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METHOD FOR TREATING COKE OVEN GAS

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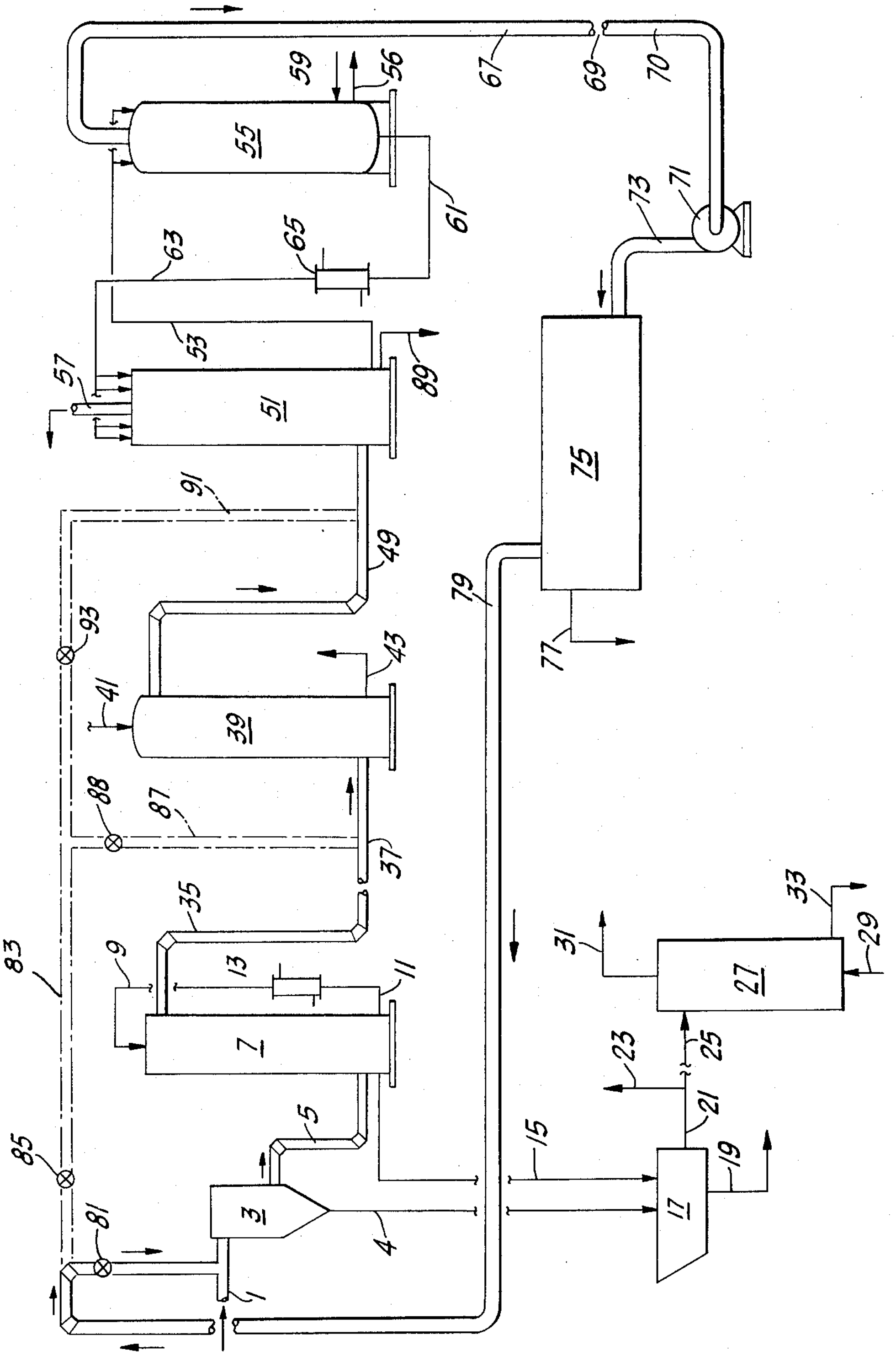

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METHOD FOR TREATING COKE OVEN GAS

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ABSTRACT OF THE DISCLOSURE

The elimination of atmospheric pollution resulting from sulfur-containing tail gases produced in a hydrogen sulfide conversion process associated with a coke oven gas by-product recovery system is described. The sulfur-containing components of the tail gas are removed by first combining the tail gas with crude coke oven gas in the by-product recovery system. Sulfur dioxide and the other gaseous sulfur-containing components of the tail gas are removed from the combined gases by the various gas-treatment phases of the by-product recovery system or pass through the system and are subsequently burned or vented to the atmosphere at less objectionable concentrations.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates generally to methods for eliminating the discharge of objectionable amounts of sulfur dioxide to the atmosphere. More particularly the invention relates to methods for eliminating the discharge of sulfur dioxide to the atmosphere from processes for producing sulfur from the hydrogen sulfide recovered from crude coke oven gas.

Prior art

Crude coke oven gas produced during the carbonization of coal contains components such as hydrogen, ammonia, hydrogen sulfide, naphthalene and other hydrocarbons that are normally removed from the coke oven gas in a by-product recovery, or gas treatment, system. The purified coke oven gas is thereafter sent to a gas distribution system and is used as a fuel for the underfiring of coke ovens or as a fuel for various steel plant furnaces or for other industrial purposes.

The chemicals recovered from the crude coke oven gas are disposed of by a variety of methods. Ammonia, for example, may be disposed of simply by burning. Hydroden sulfide, on the other hand, is usually converted to valuable by-products including sulfuric acid and elemental sulfur.

The processes for converting the hydrogen sulfide to sulfur usually produce objectionable amounts of sulfur dioxide. One such process, conventionally termed the Claus Process, produces a tail gas containing large amounts of unconverted hydrogen sulfide, sulfur dioxide, and other sulfur-containing compounds that are generally incinerated and discharged through a stack of sufficient height to provide extremely low sulfur dioxide concentrations at grade, or ground, level so as to comply with pollution codes. The incinerator and stack required for the incineration of the tail gas are major investment items. Efforts to reduce the incinerator and stack requirements and thus the initial process investment have heretoform been directed at increasing the efficiency of the Claus Process.

SUMMARY OF THE INVENTION

The present invention teaches an improvement in a process for converting hydrogen sulfide to sulfur that eliminates or at least minimizes the requirements of tail gas incinerator and exhaust stacks. The sulfur-containing

tail gas is combined with crude coke oven gas in the gas by-product recovery system. The sulfur dioxide and other sulfur-containing components react with the components of the coke oven gas or with the components of the solutions employed in the various phases of the by-product recovery system and are removed from the combined gases or pass through the by-product recovery system unchanged and are eventually burned or vented to the atmospheres at less objectionable concentrations.

The operation of the invention, however, can be better understood by referring to the drawing and the description of the preferred embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic of a crude coke oven by-product recovery, or gas treatment, system which includes inter alia a cooling phase, a benzol washing phase and a hydrogen sulfide absorption phase and of a process for converting hydrogen sulfide to sulfur. The drawing illustrates the preferred embodiments of the invention.

For clarity purposes pumps, heat exchangers, valves and other ancillary equipment not essential to a understanding of the invention have been eliminated.

DETAILED DESCRIPTION

Referring now to the drawing, there is illustrated a process for the removal of hydrogen sulfide from crude coke oven gas and for the conversion of the recovered hydrogen sulfide to elemental sulfur.

Crude coke oven gas produced during the carbonization of coal and comprising ammonia, hydrogen sulfide, hydrogen cyanide, methane, hydrogen, naphthalene and other hydrocarbons flows through an initial cooling zone **1**, which is generally a suction main, where it is cooled with a spray of flushing liquor which, in addition to cooling the gas, absorbs a portion of the ammonia. The gas then flows into a separator **3** where the flushing liquor and condensed tars are removed from the gas and flow through line **4** to flushing liquor decanter **17** where the tars settle out and are removed through line **19.** From the separator **3** the gas passes through line **5** into a primary cooler **7** where it is further cooled and ammonia removed therefrom by means of a countercurrent flow of a cooling liquor that enters the cooler **7** through line **9.** The cooling liquor after cooling the crude gas ascending the cooler **7** is removed from the bottom of cooler **7** through line **11,** cooled in heat exchanger **13** and returned to the top of the cooler **7** through line **9.** Excess cooling liquor resulting from the condensation of moisture contained in the coke oven gas is removed from the cooler **7** through line **15** and passes to flushing liquor decanter **17.** A portion of the flushing liquor from decanter **17** is returned through lines **21** and **23** to the initial cooling zone to contact another portion of crude coke oven gas. Excess flushing liquor, resulting from the condensation of the moisture contained in the crude coke oven gas, is withdrawn from decanter **17** through line **21** and passes to a crude liquor storage tank (not shown) through line **25** and is eventually passed to an ammonia still **27** where it is treated with either lime or caustic soda to free the combined ammonia. The freed ammonia is thereafter stripped from the liquor by means of stripping steam that enters the still **27** through line **29.** Stripped ammonia leaves still **27** through line **31** and the stripped liquor leaves the still through line **33.**

From the primary cooler **7** the crude coke oven gas flows through line **35** and is thereafter treated by processes (not shown) to remove tar, naphthalene, and the remaining portions of ammonia from the gas. Eventually the gas passes through line **37** into a benzol washing zone **39** where the gas is contacted with a spray of washing solution, generally petroleum wash oil, that enters the benzol washing zone **39** through line **41** and that removes the so-called light oil from the gas. The petroleum wash oil containing the light oil, conventionally termed the benzolized solution, is removed from the bottom of the benzol washing zone **39** through line **43** and is thereafter steam distilled (to remove the light oil) and subsequently cooled before being returned to washing zone **39** for contacting another quantity of the coke oven gas.

Following the removal of the light oil from the crude coke oven gas the gas passes through main **49** into a hydrogen sulfide absorption zone **51**. Although the hydrogen sulfide may be removed from the coke oven gas by any known means, the "Vacuum Carbonate Process" is used in the preferred embodiments of the invention. In the "Vacuum Carbonate Process" an alkaline metal carbonate solution, such as sodium carbonate, is employed to absorb hydrogen sulfide and other acid gases from the coke oven gas thereby forming a fouled solution. The fouled solution is thereafter heated under a vacuum to drive out the acid gases and to simultaneously regenerate the absorption solution.

In absorption zone **51** the coke oven gas is contacted with the alkaline metal carbonate solution that enters the absorption zone **51** through line **63**. The alkaline metal carbonate solution absorbs the hydrogen sulfide (and other acid gases) from the gas and forms a fouled solution. The now-purified coke oven gas containing only residual amounts of impurities leaves absorption zone **51** through main **57** and is sent to a gas distribution area (not shown) and is thereafter used as a fuel for the underfiring of coke ovens or as a fuel in various steel plant furnaces or for other industrial uses.

The fouled solution passes to an actification zone **55** through line **53** where it is actified by stripping the hydrogen sulfide under vacuum by stripping steam that is generated from a portion of the actified solution that is recirculated between actification zone **55** and heat exchanging means (not shown) through lines **56** and **59**.

The portion of actified solution not recirculated is returned to the top of absorption zone **51** through lines **61** and **63**, after first being cooled to absorption temperature in heat exchanger **65**, to contact another portion of the coke oven gas.

As mentioned above, the removal of hydrogen sulfide by absorption with dilute alkaline metal carbonate solution, while preferred, is not essential to the invention and is used by way of illustration only. It will be understood by those skilled in the art that other means of hydrogen sulfide removal may be used in the scope of this invention. Additionally, the removal of the light oil from the crude coke oven gas is not essential to the teachings of the invention and although used in accordance with one of the preferred embodiments of the invention, may be omitted depending on the chemical makeup of the crude coke oven gas and the purification requirements for a particular coke oven installation.

The hydrogen sulfide stripped from the fouled solution in actification zone **55** and containing stripping vapor leaves actification zone **55** through line **67** and is treated by some convenient means **69** (not shown) to remove the bulk of the stripping vapor.

The hydrogen sulfide gas then passes through line **70** to compressor **71** and then through line **73** to a hydrogen sulfide conversion process **75** which is, according to the preferred embodiments of the invention, the Claus Process.

The Claus Process converts hydrogen sulfide to an elemental form of sulfur known as brimstone. In the process, hydrogen sulfide is burned in less than stoichiometric amounts of oxygen to convert a portion of the hydrogen sulfide to sulfur dioxide. The remaining portion of the hydrogen sulfide and the just-produced sulfur dioxide are then catalytically reacted to form sulfur and water and a tail gas containing unconverted hydrogen sulfide, sulfur dioxide and other sulfur-containing compounds. The composition of a tail gas produced in a typical Claus Kiln Process is set out in Table I.

TABLE I

Component:	Tail gas (lbs. per hr.)
Hydrogen	5.72
Water vapor	1,089.00
Carbon monoxide	120.68
Nitrogen	2,962.40
Oxygen	None
Carbon dioxide	344.96
Hydrogen sulfide	19.89
Sulfur dioxide	18.69
Carbonyl sulfide	13.14
Carbon disulfide	2.78
Sulfur vapors	3.50

The Claus Process is described in the preferred embodiments of the invention since the problem of disposing of the sulfur-containing tail gas is very great with the Claus Process. The process of the invention, however, is applicable to other hydrogen sulfide conversion processes that produce sulfur-containing tail gases.

Heretofore, in order to meet pollution standards, the tail gas from a Claus Process has been incinerated to convert the hydrogen sulfide and other sulfur-containing compounds to sulfur dioxide. The incinerated gas is vented to the atmosphere through large stacks so that the sulfur dioxide concentration at grade is within acceptable limits. To minimize incinerator and stack requirements efforts have been aimed primarily at increasing the efficiency of the Claus Process itself. Surprisingly, it has been found that incinerator and stack requirements can be minimized if not eliminated and the discharge of sulfur dioxide minimized or eliminated by combining the tail gas from the Claus Process with the crude coke oven gas in the by-product recovery system in the manner described below. The unconverted hydrogen sulfide, sulfur dioxide, and other sulfur-containing compounds are neutralized by reaction with the components of the coke oven gas or with the constituents of the various gas-treatment solutions employed in the by-product recovery system. A minor portion of the gases may pass through the gas purification system unchanged and may be burned or vented to the atmosphere at less than objectionable concentrations.

Referring again to the drawing, hydrogen sulfide is converted in conversion process **75**, which, as stated previously, is preferably a Claus Process, to sulfur (and water) and an unwanted sulfur-containing tail gas. The sulfur is withdrawn from the convention process **75** through line **77** and sent to a sulfur recovery area (not shown). The tail gas flows through line **79** and valve **81** to, in the particularly preferred embodiment, the initial cooling zone **1** before the separator **3** where the tail gas is combined with the crude coke oven gas. The sulfur dioxide in the tail gas reacts with ammonia in the crude coke oven gas in the presence of the flushing liquor that is used to cool the gas to form aqueous ammonium sulfite that builds up in the flushing liquor. The ammonium sulfite eventually passes to the decanter **17** with the excess flushing liquor and then to ammonia still **27**. In ammonia still **27** the liquor is treated with, for example, lime or caustic soda to free the ammonia contained in the liquor in the form of salts, which salts form during the initial cooling of the crude coke oven gas with the flushing liquor. The freed ammonia is then stripped from the liquor. If lime is used to treat the liquor in the ammonia still the ammonium sulfite reacts with the lime to form calcium sulfite, an insoluble precipitate, which is discharged from the still **27** with the still bottoms through line **33**. If caustic soda is used to treat the liquor soluble sodium sulfite is produced which is also removed from the still with the still waste.

The sulfur vapors in the tail gas condense in the cooling zone **1** and are removed from the combined gases along the flushing liquor and condensed tars in separator **3** and flow to flushing liquor decanter **17** and are removed with the condensed tars through line **19**.

Hydrogen sulfied in the tail gas flows with the crude coke oven gas and is eventually removed from the gas in the hydrogen sulfide absorption zone.

The carbonyl sulfide in the tail gas is unstable and decomposes readily to carbon monoxide and sulfur. The sulfur is removed in the separator **3** as described above.

Carbon disulfide in the tail gas is neutral as to the components of the crude coke oven gas and gas-treatment solutions and flows with the crude coke oven gas through the primary cooler and other purification units to the benzol washing zone **39** where it dissolves in the petroleum wash oil. The carbon disulfide is eventually removed from the by-product recovery system during purification of the petroleum wash oil.

Water in the tail gas is condensed in the primary cooler and is eventually removed from the system as excess liquor.

The remaining components of the tail gas pass through the by-product recovery system unchanged and flow with the treated gas to the gas distribution system described above.

In a second embodiment of the disclosure, the tail gas flows through lines **79** and **83** and **87** (shown in phantom lines) and valves **85** and **88** (valve **81** is closed) and is combined with coke oven gas in line **37** leading into benzol washing zone **39**. It is desirable to cool the tail gas before discharging it into the line **37** so as to maintain a high absorption rate of light oil. Sulfur vapors condensed in the tail gas, and sulfur resulting from decomposition of the carbonyl sulfide are dissolved in the petroleum wash oil and eventually removed from the by-product recovery system as described above. Hydrogen sulfide passes through the benzol washing zone **39** and is removed in the hydrogen sulfide absorption zone **51**. Sulfur dioxide also passes to the hydrogen sulfide absorption zone **51** and reacts with the alkaline metal carbonate solution to form an alkaline metal sulfite which is removed from the system through line **89** with the waste liquor. This waste liquor can be sent to the ammonia still **27** and the sulfite removed, after lime or caustic treatment, from the system with the still bottoms.

As in the particularly preferred embodiment the small quantity of components of the tail gas inert to the gas purification system pass through the system and are either burned or vented to the atmosphere.

In a third embodiment, the tail gas passes through lines **79** and **83** and **91** (shown in phantom) and valves **85** and **93** (valves **81** and **88** are closed) into line **49** where it combines with the coke oven gas. In this embodiment the tail gas is preferably cooled before discharging it into line **49** so as to maintain a high degree of hydrogen sulfide absorption in hydrogen sulfide absorption zone **51**. The hydrogen sulfide from the tail gas is removed from the mixture of gases in the absorption zone **51** as described above. The sulfur dioxide reacts with the alkaline metal carbonate solution in the absorption zone **51** to produce an alkaline metal sulfite which builds up in the solution until it is bled from the system through line **89** with objectionable waste liquor. As in the second embodiment the waste liquor may be passed to the ammonia still **27** and treated with caustic or lime.

As an alternative to combining the tail gas with the coke oven gas at only one of the three separate locations described above, it is possible to apportion the tail gas and combine it with the coke oven gas at any two or all of the three locations.

Finally, it is posisble to contact the tail gas with an aqueous solution of ammonia formed from ammonia recovered from the crude coke oven gas. The ammonia and sulfur dioxide will react to form an ammonium sulfite solution that can be passed to the ammonia still and treated with caustic soda or lime to form sodium sulfite or calcium sulfite which is thereafter removed from the still with the still bottoms as described above. The tail gas may thereafter be sent to the gas purification system as in the preferred embodiments or, if the amounts of other sulfur-containing compounds are low, may be vented to the atmosphere or may be combined with the purified coke oven gas and sent to a gas distribution system for use as a fuel.

Thus the invention enables the elimination of costly tail gas incinerators and stacks associated with sulfur recovery units and eliminates the discharge of large amounts of sulfur dioxide and other sulfur-containing compounds into the atmosphere by utilizing existing coke oven gas purification processes and techniques.

It will be understood that the invention is not limited by the embodiments described. On the contrary, it is intended to cover all alternatives, modifications and equivalents that may be included within the spirit and scope of the invention as defined by the appended claims.

In the claims:

1. In a process wherein crude coke oven gas formed during the carbonization of coal and containing ammonia and hydrogen sulfide is treated to remove the hydrogen sulfide and wherein the so-removed hydrogen sulfide is further treated in a process that produces a sulfur-containing tail gas including sulfur dioxide, the improvement comprising: (1) combining the sulfur-containing tail gas with the crude coke oven gas thereby neutralizing the sulfur dioxide with the contained ammonia, and (2) thereafter subjecting the combined gases to the gas treatment phases of said process including a benzol washing phase and hydrogen sulfide absorption phase.

2. In a process wherein crude coke oven gas that is produced during the carbonization of coal and that contains ammonia and hydrogen sulfide is contacted with an alkaline metal carbonate solution that removes the hydrogen sulfide from the gas to form a fouled hydrogen sulfide-containing solution, said fouled hydrogen sulfide-containing solution thereafter being contacted with steam under vacuum conditions to release the hydrogen sulfide from the solution, and wherein the so-released hydrogen sulfide is burned in less than stoichiometric amounts of oxygen to convert a portion of the hydrogen sulfide to sulfur dioxide, and the so-produced sulfur dioxide and unconverted hydrogen sulfide thereafter catalytically reacted to produce elemental sulfur and a tail gas containing sulfur dioxide and other sulfur-containing gases, the improvement comprising:

combining the tail gas with the crude coke oven gas whereby the sulfur dioxide in the tail gas is neutralized by the ammonia in the coke oven gas and the other sulfur-containing components of the tail gas are removed from the combined gas in the process by selected procedures including the steps of scrubbing with aqueous solutions and wash oil, treating with reactant chemicals, distilling and steam stripping.

3. In a process wherein crude coke oven gas formed during the carbonization of coal, said gas comprising ammonia, hydrogen sulfide, light oil and other hydrocarbons, is purified in a by-product recovery system that comprises:

(a) an initial cooling zone wherein the gas is cooled with a spray of flushing liquor,

(b) a benzol washing zone wherein the gas is scrubbed with a petroleum wash oil to remove the light oil from the gas,

(c) a hydrogen sulfide absorption zone wherein the gas is scrubbed with an alkaline metal carbonate solution to form a fouled hydrogen sulfide-containing solution, and

(d) an actification zone wherein the fouled hydrogen sulfide-containing solution is contacted with steam under reduced pressure to free the hydrogen sulfide from the solution, and wherein the freed hydrogen sulfide is:

(a) burned in less than stoichiometric amounts of oxygen to convert a portion of the hydrogen sulfide to sulfur dioxide, and

(b) the remaining portion of hydrogen sulfide is catalytically reacted with the so-produced sulfur dioxide to form elemental sulfur and a tail gas containing residual amounts of hydrogen sulfide, sulfur dioxide and other sulfur-containing gases,

the improvement comprising:

combining the so-produced tail gas with the crude coke oven gas in the initial cooling zone of the by-product recovery system.

4. The process of claim **3** wherein the improvement comprises combining the so-produced tail gas with the crude coke oven gas in the benzol washing zone.

5. The process of claim **3** wherein the improvement comprises combining the tail gas with the crude coke oven gas in the hydrogen sulfide absorption zone.

6. A process for disposing of a sulfur dioxide-containing tail gas that is generated by the catalytic conversion of hydrogen sulfide to sulfur in the Claus Process comprising combining the so-generated tail gas with crude coke oven gas in the initial cooling zone of a coke oven gas by-product recovery system including the Claus Process.

7. The process of claim **6** including the step of reacting the sulfur dioxide containing tail gas with ammonia in said crude coke oven gas in the presence of flushing liquor.

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