which is slightly above that calculated in Formula II. Additions of supplemental elemental sulfur or sulfur-containing materials in excess of that required to do the job are economically unattractive and should be avoided. Further, costly downstream purification steps for the S<sub>2</sub> gas may be then avoided.

$$\log P_{(S_2)} = -17.3454 + 0.007857 T^{\circ} F - 0.0000011 T^2{}^{\circ} F \quad \text{II}$$

wherein: T is the temperature in the reaction zone is in the range of about 2100 ° F to 3000 ° F.

For example, when the temperature in the reaction zone is 2100 ° F, the equilibrium partial pressure of S<sub>2</sub> gas in the reaction zone, as determined by Formula II, is about 2 x 10<sup>-6</sup> atmospheres. This value for the partial pressure of S<sub>2</sub> gas in the reaction zone is compared with a second value for the partial pressure of S<sub>2</sub> gas which is determined by conventional calculations for the reactions going on in the reaction zone of the gasifier. When the second value for the partial pressure of S<sub>2</sub> gas is less than the value calculated from Formula II, then sufficient supplemental elemental sulfur or sulfur-containing material e.g. metal sulfides, H<sub>2</sub>S, COS, SO<sub>2</sub> are introduced into the reaction zone to restore the equilibrium partial pressure of S<sub>2</sub> gas to a value which is slightly above 2 x 10<sup>-6</sup> atmospheres, such as about 10<sup>-5</sup> atmospheres. The term "slightly above" means an increase of about 3%. Over the reaction temperature range of 2100 to 3000 ° F, the equilibrium partial pressure of sulfur in the reaction zone will increase in the range of about 2 x 10<sup>-6</sup> to 2.12 x 10<sup>-4</sup> atmospheres.

Further, it was unexpectedly found that the additional amount of free-oxygen, over and above that normally supplied to the gas generator as determined for example, by conventional thermal and weight balances may be added to the gasifier without substantially increasing the temperature in the reaction zone. Higher carbon conversions were thereby achieved at substantially the same gasification temperature. The fluidity of the molten slag was maintained, deposition of solid deposits on the gasifier walls was reduced, and the formation of metallic iron was thereby prevented. Preferably, the additional amount of free-oxygen containing gas is such that the equilibrium partial pressure of oxygen in the gas phase, as determined by Formula I, is increased about 1 to 20% over that determined from Formula I without the additional amount of free-oxygen containing gas. The additional amount of free-oxygen containing gas may be introduced into the reaction zone as a separate stream or in admixture with at least one of the following: the original free-oxygen containing gas, the original temperature moderator, the gaseous slag fluidizing agent, and mixtures thereof.

Also, the additional amount of sulfur-containing gas selected from the groups consisting of SO<sub>2</sub>, H<sub>2</sub>S, COS, and mixtures thereof may be added to the gasifier without substantially increasing the temperature in the reaction zone. Formation of metallic iron may be thereby prevented, the fluidity of the molten slag is maintained, and the deposition of solid deposits on the gasifier walls is reduced. Preferably, the additional sulfur-containing gas is such that the equilibrium partial pressure of sulfur in the gas phase as determined by Formula II, is increased about 0.1 to 5% over that determined from Formula II without the additional amount of sulfur-containing gas. The additional amount of sulfur-containing gas may be introduced into the reaction zone as a separate stream, or in admixture with the gaseous slag fluidizing agent, and mixtures thereof.

A suitable amount of iron-containing additive is introduced into the reaction zone along with the fuel feedstock in order to satisfy the following two ratios: (i) a wt. ratio of iron-containing additive to ash (noncombustible material) in the reaction zone in the range of about 0.1 - 10.0 to 1.0, such as in the range of about 1-6 to 1; and (ii) at least 2 parts by weight, such as about 10-30, say 20 parts by weight of iron for each part by weight of vanadium. Further, the total atoms of iron in the reaction zone is in the range of about 1.3 to 3.0 times the atoms of sulfur in the fuel plus about 0.5 to 2.0 times the atoms of silicon in the ash.

Advantageously by the subject process, the two washing phases of the molten slag which are produced in the reaction zone have low viscosities in comparison with prior art high viscosity slag. This facilitates slag removal. Further, at shut-down of the gasifier, the inside surfaces of the top dome and refractory walls of the reaction zone are provided clean and with substantially no deposits of slag.

The partial oxidation reaction takes place in a reducing atmosphere under the following conditions: temperature 2100 ° F to 3000 ° F, such as about 2300 ° F to 2600 ° F; say about 2725 ° F to 2825 ° F; pressure - about 2 to 250 atmospheres, H<sub>2</sub>O/fuel weight ratio is in the range of about 0.1 to 5.0, such as about 0.2 to

0.9; and atomic ratio of free oxygen to carbon in the fuel (O/C ratio) is in the range of about 0.6 to 1.6, such as about 0.8 to 1.4. About 90 to 99.9 wt. % of the carbon in the fuel is converted into carbon oxides.

The composition of the hot, raw effluent gas stream directly leaving the free-flow unobstructed vertical refractory lined reaction zone of the partial oxidation gas generator is about as follows, in mole percent: H<sub>2</sub> 10 to 70, CO 15 to 57, CO<sub>2</sub> 0.1 to 30, H<sub>2</sub>O 0.1 to 20, CH<sub>4</sub> nil to 60, H<sub>2</sub>S nil to 0.5, COS nil to 0.05, N<sub>2</sub> nil to 60, and A<sub>r</sub> nil to 2.0. Particulate carbon is present in the range of about 0.2 to 20 weight % (basis carbon content in the feed). Ash is present in the range of about 0.5 to 5.0 wt. %, such as about 1.0 to 3.0 wt. % (basis total weight of fuel feed). Depending on the composition after removal of the entrained particulate carbon and ash by quench cooling and/or scrubbing, the gas stream may be employed as synthesis gas, reducing gas or fuel gas.

The preferred iron-containing additive for mixing with the heavy liquid hydrocarbonaceous material having a nickel and vanadium-containing ash or petroleum coke having a nickel and vanadium-containing ash is selected from the group consisting of elemental iron; iron compounds including oxides, sulfides, sulfates, carbonates, cyanides, nitrates; and mixtures thereof. In another embodiment, the iron compound is a water soluble iron salt. In still another embodiment, the iron compound is a ferro or ferri organic compound selected from the group consisting of naphthenates, oxalates, acetates, citrates, benzoates, oleates, tartrates, and mixtures thereof.

In the subject invention the aforesaid mixture of fuel feedstock comprising heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash and/or the petroleum coke having a nickel and vanadium-containing ash, and the iron-containing additive are introduced into the partial oxidation gasifier. In another embodiment, the iron-containing additive is mixed with the heavy liquid hydrocarbonaceous material having a nickel and vanadium-containing ash and the mixture is then fed into a conventional coking unit to produce petroleum coke. By this means, the finely ground iron-containing additive may be intimately mixed throughout the petroleum coke product. The preferable particle size of the comminuted iron-containing additive and the comminuted petroleum coke is in the range of ASTM E-11 Standard Sieve Designation about 210 microns to 37 microns, or below. The ingredients of the aforesaid mixtures may be separately ground and then mixed together. Alternatively, the ingredients may be wet or dry ground together. Intimate mixing of the solid materials is thereby achieved, and the particle sizes of each of the solid materials in the mixture may be substantially the same. The dry ground mixture may be mixed with water or a liquid hydrocarbonaceous material or both to produce a pumpable slurry having a solids content in the range of about 50-65 wt. %. Alternatively, the solid materials may be wet ground with the liquid slurry medium. Alternatively, the mixture of particulate solids may be entrained in a gaseous medium and then introduced into the gas generator. The gaseous transport medium may be selected from the group consisting of steam, CO<sub>2</sub>, N<sub>2</sub>, free-oxygen containing gas, recycle synthesis gas, and mixtures thereof.

For example, a mixture comprising a high boiling liquid petroleum i.e. heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash and the comminuted iron-containing additive at a temperature in the range of about 650 °F to 930 °F is introduced into a delayed coking zone, for example, by way of line 33, such as shown and described in coassigned U.S. Patent No. 3,673,080, which is incorporated herein by reference. At a temperature in the range of about 800 °F to 895 °F and a pressure in the range of about 20 to 60 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and petroleum coke in admixture with iron-containing additive is removed from the bottom of said delayed coking zone.

In another embodiment, a mixture comprising a high boiling liquid petroleum having a nickel and vanadium-containing ash and the comminuted iron-containing additive at a temperature in the range of about 550 °F to 750 °F is introduced into a fluidized bed coking zone for example by way of line 31, such as shown and described in U.S. Patent No. 2,709,676, which is incorporated herein by reference. At a temperature in the range of about 1000 °F to 1200 °F and a pressure in the range of about 10 to 20 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and said petroleum coke is removed from the bottom of said coking zone.

In other embodiments, this invention may be applied to other similar petroleum processes that produce a stream suitable for gasification. Any "bottom of the barrel" process that does not upgrade the bottoms or residue stream to extinction must ultimately produce such a stream. These streams, either liquid or normally solid but pumpable at elevated temperatures, will produce the same gasification problems discussed for coke. Thus, the invention of introducing an iron-containing additive as part of the petroleum processing prior to gasification should, depending on the specific process, produce a feedstock that will be free of the gasification problems mentioned above. Most of these processes employ vacuum distillation as a pretreatment. Accordingly, as described above, the iron-containing addition agent may be mixed with the vacuum distillation feed having a nickel and vanadium-containing ash. The additive will then emerge from

the distillation column in the bottoms stream. In turn, the bottoms stream is the feed stream for the upgrading process. This incorporation of the iron-containing additive should not adversely affect these processes, and the iron-containing addition agent should ultimately emerge with the vanadium-rich residue stream from each respective process. In all of these processes, this residue stream should be suitable for gasification by partial oxidation.

In applicants' process, simultaneously with the gasification of the fuel in the reaction zone, at least about 20 wt. % of the sulfur in the fuel reacts with iron and nickel in the reaction zone to produce iron and nickel sulfide particulate matter. The remainder of the sulfur is converted into H<sub>2</sub>S and COS which leave the reaction zone in the hot raw effluent gas stream. In one embodiment the H<sub>2</sub>S and COS is separated from the effluent gas stream, for example by well-known solvent absorption processes, and recycled to the reaction zone in the gasifier, for example, along with the gaseous slag fluidizing agent. The metal sulfide particulate matter leaves the reaction zone along with the molten slag. When the molten slag drops into a water bath located in the bottom of a quench tank, such as quench water 31 in coassigned U.S. Patent No. 4,328,008, which is incorporated herein by reference, reaction of the metal sulfides with H<sub>2</sub>O takes place to produce a gaseous stream comprising H<sub>2</sub>S and H<sub>2</sub>O. In one embodiment this gaseous stream is recycled to the reaction zone, for example in admixture with said slag fluidizing agent.

Various modifications of the invention as herein before set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be made as are indicated in the appended claims.

## Claims

1. A process for the production of gaseous mixtures comprising H<sub>2</sub> + CO by the partial oxidation of a feedstock comprising a heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash or petroleum coke having a nickel and vanadium-containing ash, or mixtures thereof; and said feedstock includes a minimum of 0.1 wt. % of sulfur, and greater than about 7 parts per million of silicon; and said ash includes a minimum of 2.0 wt. % vanadium, and a minimum of 1.0 wt. % of nickel; said process comprising:

(1) mixing together an iron-containing additive with said feedstock; wherein the weight ratio of iron-containing additive to ash in the reaction zone in (2) is in the range of about 0.1 - 10.0 to 1.0, and there is at least 2 parts by weight of iron for each part by weight of vanadium;

(2) reacting said mixture from (1) at a temperature in the range of 1700 ° F to 3000 ° F and a pressure in the range of about 5 to 250 atmospheres in a free-flow refractory lined partial oxidation reaction zone with a free-oxygen containing gas in the presence of a temperature moderator and in a reducing atmosphere to produce a hot raw effluent gas stream comprising H<sub>2</sub> + CO and entrained molten slag; and where in said reaction zone a first portion of the said iron-containing additive combines with at least a portion of the nickel, iron and sulfur constituents found in the feedstock to produce a first liquid phase washing agent; a second portion of said iron-containing additive combines with at least a portion of the silicon, aluminum, calcium, sodium and/or potassium, and iron constituents found in the feedstock to produce a second liquid phase washing agent; and wherein the first and second liquid phase washing agents collect and transport at least a portion of the vanadium-containing oxide laths and spinels and other ash components and refractory out of the reaction zone; and

(3) separating non-gaseous materials from said hot raw effluent gas stream.

2. A process according to Claim 1 wherein a calcium compound in the amount of about 2.0 to below 8.0 wt. % of said iron-containing addition agent is only introduced into the reaction zone of the partial oxidation reaction zone at start-up to reduce the softening temperature of the iron-containing addition agent, and is then discontinued.

3. A process according to Claim 1 or Claim 2 wherein said first liquid phase washing agent substantially comprises in wt. % iron about 40 to 80, nickel about 0.1 to 5 and sulfur about 10 to 32; and, said second liquid phase washing agent substantially comprises in wt. % iron about 5 to 40, aluminum about 5 to 20, silicon about 20 to 50, calcium about 1.0 to 35, and sodium and/or potassium about 0.01 to 5.

4. A process according to any one of Claims 1 - 3 provided with the step of increasing the amount of second liquid phase washing agent in the reaction zone to a value in the range of about 30 to 95 wt. % (basis total weight of first and second liquid phase washing agents) by introducing a supplemental silicon-containing addition agent into the reaction zone.

5. A process according to Claim 4 wherein said supplemental silicon-containing addition agent is selected from the group consisting of oxides and sulfides of silicon; coal; coal ash; tar sand; sand; earth;

and mixtures thereof.

6. A process according to Claim 4 or Claim 5 wherein said feedstock is petroleum coke; and provided with the step of introducing coal into the reaction zone as said silicon-containing addition agent and as a portion of the fuel; and wherein coal is introduced into the reaction zone along with said petroleum coke to provide in said reaction zone a weight ratio of coal ash in the range of about 0.1 to 100 for each part by weight of petroleum coke ash.

7. A process according to any one of Claims 1 - 6 provided with the step of introducing sufficient supplemental oxygen-containing material and/or sulfur-containing material into the reaction zone so as to keep the equilibrium partial pressure of oxygen and/or S<sub>2</sub> gas in the reaction zone slightly above that calculated by Formulae I and/or II below; whereby elemental iron is prevented from forming in the reaction zone:

$$\log P_{(O_2)} = -38.9691 + 0.01744T^{\circ}F - 0.0000024 T^2{}^{\circ}F \quad I$$

where: log P<sub>(O<sub>2</sub>)</sub> is the equilibrium partial pressure of oxygen in the reaction zone, and T is the temperature in the reaction zone in °F.

and

$$\log P_{(S_2)} = -17.3454 + 0.007857 T^{\circ}F - 0.0000011 T^2{}^{\circ}F \quad II$$

where: log P<sub>(S<sub>2</sub>)</sub> is the equilibrium partial pressure of S<sub>2</sub> gas, in the reaction zone, and T is the temperature in the reaction zone in °F.

8. A process according to any one of Claims 1 - 7 where included in the iron-containing additive in (1) is an additional material selected from the group of elements consisting of magnesium, chromium, and mixtures thereof.

9. A process for the production of gaseous mixtures comprising H<sub>2</sub> + CO by the partial oxidation of a feedstock comprising a low silicon-containing heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash, or a low-silicon containing petroleum coke having a nickel and vanadium-containing ash, or mixtures thereof; and said feedstock includes a minimum of 0.1 wt. % of sulfur, and less than about 350 parts per million of silicon; and said ash includes a minimum of 1.0 wt. % vanadium, and a minimum of 1.0 wt. % of nickel; said process comprising:

(1) mixing together an iron-containing additive with said feedstock; wherein the weight ratio of iron-containing additive to ash in the reaction zone in (2) is in the range of about 0.1 - 10.0 to 1.0, and there is at least 2 parts by weight of iron for each part by weight of vanadium;

(2) reacting said mixture from (1) at a temperature in the range of about 2100 °F to 3000 °F and at a pressure in the range of about 2 to 250 atmosphere in a free-flow vertical refractory lined partial oxidation zone with a free-oxygen containing gas in the presence of a temperature moderator and in a reducing atmosphere to produce a hot raw effluent gas stream comprising H<sub>2</sub> + CO and entrained molten slag; wherein said refractory lining comprises in weight percent: MgO 85 to 98, Fe<sub>2</sub>O<sub>3</sub> 0.03 to 3.0; Al<sub>2</sub>O<sub>3</sub> 0.02 to 2.0, CaO 0.1 to 10 and SiO<sub>2</sub> 0.02 to 2.0; and where in said reaction zone a first portion of the said iron-containing additive combines with at least a portion of the nickel, iron and sulfur constituents found in the feedstock and refractory components to produce a first liquid phase washing agent substantially comprising in wt. % iron about 40 to 80; nickel about 0.1 to 5; and sulfur about 10 to 32; and optionally a minor amount of at least one element selected from the group consisting of Al, Ca, V, Si, Ti, Mg, Mn, Na, K and mixtures thereof; a second portion of said iron-containing additive combines with at least a portion of the silicon, aluminum, calcium, sodium and/or potassium, and iron constituents found in the feedstock and refractory components to produce a second liquid phase washing agent substantially comprising in wt. % iron about 5 to 40; magnesium about 0.01 to 2.0; aluminum about 5 to 20; silicon about 20 to 50; calcium about 1.0 to 35; and sodium and/or potassium about 0.01 to 5; and wherein the first and second liquid phase washing agents collect and transport at least a portion of the vanadium-containing oxide laths and spinels and other ash and refractory components out of the reaction zone as said molten slag, and said molten slag combines with a portion of said refractory in the amount of about 0.001 to 2.0 wt. % of the weight of said iron-containing additive to produce localized vanadium-containing spinels and substantially no interlocking laths;

(3) separating nongaseous materials from said hot raw effluent gas stream.

10. A process according to Claim 9 where included in the iron-containing additive in (1) is an additional material selected from the group of elements consisting of magnesium, manganese, and mixtures thereof.

11. A process according to Claim 8 or 10 wherein said additional materials are provided as compounds in the total amount of about 1.0 to 10.0 wt. % of said additive.

12. A process according to any one of Claims 9 - 11 provided with the step of introducing sufficient supplemental oxygen-containing material and/or sulfur-containing material into the reaction zone so as to maintain at a temperature of 2100 °F said oxygen and/or sulfur in the gaseous phase in the reaction zone at



a partial pressure in atmospheres of  $1.18 \times 10^{-13}$  and  $2 \times 10^{-6}$ , respectively.

13. A process according to any one of Claims 1 - 12, including the steps of:

(A) coking said mixture from step (1) to produce petroleum coke having a nickel and vanadium-containing ash and having dispersed therein said iron-containing additive;

5 (B) introducing the petroleum coke from step (A) into the partial oxidation reaction zone in step (2) as a pumpable slurry of petroleum coke in water, liquid hydrocarbonaceous fluid or mixtures thereof, or as substantially dry petroleum coke entrained in a gaseous transport medium.

14. A process according to Claim 13 where in (2) the mixture from (1) at a temperature in the range of about  $650^{\circ}\text{F}$  to  $930^{\circ}\text{F}$  is introduced into a delayed coking zone where at a temperature in the range of about  $800^{\circ}\text{F}$  to  $895^{\circ}\text{F}$  and a pressure in the range of about 20 to 60 psig uncondensed hydrocarbon effluent vapor and steam are removed overhead and said petroleum coke having a nickel and vanadium-containing additive is removed from the bottom.

15. A process according to Claim 13 where in (2) the mixture from (1) at a temperature in the range of about  $550^{\circ}\text{F}$  to  $750^{\circ}\text{F}$  is introduced into a fluidized bed coking zone where at a temperature in the range of about  $1000^{\circ}\text{F}$  to  $1200^{\circ}\text{F}$  and a pressure in the range of about 10 to 20 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and said petroleum coke is removed from the bottom.

16. A process for the production of gaseous mixtures comprising  $\text{H}_2 + \text{CO}$  by the partial oxidation of a sulfur-containing feedstock comprising a heavy liquid hydrocarbonaceous fuel having a nickel and vanadium-containing ash or solid carbonaceous fuel having a nickel and vanadium-containing ash, or mixtures thereof; and said feedstock includes a minimum of 0.1 wt. % of sulfur, and greater than about 7 parts per million of silicon; and said ash includes a minimum of 2.0 wt. % vanadium, and a minimum of 1.0 wt. % of nickel; said process comprising:

(1) mixing together an iron-containing additive with said feedstock; wherein the weight ratio of iron-containing additive to ash in the reaction zone in (2) is in the range of about 0.1 - 10.0 to 1.0, and there is at least 2 parts by weight of iron for each part by weight of vanadium;

(2) reacting said mixture from (1) at a pressure in the range of about 2 to 250 atmosphere in a down-flowing free-flow unobstructed refractory lined vertical reaction zone of a partial oxidation gas generator with a free-oxygen containing gas in a reducing atmosphere and in the presence of a gaseous slag fluidizing agent which is introduced at the top of the reaction zone in a sufficient amount so as to maintain a uniform temperature throughout the reaction zone in the range of about  $2100^{\circ}\text{F}$  to  $3000^{\circ}\text{F}$  and said gaseous slag fluidizing agent is selected from the group consisting of superheated steam,  $\text{CO}_2$ , and mixtures thereof, to produce a hot raw effluent gas stream comprising  $\text{H}_2 + \text{CO}$  and entrained molten slag; wherein an equilibrium oxygen concentration is provided in the gas phase in the reaction zone with a partial pressure in the range of about  $1.18 \times 10^{-13}$  to  $5.64 \times 10^{-9}$  atmospheres, an equilibrium sulfur concentration is provided in the gas phase in the reaction zone with a partial pressure in the range of about  $2 \times 10^{-6}$  to  $2.12 \times 10^{-4}$  atmospheres, the free O/C atomic ratio is in the range of about 0.6 to 1.6, the  $\text{H}_2\text{O}/\text{liquid hydrocarbonaceous fuel and/or solid carbonaceous fuel}$  weight ratio is in the range of about 0.1 to 5.0, and about 90 to 99.9 wt. % of the carbon in said liquid hydrocarbonaceous fuel and/or solid carbonaceous fuel is converted into carbon oxides; and where in said reaction zone a first portion of the said iron-containing additive combines with at least a portion of the nickel, iron and sulfur constituents found in the feedstock to produce a first liquid phase washing agent; a second portion of said iron-containing additive combines with at least a portion of the silicon, aluminum, calcium, sodium and/or potassium, and iron constituents found in the feedstock to produce a second liquid phase washing agent; and wherein the first and second liquid phase washing agents collect and transport substantially all of the vanadium-containing oxide laths and spinels and other ash components and refractory out of the reaction zone, and there is substantially no build-up of slag on the inside walls of the reaction zone; and

(3) separating nongaseous materials from said hot raw effluent gas stream.

17. A process according to Claim 16 including the additional steps of :-

(A) coking said mixture from step (1) by introducing said mixture at a temperature in the range of about  $650^{\circ}\text{F}$  to  $920^{\circ}\text{F}$  into a delayed coking zone where at a temperature in the range of about  $800^{\circ}\text{F}$  to  $895^{\circ}\text{F}$  and a pressure in the range of about 20 to 60 psig, uncondensed hydrocarbon effluent vapor and steam are removed overhead and said petroleum coke having a nickel and vanadium-containing ash and having uniformly dispersed therein said iron-containing additive is removed from the bottom;

55 (B) introducing the petroleum coke from step (A) into the partial oxidation reaction zone in step (2) as a pumpable slurry having a solids content in the range of about 50 to 70 wt. % and comprising petroleum coke in water, liquid hydrocarbonaceous fluid or mixtures thereof; or as substantially dry petroleum coke entrained in a gaseous transport medium.

18. A process according to Claim 16 or 17 wherein said gaseous fluidizing agent in step (2) is

introduced into said reaction zone in any one or more of the following ways:

(a) in admixture with said free-oxygen containing gas and/or in admixture with said liquid hydrocarbonaceous or solid carbonaceous fuel;

(b) by way of a separate passage in a partial oxidation annular-type burner; and

5 (c) by way of at least one injection port passing through the dome or side walls of said gasifier.

19. A process according to any one of Claims 16 - 18 wherein substantially all of the sulfur in said fuel is converted into iron sulfide and nickel sulfide which leave the reaction zone in said molten slag; and the remainder of said sulfur in the fuel is converted into H<sub>2</sub>S and COS which leave said reaction zone in said hot raw effluent gas stream; and provided with the steps of separating said H<sub>2</sub>S and COS from said effluent  
10 gas stream and recycling same to the reaction zone in (2).

20. A process according to any one of Claims 16 - 19 wherein said solid carbonaceous fuel is introduced into said reaction zone as a pumpable slurry entrained in a liquid carrier, or as ground particulate matter entrained in a gaseous carrier.

21. A process according to any one of Claims 1 - 20 wherein said iron-containing additive is selected  
15 from the group consisting of elemental iron; iron compounds selected from the group consisting of oxides, sulfides, sulfates, carbonates, cyanides, chlorides, and nitrates; and mixtures thereof.

22. A process according to any one of Claims 1 - 21 wherein the iron containing portion of said iron-containing additive is a ferro or ferri organic compound selected from the group consisting of naphthenates, oxalates, acetates, citrates, benzoates, oleates, tartrates, and mixtures thereof.

20 23. A process according to any one of Claims 1 - 22 wherein the iron-containing portion of said iron-containing additive is a water soluble iron salt.

24. A process according to any one of Claims 1 - 23 wherein an additional supplemental gaseous material selected from the group consisting of free-oxygen containing gas, H<sub>2</sub>S, COS, SO<sub>2</sub> and mixtures thereof is introduced into the reaction zone.

25 25. A process according to any one of Claims 1 - 24 wherein said mixture of iron-containing additive and feedstock from (1) has a particle size of ASTM E-11 Standard Sieve Designation in the range of about 210 microns to 37 microns, or below.

26. A process according to any one of Claims 1 - 25 wherein said iron-containing additive comprises about 30.0 to 100.0 wt. % of an iron compound.

30 27. A process according to any one of Claims 1 - 26 wherein the first liquid phase washing agent is present in the amount of about 90 to 99.5 wt. %, (basis total weight of said first and second liquid phase washing agents).

28. A process according to any one of Claims 1 - 27 wherein a sufficient amount of gaseous slag fluidizing agent is introduced into the reaction zone so as to maintain a uniform temperature throughout the  
35 reaction zone of about 2100° F to 3000° F ± 150° F.

29. A process according to any one of Claims 16 - 20 wherein supplemental free-oxygen containing gas is introduced into the reaction zone; and wherein the amount of said supplemental free-oxygen containing gas is such that the equilibrium partial pressure of oxygen in the gas phase, as determined by Formula I, below, is increased about 1 to 20% over that determined by Formula I without the additional amount of free-  
40 oxygen containing gas;

$$\log P_{(O_2)} = -38.9691 + 0.01744 T^\circ F - 0.0000024 T^2^\circ F \quad I$$
 wherein: T is the temperature in the reaction zone and is in the range of about 2100° F to 3000° F.

30. A process according to any one of Claims 16 - 20 wherein supplemental gaseous material selected from the group of sulfur-containing gases consisting of H<sub>2</sub>S, COS, SO<sub>2</sub>, and mixtures thereof is introduced  
45 into the reaction zone; and wherein the amount of said additional sulfur-containing gas is such that the equilibrium partial pressure of sulfur in the gas phase as determined from Formula II is increased about 0.1 to 5% over that determined from Formula II without the additional amount of said sulfur-containing gas;

$$\log P_{(S_2)} = -17.3454 + 0.007857 T^\circ F - 0.0000011 T^2^\circ F \quad II$$
 wherein: T is the temperature in the reaction zone and is in the range of about 2100° F to 3000° F.

50 31. A process according to any one of Claims 1 - 30 wherein there is present in said first liquid phase washing agent at least one additional element selected from the group consisting of Al, Ca, V, Si, Ti, Mg, Mn, Na, K, and mixtures thereof; and wherein there is present in said second liquid phase washing agent at least one additional element selected from the group consisting of Ni, V, S, Mg, Cr and mixtures thereof.

FIG. 1

SLAG FROM FIRST LIQUID PHASE WASHING AGENT  
(FIELD OF VISION = 0.55mm)

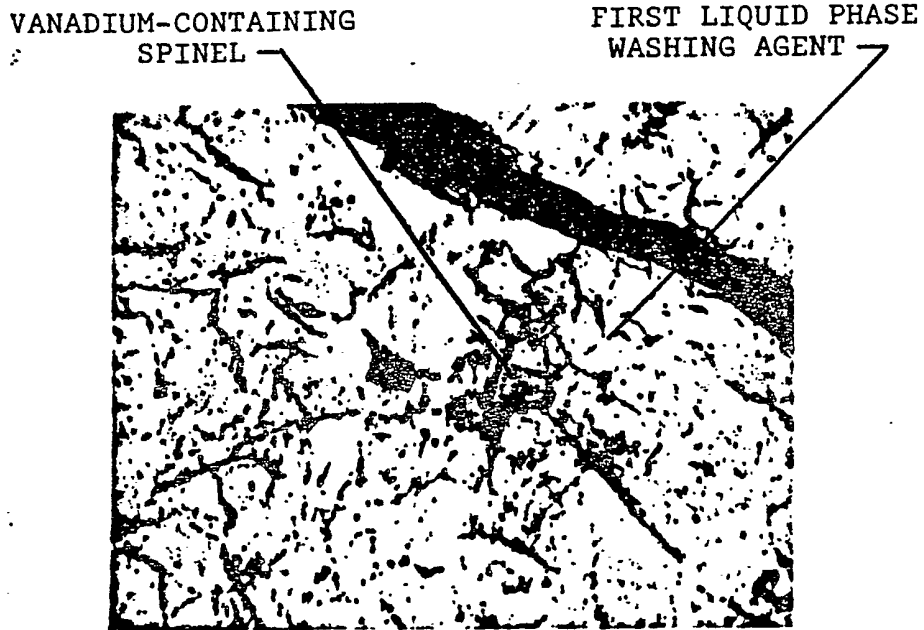
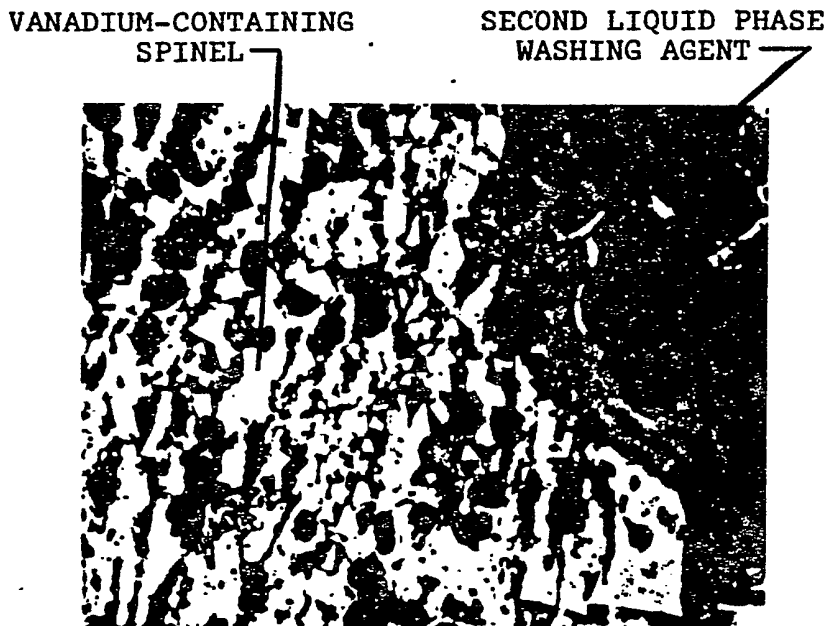


FIG. 2

SLAG FROM SECOND LIQUID PHASE WASHING AGENT  
(FIELD OF VISION = 1.1mm)



**FIG. 3**

SLAG FROM SECOND LIQUID PHASE WASHING AGENT  
WITH SUPPLEMENTAL ADDITION OF SILICON  
(FIELD OF VISION = 0.6mm)

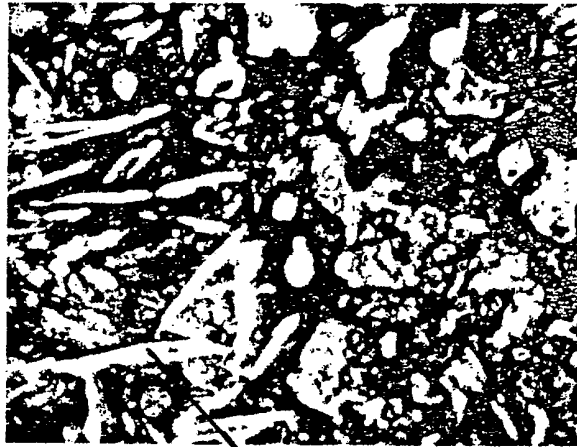
VANADIUM-CONTAINING  
SPINEL

SECOND LIQUID PHASE  
WASHING AGENT



**FIG. 4**

SLAG FROM PARTIAL OXIDATION OF LOW SILICON-CONTAINING PETROLEUM COKE WITHOUT AN ADDITIVE  
(FIELD OF VISION = 0.6MM)



SPINEL

LATH

**FIG. 5**

SLAG FROM PARTIAL OXIDATION OF LOW SILICON-CONTAINING PETROLEUM COKE WITH IRON-OXIDE ADDITIVE IN CHROMA-ALUMINA REFRACTORY LINED GASIFIER  
(FIELD OF VISION = 1.2MM)



INTERLOCKING LATHS

**FIG. 6**

SLAG FROM PARTIAL OXIDATION OF LOW  
SILICON-CONTAINING PETROLEUM COKE WITH  
IRON-OXIDE ADDITIVE IN HIGH MgO  
REFRACTORY LINED GASIFIER  
(FIELD OF VISION = 0.55MM)



SPINEL



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 778 485 (R.M. SUGGITT et al.) ---		C 01 B 3/36
A	US-A-4 732 700 (M.S. NAJJAR et al.) ---		C 10 J 3/46
A	US-A-4 705 539 (M.S. NAJJAR et al.) ---		
A	US-A-4 803 061 (M.S. NAJJAR et al.) ---		
A	US-A-4 705 538 (M.S. NAJJAR et al.) ---		
A	US-A-4 705 536 (M.S. NAJJAR et al.) ---		
A	US-A-4 671 804 (M.S. NAJJAR et al.) ---		
A	EP-A-0 209 261 (TEXACO DEVELOPMENT CORP.) -----		
			<b>TECHNICAL FIELDS SEARCHED (Int. Cl.5)</b>
			C 01 B C 10 J
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>09-11-1989</b>	Examiner <b>VAN BELLINGEN I.C.A.</b>
<b>CATEGORY OF CITED DOCUMENTS</b>		<b>T</b> : theory or principle underlying the invention <b>E</b> : earlier patent document, but published on, or after the filing date <b>D</b> : document cited in the application <b>L</b> : document cited for other reasons ..... <b>&amp;</b> : member of the same patent family, corresponding document	
<b>X</b> : particularly relevant if taken alone <b>Y</b> : particularly relevant if combined with another document of the same category <b>A</b> : technological background <b>O</b> : non-written disclosure <b>P</b> : intermediate document			