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(54) **GASIFICATION OF SULFUR-CONTAINING CARBONACEOUS FUELS**

(52) **U.S. Cl. 48/197 R**

(57) **ABSTRACT**

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A process for converting sulfur-containing carbonaceous fuel into a combustible product gas is described. The fuel, in the form of fine particles, is mixed with a first aqueous solution containing dissolved alkali metal carbonate at approximately atmospheric pressure to form concentrated slurry. The slurry is pressurized and fed into a gasifier operating at an elevated pressure. An oxygen-containing gas is also fed into the gasifier where it reacts with the fuel to produce hydrogen and carbon monoxide-containing gases and heat the reacting mixture to about 900-1400° C. Oxygen combined with steam may also be used as the oxidizer to produce hydrogen-rich product gas. Alkali metal salts in the slurry are melted and absorb sulfur from the reacting fuel to form a liquid smelt containing alkali metal sulfide. The smelt is dissolved in water to form a second aqueous solution which is regenerated by converting dissolved alkali metal sulfide into dissolved alkali metal carbonate and hydrogen sulfide gas which is released from the solution. The regenerated solution is recycled as the principal ingredient of the first aqueous solution. The hydrogen and carbon monoxide-containing gases are cooled, separated and purified to produce combustible product gases.

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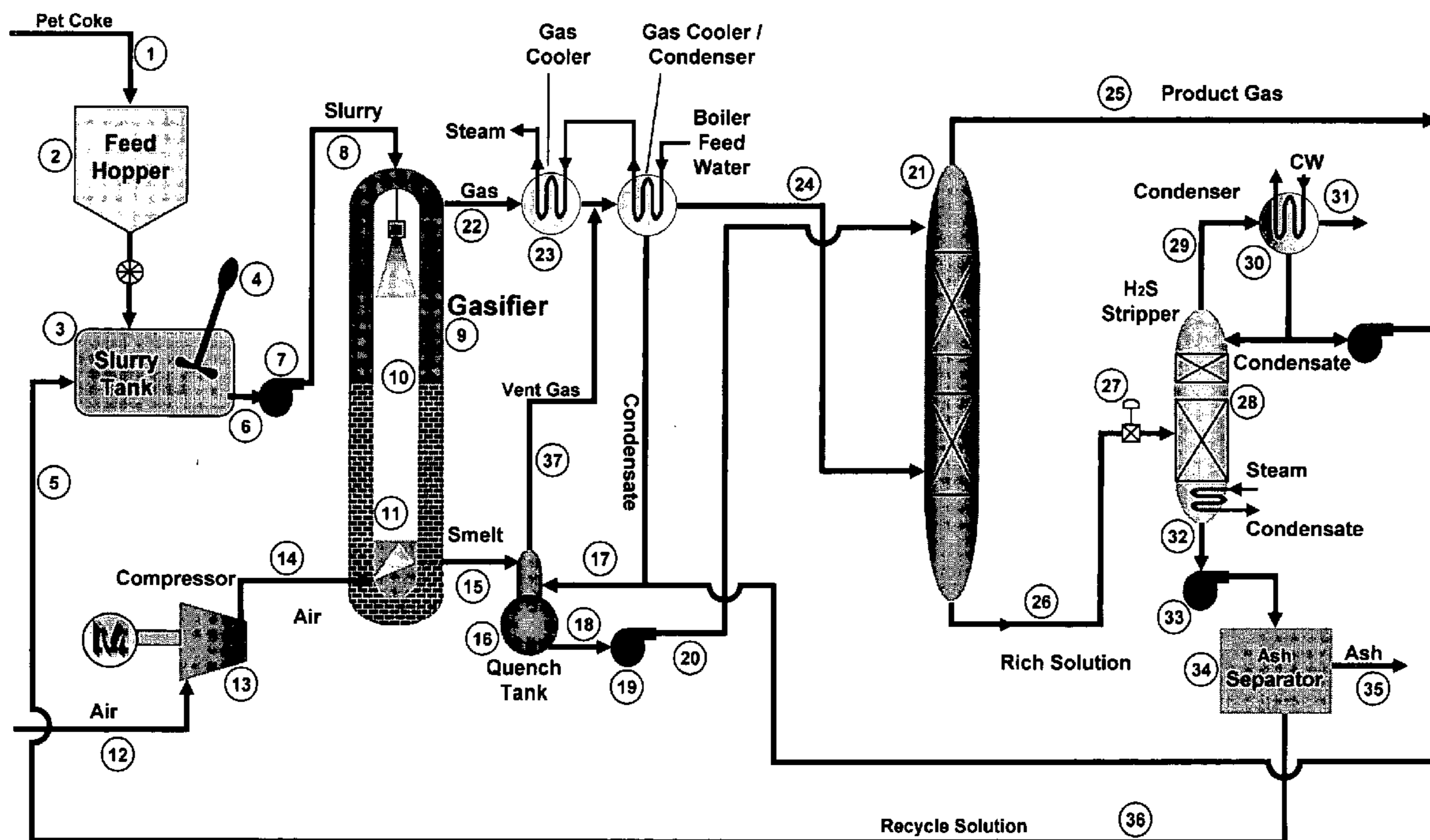
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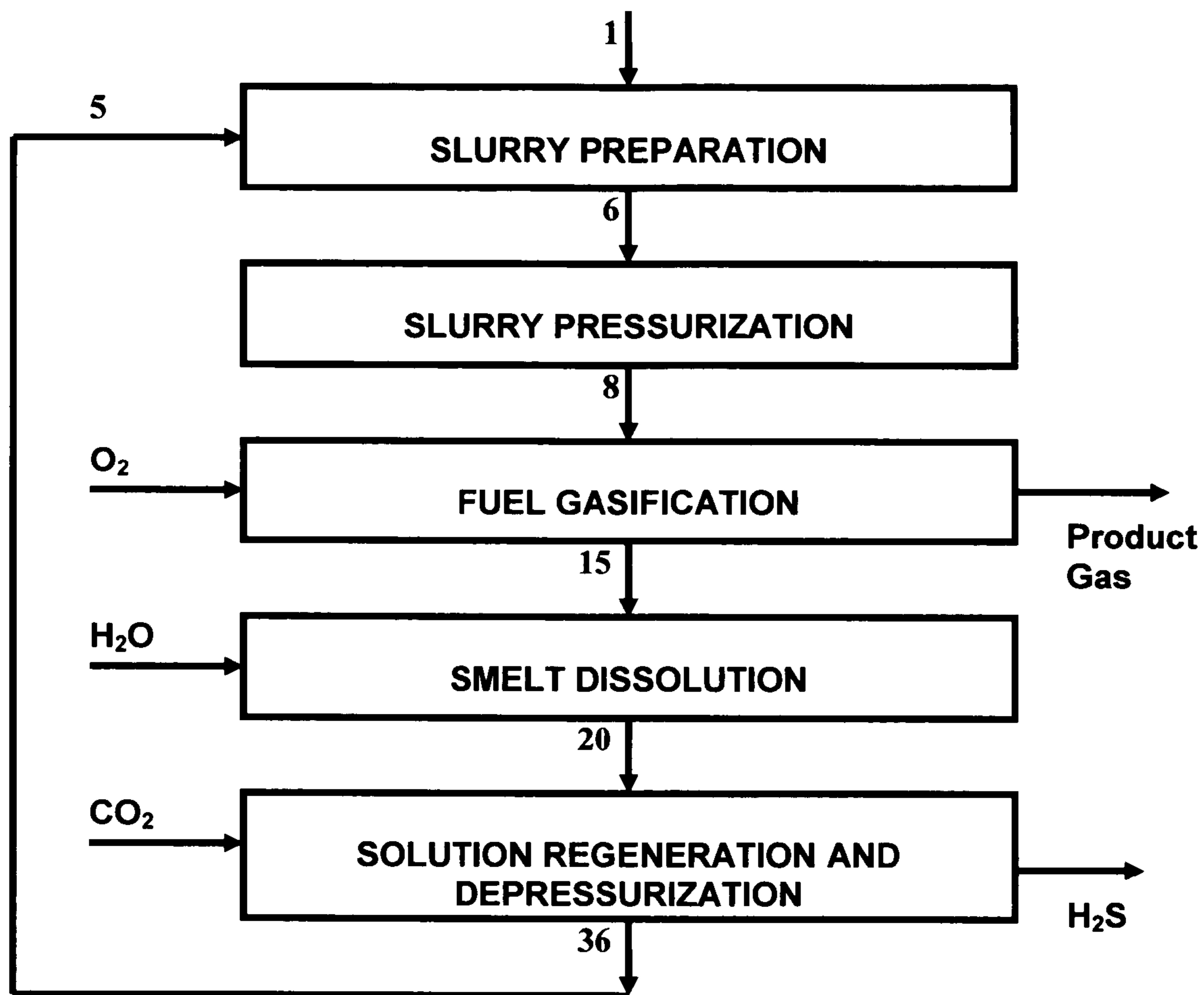
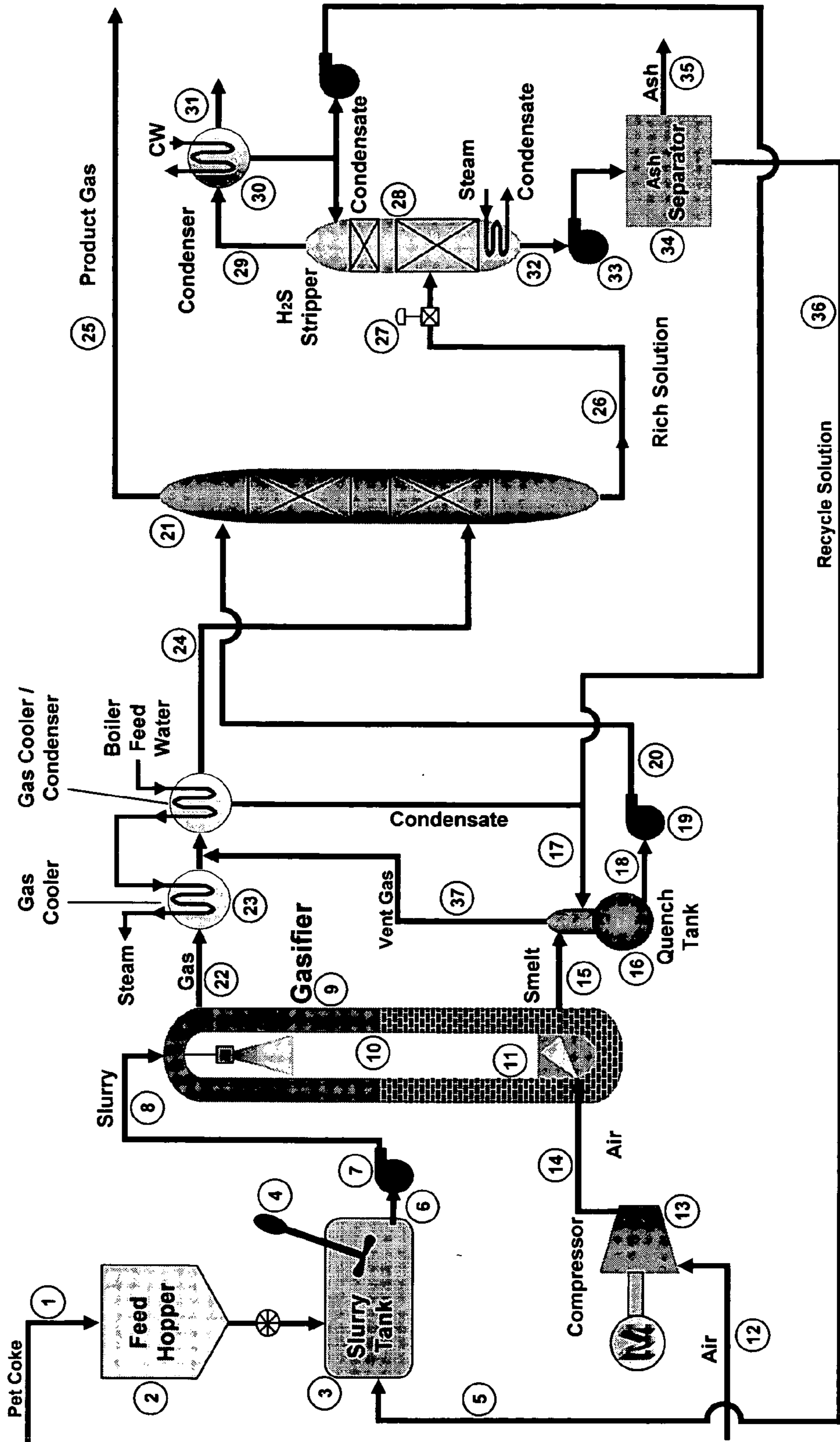


Figure 1

Figure 2.



GASIFICATION OF SULFUR-CONTAINING CARBONACEOUS FUELS

BACKGROUND

[0001] 1. Field of Application

[0002] This application relates to the gasification of carbonaceous fuels. More particularly, this technique of the application relates to a process for converting a sulfur-containing carbonaceous fuel into hydrogen and carbon monoxide-containing combustible gases by reaction with an oxygen-containing gas, or by reaction with a mixture of oxygen and steam, in the presence of a molten alkali metal salt catalyst.

[0003] 2. Description of the Related Art

[0004] Numerous techniques are known for gasifying coal and other carbonaceous fuels. In a review report published in 1983 by the Electric Power Institute (EPRI AP-3109) 22 different coal gasification processes are listed as being in commercial use, being demonstrated, or under active development. In general, the known coal gasification processes are categorized as moving bed, fluidized bed, entrained flow, or molten bath.

[0005] The moving bed process employs a dense settled bed of large fuel particles which move slowly downward in the bed while reacting with gases that move upward. The Lurgi gasifier is an example of a moving bed process. Difficulties with the moving bed gasifier, when operated at elevated pressure, include feeding the large fuel particles, handling fines, and handling hydrocarbon liquids which are distilled out with the product gas.

[0006] The fluidized bed process employs a dilute bed of small solid particles which are fluidized and continuously mixed by up-flowing gases. The High Temperature Winkler (HTW) process is an example of a fluidized bed system. Typical difficulties with fluidized bed processes include entrainment of small particles in the product gas and poor conversion efficiency with low reactivity fuels.

[0007] The entrained flow process uses powdered fuel in a plug flow reactor where the fine particles of coal react with the oxidant and steam in high velocity co-current flow. Examples of entrained flow systems are the Koppers-Totzek gasifier, which utilizes a solids feed system, and the Texaco gasifier, which uses slurry of powdered coal in water as feed. Difficulties with entrained flow gasifiers include the need for an oxygen plant, materials corrosion due to the high operating temperature and the presence of molten slag, and handling the high temperature product gas.

[0008] The molten bath process uses a pool of molten metal or salt in the reaction zone. U.S. Pat. No. 3,916,617 is an example of the molten salt process. Common difficulties with molten bath processes include excessive corrosion of materials used to retain the molten bath and the need to feed solid materials into the gasifier as fuel and makeup bath material.

[0009] U.S. Pat. No. 4,083,930 describes a process for removing and recovering sulfur values from a molten mixture of alkali metal sulfide and carbonate and producing a purified alkali metal carbonate solid suitable for recycle to a gasifier of the type described in U.S. Pat. No. 3,916,617. The process of U.S. Pat. No. 4,083,930 includes quenching the molten salt, dissolving it in an aqueous medium, reducing the pressure on the resulting solution to evaporate water, carbonating the solution, vacuum stripping the solution to release H₂S, recarbonating the stripped solution with pure CO₂, to produce alkali metal bicarbonate crystals, removing the crystals from

the residual solution, and drying and calcining the bicarbonate crystals to produce solid alkali metal carbonate.

[0010] Any attempt to combine the processes shown in U.S. Pat. Nos. 3,916,617 and 4,083,930 results in an overall process which is much more complicated than the subject technique of the application and has the undesirable features of a solid feeding system and a molten salt pool with air and solids injection beneath the surface.

[0011] U.S. Pat. Nos. 4,682,985, 4,773,918 and 5,984,987 describe gasification processes designed to handle concentrated black liquor, a liquid byproduct of the pulp and paper industry. Such processes are not applicable to solid fuels and do not involve the recycle of an alkali metal carbonate solution and the use of said recycle solution to form a slurry with the carbonaceous fuel feed.

[0012] The use of an alkali metal carbonate solution to remove and recover H₂S and CO₂ from gas streams is known. U.S. Pat. Nos. 1,533,733; 2,094,070; and 2,243,323 describe typical processes. However, the prior art does not suggest the integration of gas purification steps with the gasification of sulfur-containing carbonaceous fuel including the absorption of sulfur into molten alkali metal salt within the gasifier and the use of regenerated alkali metal carbonate solution to form a slurry with the fuel feed for the purpose of conveying it into the gasifier.

SUMMARY OF THE INVENTION

[0013] In its broadest aspects the process consists of mixing sulfur-containing carbonaceous fuel, in particulate form, with an aqueous solution of an alkali metal carbonate to produce a slurry; pressurizing the slurry and feeding it into a gasifier operating at superatmospheric pressure; feeding a pressurized oxygen-containing gas into the gasifier and reacting the oxygen with the carbonaceous fuel by exothermic partial combustion reactions in the presence of molten alkali metal salts to form a carbon monoxide-containing gas and an alkali metal sulfide-containing molten salt smelt; recovering the carbon monoxide-containing gas as the combustible product gas; dissolving the smelt in water and regenerating the resulting solution by converting dissolved alkali metal sulfide into dissolved alkali metal carbonate and gaseous hydrogen sulfide; and recycling the aqueous solution of alkali metal carbonate to the slurry preparation step.

[0014] In its more specific and preferred aspects the process includes the following steps:

[0015] Sulfur-containing carbonaceous fuel, in the form of fine particles, is mixed with a first aqueous solution of alkali metal salts containing about 5% to 35% by weight, preferably 10% to 30%, alkali metal carbonate and minor amounts of other salts such as alkali metal bisulfide, thiosulfate, and sulfate to form a concentrated slurry containing about 25% to 75% by weight, preferably 35% to 65%, undissolved fuel particles. The slurry is pressurized and fed into a gasifier operating at an elevated pressure in the range of about 4 to 50 atmospheres, preferably 6 to 40 atmospheres, and containing a drying zone and gasification zone.

[0016] The slurry contacts a hot gas in the drying zone producing water vapor, which mixes with the gas, and a dried mixture of carbonaceous fuel and salts. The dried mixture enters the gasification zone where it is contacted with an oxygen-containing gas (the oxidizer) which is fed into the gasification zone in an amount less than about 60% of the amount required for complete combustion of the carbonaceous fuel, and preferably in the range of 35% to 50%. The

oxygen reacts with the carbonaceous fuel by exothermic, partial combustion, reactions forming hydrogen and carbon monoxide-containing gases and producing a temperature in the gasification zone in the range of about 900-1400° C., preferably in the range of about 950-1300° C.

[0017] To prevent the presence of excessive nitrogen gas in the product gas, pure oxygen can be used as the oxidizer. In this process, the temperature of the gasification zone is moderated by steam injection into the gasifier at above the molten pool. This combined oxygen/steam oxidizer will produce hydrogen rich, medium-Btu gas (higher heating value (HHV) of about ≈ 290 Btu/scf).

[0018] The salts, which enter the gasification zone in the dried mixture, melt at the high temperature in the gasification zone, forming a liquid smelt that catalyzes the gasification reaction and absorbs sulfur from the reacting fuel resulting in the conversion of alkali metal carbonate to the corresponding sulfide in the smelt. The smelt drains out of the gasifier into a quench tank operating at the same pressure as the gasifier where it is dissolved in water to form a second aqueous solution containing alkali metal sulfide, unconverted alkali metal carbonate, and minor amount of other salts. The second aqueous solution is depressurized; treated to convert dissolved alkali metal sulfide into hydrogen sulfide gas, which is released from solution, and alkali metal carbonate, which remains in the solution, and is then recycled as regenerated solution for use as the principal ingredient of the first aqueous solution.

[0019] The hydrogen and carbon monoxide-containing gases generated in the high temperature gasification zone leaves the gasifier as impure off-gas. Its carbon monoxide concentration may vary over a wide range because of the effects of both the carbon content of the fuel and the oxygen content of the oxygen-containing gas. It is typically in the range of about 15 to 70% CO by volume, dry basis, and is preferably in the range of 20 to 60% CO. The hydrogen concentration, typically, ranges from 5% by volume—dry basis—when oxidant agent is air and it is as high as 38% when gasification is performed in combined oxygen and steam environment. The main impurities in the off-gas are water vapor, hydrogen sulfide, and salt fume particles. For some applications it may be used without further treatment, but preferably it is cooled and purified to produce the final product gas. In addition to hydrogen, carbon monoxide and the above mentioned impurities, the product gas typically contains nitrogen, hydrogen, carbon dioxide, and some methane, and has a higher heating value (HHV) of at least 100 Btu/scf (3720 kJ/m^3), preferably in the range of about 115 to 260 Btu/Std cu ft (4280 to 9670 kJ/m^3).

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 is a block diagram of one embodiment of the techniques of the present application.

[0021] FIG. 2 is a flow diagram of one embodiment of the techniques of the present application.

[0022] The same reference numbers are used in the two figures to denote similar elements.

DETAILED DESCRIPTION OF THE DRAWINGS

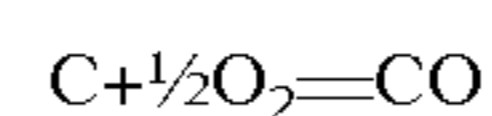
[0023] Referring to FIG. 1, particles of sulfur-containing carbonaceous fuel, **1**, are mixed with an aqueous solution containing alkali metal carbonate, **5**, in a slurry preparation step. The resulting slurry, or suspension, **6**, passes through a

pressurization step, which may be a simple liquid pump, and the pressurized slurry, **8**, is, fed into a pressurized gasification step. Pressurized oxygen-containing gas is also fed into the gasification step where it reacts with the slurry to produce a combustible product gas and a molten smelt, **15**. The smelt contains sulfur absorbed from the fuel, in the form of alkali metal sulfide. The smelt flows to a smelt dissolution step where it is dissolved in water to form an aqueous solution at essentially the same pressure as the gasification step. The aqueous solution, **20**, flows through a solution regeneration and depressurization step which uses the reaction of CO_2 , and H_2O with alkali metal sulfide in solution to produce dissolved alkali metal carbonate and gaseous H_2S . The required CO_2 may be absorbed from the product gas stream or provided from an outside source. The H_2S is recovered as a byproduct acid gas stream which typically also contains CO_2 and water vapor. The regenerated and depressurized aqueous solution containing alkali metal carbonate, **36**, is recycled to the slurry preparation step.

[0024] Operation of the gasifier at elevated pressure is required because it greatly reduces the volume of gas handled and, therefore, the size of the gasifier vessel, gas lines, and downstream gas handling equipment. Elevated pressure also increases the efficiency of gas absorption operations and permits the product gas to be used directly in gas turbines or other devices which require a pressurized feed gas. The present technique of the application avoids the problem of feeding solid particles into a high pressure system by converting the fuel feed into a liquid slurry form so that it can be pressurized and forced into the elevated pressure gasifier using simple liquid pumps.

[0025] The sulfur-containing carbonaceous fuel may be any such material that can be dispersed in a liquid aqueous medium to form a concentrated pump-able suspension or slurry, including coal, petroleum coke, and petroleum residuals. The process is most advantageous when used with fuels that are solid at the temperature of the feed slurry because liquid fuels do not need to be mixed with an aqueous medium to become pump-able; however, a dispersion of liquid or semisolid particles of sulfur-containing carbonaceous fuel in the aqueous solution represents an acceptable feed slurry for the practice of the present technique of the application.

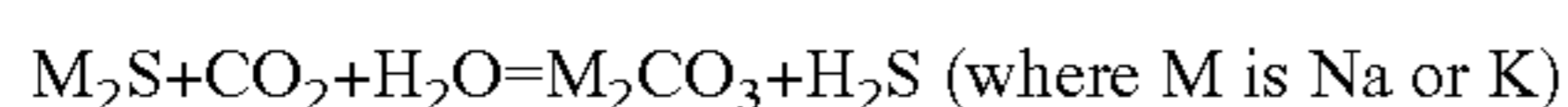
[0026] Other processes for gasifying sulfur-containing carbonaceous fuels in the presence of molten salts have the requirement to provide solid alkali metal carbonate feed as make-up for a molten salt pool. The present technique of the application avoids this requirement by recycling alkali metal carbonate as an aqueous solution. The recycled solution need not be highly purified because the presence of unconverted sulfide or bi-sulfide in the feed will not adversely affect gasifier operation. With solid salt recycle alkali metal sulfide and bi-sulfide cannot be included in the recycle stream in significant quantities because these salts are very difficult to crystallize out of solution and the solid forms tend to absorb water from the air causing sticking and plugging problems in the solids feed system. In one mode of operation of the present technique of the application, the carbonaceous fuel is a low ash material such as petroleum coke, the oxidant is air, and the alkali metal is sodium or potassium. The fuel, in the form of small particles, is mixed with a first aqueous solution to form concentrated slurry which is pumped into the gasifier. The key reaction in the gasification of carbonaceous fuel with oxygen is:



[0027] Other known reactions that result in the formation of CO_2 , H_2 , H_2O , H_2S , CH_4 , and other products may also occur.

[0028] The overall gasification reactions are exothermic, generating a temperature in the gasification zone in the range of 900-1400° C. which is sufficiently high to melt the alkali metal salts. The molten salt acts as a catalyst for the gasification reactions and also serves to absorb sulfur from the reacting fuel, by forming alkali metal sulfide. The molten salt, or smelt, is drained from the gasifier and dissolved in water at the gasifier operating pressure to form a second aqueous solution. The second aqueous solution is depressurized and regenerated for use as the principal ingredient of the first solution by converting dissolved alkali metal sulfide into hydrogen sulfide gas which is released from solution and alkali metal carbonate which remains in the recycled solution.

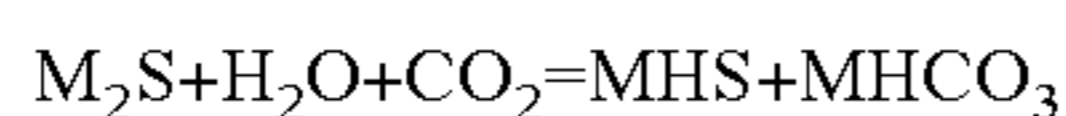
[0029] Solution regeneration may be accomplished, by various known techniques; however, the overall chemical reaction is generally represented by the equation:



[0030] The required CO_2 may be absorbed from a dilute gas, injected as pure CO_2 , or generated in situ by decomposing MHCO_3 .

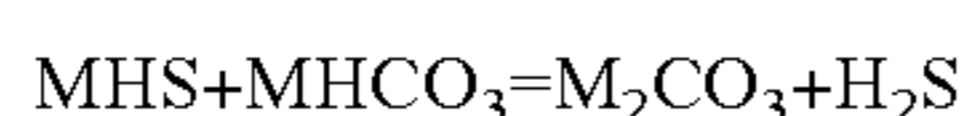
[0031] The regeneration system typically includes using the second solution to absorb carbon dioxide from the gasifier off-gas at approximately the gasifier pressure; depressurizing and stripping hydrogen sulfide gas from the solution; separating at least a portion of the ash components such as silicon, aluminum, and vanadium compounds, if present, from the solution; and recycling the resulting solution as the principle ingredient of the first aqueous solution. Valuable ash components, such as vanadium, may be recovered as a byproduct as part of the ash separation step.

[0032] The solution leaving the quench tank is very alkaline with a pH typically in the 12-14 range. Its principal ingredients are alkali metal sulfide and carbonate; however it typically contains small amounts of other compounds such as alkali metal hydroxide, sulfate, and thiosulfate. When it is used to absorb acid gases from the gasifier off-gas or other source of CO_2 , the alkalinity is neutralized to a considerable extent by reactions such as:



[0033] As a result of such reactions, the carbonated solution from the absorber contains alkali metal bicarbonate and bi-sulfide and is only mildly alkaline, with a pH in the range of about 7.5 to 10.5. The absorption reactions are carried to the point where the solution contains essentially no hydroxide or sulfide, but it may contain a significant fraction of un-reacted carbonate.

[0034] Typically, the carbonated solution is fed into a stripper where the combined effects of heat, reduced pressure, and stripping vapor cause the following reactions to occur:

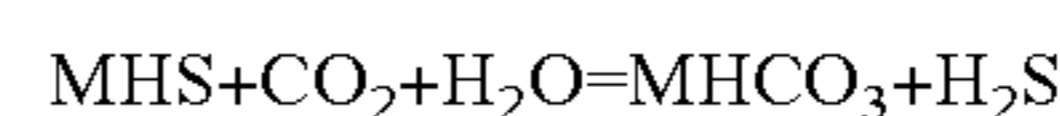


[0035] The regenerated solution from the stripper has an alkalinity intermediate between the quench solution and the carbonated solution with a pH typically in the range of about 9 to 13. It contains primarily alkali metal carbonate with small

amounts of other salts such as alkali metal bi-sulfide, sulfate, and thiosulfate. The regenerated solution is recycled to the feed preparation step as the principal ingredient of the first aqueous solution. Additional alkali metal carbonate or water may be added prior to recycle to adjust the concentration and make up for salt losses that may occur in the system.

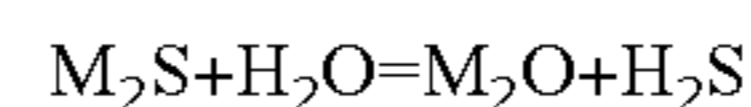
[0036] The separation of ash components from the solution may be carried out at any point in the solution flow circuit and may be accomplished by settling, filtration, centrifugation, or other means. When essentially ash free fuel is used, no separate ash removal step is required.

[0037] In one alternative regeneration step, the solution from the quench tank is carbonated by the absorption of carbon dioxide from a source other than the gasifier off-gas. The resulting carbonated solution is stripped to remove H_2S then recycled to the feed preparation step. In another alternative regeneration system the quench solution, which may first be pre-carbonated by contact with dilute CO_2 gas, is regenerated by contact with pure CO_2 gas. In this technique, H_2S is displaced from the dissolved salts by CO_2 because of the greater effective acidity of CO_2 relative to H_2S . The overall chemical reaction is:



[0038] The product acid gas is a mixture of released H_2S and un-reacted CO_2 . This technique may result in the precipitation of alkali metal bicarbonate crystals, particularly when sodium salts are used, but these can be re-dissolved in a separate step where the mixture is heated to decompose the bicarbonate and produce the pure CO_2 required by the previous step while forming the more soluble carbonate salt for recycle to the feed preparation step.

[0039] The molten salt catalyzes gasification reactions in the gasifier and absorbs sulfur from the reacting fuel; however a portion of the sulfur normally leaves the gasifier as H_2S in the off-gas due to reactions such as:



[0040] The H_2S may be removed, from the off-gas by absorption in the quench solution, absorption in a recycle stream of regenerated solution, or use of an auxiliary gas purification system.

[0041] Referring to FIG. 2, a sulfur-containing carbonaceous fuel, **1**, such as petroleum coke, in the form of a fine powder is fed into a hopper, **2**, from which it is fed into slurry tank, **3**, which is equipped with a mixing device, **4**. A first aqueous solution of alkali metal salts, **5**, is also fed into the slurry tank to form a suspension, or slurry, of fuel particles in alkali metal salt solution. The slurry flows out of the slurry tank through line **6** to pressurizing pump, **7**, which, forces it through line **8** to gasifier **9**. The gasifier shown is of a type that has a drying zone, **10**, and a gasification zone, **11**. Inside the gasifier the slurry is dried in the drying zone by contact with hot gas originating in the gasification zone. The dried slurry, a mixture of fuel and alkali metal salt solids, enters the gasification zone where it is gasified by reaction with oxygen. Alternative gasifier designs that bring about the reaction of the feed slurry with an oxygen containing gas to produce a molten salt smelt and a CO-containing product gas may be employed.

[0042] Air, **12**, is compressed by compressor, **13**, to a pressure slightly higher than the gasifier pressure, and flows into the gasifier through high pressure air line, **14**. The air enters the gasification zone of the gasifier where the oxygen reacts, with the carbonaceous fuel, raising the temperature in the

gasification zone to about 900 to 1400° C. The amount of air added is less than about 60% of the amount required for complete combustion of the carbonaceous fuel, and preferably in the range of 35 to 50%. An excessive amount of air will raise the gasification zone temperature above the desired range and also reduce the heating value of the product gas. Too little air will cause excessive build-up of un-reacted fuel in the gasifier.

[0043] At the high temperature in the gasification zone, the alkali metal salt solids that enter with the dried slurry are melted and the resulting molten salt, or smelt, wets the reacting fuel particles, catalyzing the gasification reactions. Sulfur in the fuel reacts with the molten salt to form alkali metal sulfide. A portion of the fuel sulfur may also form alkali metal sulfate and thiosulfate in the smelt and hydrogen sulfide in the gas phase.

[0044] The smelt, consisting primarily of alkali metal sulfide and un-reacted alkali metal carbonate flows out of the gasifier through line 15 into quench tank, 16, which operates at the same elevated pressure as the gasifier. Water is added to the quench tank through line 17. All or a portion of the water may be produced by condensing water vapor out of the gasifier and stripper off-gas streams as shown in the figure. The amount of water added to the quench tank is controlled to dissolve the smelt and produce a quench solution, or second aqueous solution, containing about 5% to 40% total dissolved solids.

[0045] The quench solution is withdrawn from the quench tank through line 18 to pump 19 which forces it to flow through line 20 to the gas purification system, 21. For simplicity, the gas purification system is shown as a single vessel with solution feed near the top and gas entry near the bottom. In practice the system may involve multiple contactors or sections, split stream liquid or gas feed, solution recycle loops, and other features known to improve gas purification and absorption operations. The purpose of this system is to carbonate the solution by the absorption of carbon dioxide and also to reduce the hydrogen sulfide content of the gas to a level that is acceptable in the final product gas.

[0046] Gasifier off-gas leaves the drying zone of the gasifier via line 22 and passes through gas cooler-condenser system 23, which serves to reduce the temperature and water vapor content of the gasifier off-gas. The gas then flows through line 24 to the gas purification system, 21 where carbon dioxide and hydrogen sulfide are absorbed. It leaves this system as the final product gas via line 25.

[0047] The carbonated solution flows out of the gas purification system through line 26 and pressure reduction valve, 27, into the acid gas stripper 28 which may include a heating coil as shown in the figure. The stripper operates at a significantly lower pressure than the gas purification system and gasifier. The stripper operates at a pressure between about 0.1 and 2.0 atmospheres, and preferably in the range of 0.2 to 1.0 atmospheres. The acid gases, hydrogen sulfide and carbon dioxide, and water vapor produced in the stripper flow through line 29 into condenser 30 where the gas stream is cooled, to condense water. The resulting liquid water may be returned to the stripper or used in the quench tank as shown in the figure. The acid gas stream leaves the condenser via line 31 and is typically sent to a sulfur recovery plant (not shown on the drawing) for recovery of sulfur values. In this embodiment of the technique of the application the gas purification system and acid gas stripper combined represent the solution regeneration and depressurization step of FIG. 1.

[0048] Regenerated solution flows out of the acid gas stripper through line 32 to pump 33 which forces it through separator 34 and line 36 back to the slurry tank where it serves as the aqueous solution of alkali metal salts, 5, referred to previously. Ash components, removed from the solution by separator 34, are discharged from the system via line 35 for disposal or recovery of byproducts. A small amount of un-gasified carbonaceous material may be suspended in the quench solution. This material may be removed with the ash components but preferably is recycled to the slurry tank and ultimately to the gasifier.

[0049] All or a portion of the product gas may flow out of the gasification zone with smelt. This gas is separated from the molten smelt and flows through vent line 37 to the product gas line.

EXAMPLE

[0050] Sound prediction of the techniques of the present application is based, on small scale test data for individual operations and computer model calculations. The feed material is petroleum coke of the composition shown in Table 1. Performance data are based on 100 grams of dry coke feed.

[0051] The coke is mixed with an equal weight of aqueous solution containing approximately 18% sodium carbonate and 2% sodium bi-sulfide. The resulting slurry is fed into a gasifier operating at a pressure of 20 atmospheres (294 psia) and a temperature of about 1000° C. in the gasification zone. An approximate material balance around the gasifier is given in Table 2.

[0052] Molten smelt flows from the gasifier into a quench tank operating at the same pressure as the gasifier and is dissolved in approximately 80 grams of water to yield about 98.7 grams of quench solution. The quench solution is regenerated by carbonating it in an absorber used to scrub the gasifier off-gas then stripping H₂S and CO₂ from it in a sub-atmospheric pressure stripper. The stripper produces an acid gas stream containing approximately 50% H₂S and 50% CO₂ by volume, dry basis. Ash is removed from the regenerated solution by filtration and the filter cake is washed with water to remove soluble salts. The filtered regenerated solution is recycled, to the slurry preparation step.

[0053] A material balance around the quench tank and solution regeneration system is given in Table 3. The material balance envelope for this table includes all steps relating to solution processing including smelt dissolution; product gas cooling, water condensation, and scrubbing; solution stripping; acid gas cooling and water condensation, and ash separation.

TABLE 1

Typical Petroleum Coke Composition	
Components	Concentration (wt. %, dry basis)
Carbon	88.9
Hydrogen	3.9
Nitrogen	2.2
Sulfur	2.1
Oxygen	1.3
Ash	1.6
Total	100

TABLE 2

Gasifier Material Balance			
Input		Output	
Feed Slurry		<u>Off-Gas</u>	
<u>Solid Phase</u>		CO	185.1 grams
Carbon	88.9 grams	CO ₂	35.8
Hydrogen	3.9	H ₂	4.8
Nitrogen	2.2	N ₂	403.4
Sulfur	2.1	CH ₄	1.2
Oxygen	1.3	H ₂ O	71.9
Ash	1.6	H ₂ S	0.1
<u>Aqueous Phase</u>		<u>Smelt</u>	
Na ₂ CO ₃	18.0	Na ₂ S	7.7
NaHS	2.0	Na ₂ CO ₃	9.4
H ₂ O	80.0	Ash	1.6
<u>Compressed Air</u>			
Oxygen	119.8		
Nitrogen	401.8		
Total Input	721.0 grams	Total Output	721.0 grams

TABLE 3

Quench Tank and Solution Regeneration System Material Balance				
Input		Output		
	grams	grams	Vol %	
Gasifier		<u>Purified Gas</u>		
<u>Off-Gas</u>				
CO	185.1	CO	185.1	27.1
CO ₂	35.8	CO ₂	29.3	2.7
H ₂	4.8	H ₂	4.8	9.8
N ₂	403.4	N ₂	403.4	59.1
CH ₄	1.2	CH ₄	1.2	0.3
H ₂ O	71.9	H ₂ O	4.3	1.0
H ₂ S	0.1	H ₂ S	negligible	0.0
<u>Smelt</u>		<u>Acid Gas</u>		
Na ₂ S	7.7	H ₂ S	2.2	50
Na ₂ CO ₃	9.4	CO ₂	2.9	50
Ash	1.6	<u>Regenerated Solution</u>		
<u>Make-up Water</u>		Na ₂ CO ₃	18.0	
H ₂ O	15.4	NaHS	2.0	
		H ₂ O	80.0	
		<u>Ash Cake</u>		
		Ash	1.6	
		H ₂ O	1.6	
Total Input	736.4 grams	Total Output	736.4 grams	

[0054] Table 3 also presents the approximate composition of the product and byproduct gas streams. The product gas is calculated to have a higher heating value (HHV) of about 124 Btu/scf (4600 kJ/m³), dry basis, which is suitable for fuel to a gas turbine. The material balances are approximate and include only the principal components in each stream. For example, a small amount of alkali metal salt may be present in the ash filter cake, and minor amounts of oxidized sulfur compounds such as sulfate and thiosulfate may be present in

the smelt and aqueous solutions. Also, traces of higher hydrocarbons and other sulfur compounds may be present in the product gas stream.

[0055] Although certain embodiments of the techniques of the present application have been described, the spirit and scope of the application is by no means restricted to what is described above. Persons having ordinary skill in the art will be able to make variations, permutations, and combinations, in view of the above description, all of which are within the scope of the present application.

Process Advantages:

[0056] Significant technical advantages are offered by this gasification process in both production cases of either low- or medium-Btu gas:

[0057] 1. A wide variety of carbonaceous materials can be and indeed have been handled, including anthracite, bituminous and lignite coals; several types of petroleum coke; organic waste; photographic film; wood chips, and heavy residual hydrocarbons. Fuel particles are pneumatically injected into the melt and are immediately wetted and dispersed so there is no opportunity for caking or swelling to affect operation.

[0058] 2. Feed need not be closely sized. Pulverization and fines removal are unnecessary. The only requirement for solid feed is that it be pneumatically conveyable, which generally requires particles of less than 4 mesh.

[0059] 3. The product gas is essentially free of sulfur. Approximately 90 to 99 percent of feed sulfur is recovered in the regeneration system. This level of removal is generally adequate to meet environmental requirements for combustion use of product gas. However, if product gas is to be used in synthesis of chemicals, further sulfur removal may be required to prevent poisoning catalyst.

[0060] 4. Negligible amounts of tar, heavy hydrocarbons and NO_x are produced. The catalytic effect of the melt apparently causes almost complete destruction of heavy hydrocarbons and organic nitrogen compounds at the gasifier operating temperature.

[0061] 5. Oxygen requirement is relatively low. For a typical petroleum coke, about 0.8 pounds of oxygen per pound of coke is required.

[0062] 6. The gasifier turndown capability is excellent because a gas-sparged molten pool is relatively insensitive to gas velocity.

[0063] 7. There is no explosion hazard when the fuel feed stops. Any oxygen that flows into the molten salt pool is absorbed by an inventory of reduced compounds (sodium sulfide, residual carbon).

[0064] 8. Thermal efficiency is high. Although actual efficiency is a function of fuel composition and other design parameters, a relatively high efficiency is possible because no char is produced and carbon utilization is generally over 98%; heat losses are low because the reaction zone is not actively cooled, and product gas is amenable to efficient heat recovery because of its moderate temperature and relative freedom from tar, ash and other objectionable impurities.

[0065] 9. Valuable byproducts such as sulfur and vanadium can be recovered relatively easily. All ash constituents are retained in the melt which is processed to return sodium carbonate to the gasifier. A vanadium-recovery step may be added to the melt-regeneration system.

What is claimed is:

1. A process for converting a sulfur-containing carbonaceous fuel into a combustible product gas having a higher heating value of at least 100 Btu/scf, dry basis, by reaction with oxygen in the presence of a molten alkali metal salt comprising steps of:

- (a) Mixing particles of said fuel with a first solution containing about 5% to 35% by weight alkali metal carbonate, at approximately atmospheric pressure to form slurry containing about 25% to 75% by weight un-dissolved fuel particles;
- (b) Pressurizing and feeding said slurry into a gasifier operating at an elevated pressure in the range of 4 to 50 atmospheres, said gasifier containing a drying zone and a gasification zone;
- (c) Feeding pressurized oxygen-containing gas into said gasifier;
- (d) Drying said slurry in said drying zone and gasifying the resulting dried mixture of fuel and salts by reaction with said oxygen at a temperature in the range of about 900 to 1400° C. in said gasification zone to produce a gasifier off-gas, containing carbon monoxide and water vapor, and a hot liquid smelt containing molten alkali metal sulfide;
- (e) Draining said smelt into a quench tank operating at essentially the same pressure as the gasifier, and dissolving it in an aqueous medium to form a second solution containing 5% to 35% by weight, alkali metal salts including alkali metal sulfide;
- (f) Recovering said gasifier off-gas as said combustible product gas;
- (g) Reducing the pressure on said second solution and regenerating it by converting said alkali metal sulfide to alkali metal carbonate in said solution and hydrogen sulfide gas which is released from solution; and
- (h) Utilizing the depressurized and regenerated second solution as the principal ingredient of said first solution.

2. The process of claim 1 wherein said alkali metal is sodium.

3. The process of claim 1 wherein said alkali metal is potassium.

4. The process of claim 1 wherein said oxygen-containing gas is air.

5. The process of claim 1 wherein said oxygen-containing gas is a mixture of oxygen and steam.

6. The process of claim 1 wherein said sulfur-containing carbonaceous fuel is petroleum coke.

7. The process of claim 1 wherein the amount of oxygen fed into the gasification zone is less than about 60% of the amount needed for complete combustion of the fuel.

8. The process of claim 1 wherein step (g) includes the removal of ash components from said second solution.

9. The process of claim 1 wherein step (g) includes contacting said second solution with a carbon dioxide-containing gas to form alkali metal bi-sulfide and bicarbonate in solution, depressurizing the solution, and stripping hydrogen sulfide gas from it to produce a stream of hydrogen sulfide-rich gas and a stream of depressurized and regenerated second solution.

10. The process of claim 1 wherein steps (f) and (g) include treating said gasifier off-gas by contacting it with said second solution at an elevated pressure, thereby purifying said combustible product gas and absorbing carbon dioxide into said second solution; depressurizing the carbonated second solution and stripping hydrogen sulfide gas from it at a reduced pressure in the range of 0.1 to 2.0 atmospheres to produce a stream of hydrogen sulfide-rich gas and a stream of depressurized and regenerated second solution.

11. The process of claim 1 wherein step (g) includes contacting said second solution with a carbon dioxide-containing gas and absorbing sufficient carbon dioxide to convert alkali metal sulfide and bi-sulfide into alkali metal bicarbonate thereby displacing hydrogen sulfide gas from solution; and heating the resulting bicarbonate solution to produce a stream of carbon dioxide gas and a stream of depressurized and regenerated second solution.

12. The process of claim 1 wherein step (b) includes feeding said slurry into the drying zone of said gasifier in the form of a spray.

13. The process of claim 1 wherein step (c) includes feeding pressurized oxygen-containing gas into the gasification zone of said gasifier.

14. The process of claim 1 wherein step (d) includes discharging said gasifier off-gas from the drying zone of said gasifier.

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