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(54) Title: LEAN ACID GAS ENRICHMENT WITH SELECTIVE HINDERED AMINES

(57) Abstract

Lean acid gas consisting essentially of H_2S and CO_2 wherein the H_2S content is less than about 20 % by volume and the balance is essentially CO_2 can be enriched by use of selective hindered amines to produce an acid gas containing about 20-80 % H_2S which can then be treated in a Claus plant.

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LEAN ACID GAS ENRICHMENT WITH SELECTIVE HINDERED AMINES

Background of the Invention

Field of the Invention

This invention relates to a method whereby lean acid gases containing less than 20% by volume H_2S and the balance essentially CO_2 are enriched to contain 20% or more H_2S by volume, preferably between 20-80% H_2S by means of selective hindered amines, which selectively removes H_2S from the lean acid gas stream, the enriched acid gas being suitable for treatment in Claus process units.

Description of Related Patents

It is well known in the art to treat gases and liquids such as mixtures containing acidic gases including CO_2, H_2S, CS_2, HCN, COS, and oxygen and sulfur derivatives of C_1 to C_4 hydrocarbons with amine solutions to remove these acidic gases. The amine usually contacts the acidic gases and the liquids as an aqueous solution containing the amine in an absorber tower with the contacting being conducted counter currently.

The treatment of acid gas mixtures containing CO_2 and H_2S, along with other components, with amine solutions typically results in the simultaneous removal of substantial amounts of both CO_2 and H_2S.

U.S. Patent 4,112,052 describes a process employing sterically hindered amines to obtain nearly complete removal of acid gases such as CO_2 and H_2S simultaneously.

In many instances it is desirable to selectively remove H_2S from the acid gas mixture, minimizing the amount of CO_2 removed. This is desirable because the separated gas then contains a relatively high H_2S/CO_2 ratio. High H_2S concentration in the separated gas facilitates conversion of the H_2S to elemental sulfur using the Claus process.

The typical reactions of aqueous secondary and tertiary amines with CO_2 and H_2S can be represented as follows:

$$H_2S+R_3N \rightleftarrows R_3NH^{+}+SH^{-} \quad (1)$$
$$H_2S+R_2NH \rightleftarrows R_2NH_2^{+}+SH^{-} \quad (2)$$
$$CO_2+R_3N+H_2O \rightleftarrows R_3NH^{+}+HCO_3^{-} \quad (3)$$
$$CO_2+2R_2NH \rightleftarrows R_2NH_2^{+}+R_2NCOO^{-} \quad (4)$$

wherein R is an organic radical which may be the same or different and may be substituted with a hydroxy group. The above reactions are reversible, and the partial pressures of both CO_2 and H_2S are thus important in determining the degree to which the above reactions occur.

While selective H_2S removal is applicable to a number of gas treating operations including treatment of hydrocarbon gases from shale pyrolysis, refinery gas, and natural gas having a low H_2S/CO_2 ratio, it is particularly desirable in the treatment of gases wherein the partial pressure of H_2S is relatively low compared to that of CO_2 because the capacity of an amine to absorb H_2S from the latter type gases is very low. Examples of gases with relatively low partial pressures of H_2S include synthetic gases made by coal gasification, sulfur plant tail gas, and low-Joule fuel gases encountered in refineries where heavy residual oil is being thermally converted to lower molecular weight liquids and gases.

Although it is known that solutions of primary and secondary amines such as monoethanolamine (MEA), diethanolamine (DEA), dipropanolamine (DPA), and hydroxyethoxyethylamine (DGA) absorb both H_2S and CO_2 gas, they have not proven especially satisfactory for preferential absorption of H_2S to the exclusion of CO_2 because the amines undergo a facile reaction with CO_2 to form carbamates.

Diisopropanolamine (DIPA) is relatively unique among secondary aminoalcohols in that it has been used industrially, alone or with a physical solvent such as sulfolane, for selective removal of H_2S from gases containing H_2S and CO_2, but contact times must be kept relatively short to take advantage of the faster reaction of H_2S with the amine compared to the rate of CO_2 reaction shown in Equations 2 and 4 hereinabove.

In 1950, Frazier and Kohl, Ind. and Eng. Chem., 42, 2288 (1950) showed that the tertiary amine, methyldiethanolamine (MDEA), has a high degree of selectivity toward H_2S absorption over CO_2. This greater selectivity was attributed to the relatively slow chemical reaction of CO_2 with tertiary amines as compared to the rapid chemical reaction of H_2S. The commercial usefulness of MDEA, however, is limited because of its restricted capacity for H_2S loading and its limited ability to reduce the H_2S content to the level at low pressures which is necessary for treating, for example, synthetic gases made by coal gasification.

U.K. Patent Publication 2,017,524A to Shell disclosed that aqueous solutions of dialkylmonoalkanolamines, and particularly diethylmonoethanolamine (DEAE), have higher selectivity and capacity for H_2S removal at higher loading levels than MDEA solutions. Nevertheless, even DEAE is not very effective for the low H_2S loading frequently encountered in the industry. Also, DEAE has a boiling point of 161°C., and as such, it is characterized as being a low-boiling, relatively highly volatile amino alcohol. Such high volatilities under most gas scrubbing conditions result in large material losses with consequent losses in economic advantages.

Other absorbent solutions which are selective to H_2S removal but have selectivity and/or capacity limitations similar to those of MDEA include solutions of 1-formylpiperidine as described in U.S. Pat. No. 4,107,270, piperazine as described in U.S. Pat. No. 4,112,049, and solutions, in N-methyl-2-pyrrolidone, of cyanopyridine, an aromatic nitrile, an anhydride, or a piperazine, as described in U.S. Patent

Nos. 3,656,887, 3,767,766, 3,642,431 and G.B. Pat. No. 1,560,905, respectively.

Recently, adsorbent solutions containing certain amino compounds defined as severely sterically hindered tertiary amine compounds have been found to maintain their high selectivity for H_2S at high H_2S and CO_2 loadings.

U.S. Patent 4,483,833 teaches that nitrogen heterocyclic tertiary aminoalkanols and aminoether alkanols have a high selectivity for H_2S as compared to CO_2 and maintain this selectivity at high H_2S and CO_2 loadings.

The nitrogen heterocyclic tertiary aminoalkanol or aminoetheralkanol is defined as a compound wherein the heterocycle portion contains 4-8 ring atoms, preferably 4-7 ring atoms, most preferably five ring atoms, of which one is nitrogen, and may be unsubstituted or substituted, e.g., with hydroxyl, alkyl or hydroxyalkyl radicals, and wherein the alkanol portion is arranged in a liner or branched fashion, connected to the heterocycle portion via a ring nitrogen or ring carbon atoms, preferably 2-10 carbon atoms, when the alkanol carbon atoms is attached to the nitrogen atom. The hydroxy carbon group can be attached directly to a ring carbon atom or separated from a ring carbon atom by 1-5 carbon atoms. The hydrocarbon chain of the alkanol portion may be alkoxylated, i.e., may contain one or more ether oxygen atoms. The hydroxyl functionality of the alkanol chain may be primary or secondary.

U.S. Patent 4,405,581 teaches that severely sterically hindered amino alcohols have a high selectivity for H_2S as compared to CO_2, and maintain this selectivity at high H_2S and CO_2 loadings.

The severely sterically hindered secondary amino alcohols herein may have either acyclic (linear or branched) or cyclic moieties attached to the nitrogen atom(s) of the amino alcohols.

Representative severely sterically hindered secondary amino alcohols include tertiarybutylaminoethanol, 2-(isopropylamino)-1-propanol, 3-(tertiarybutylamino)-n-butanol, 2-(tertiarybutylamino)-1-propanol, 3-(tertiarybutylamino)-1-propanol, 3-aza-2,2-dimethyl-1,6-hexanediol, and 2,5-diaza-2,4,4-trimethyl-7-heptanol.

U.S. Patent 4,405,811 teaches that severely sterically hindered tertiary amino compounds such as N-methyl-N-tertiarybutylaminoethoxyethanol, 2-(N-isopropyl-N-methylamino) propoxyethanol and 3-aza 2,2,3-trimethyl-1,6-hexanediol have a high selectivity for H_2S as compared to CO_2, and maintain this selectivity at high H_2S and CO_2 loadings and are useful in sulfur plant tail gas clean-up operations.

U.S. Patent 4,405,585 teaches that severely sterically hindered aminoether alcohols have a high selectivity for H_2S as compared to CO_2 and maintain this selectivity at high H_2S and CO_2 loadings.

The amino compound is preferably one or more compounds selected from the group consisting of tertiarybutylaminoethoxyethanol, 2-(2-tertiarybutylamino)propoxyethanol, tertiaryamylaminoethoxyethanol, (1-methyl-1-ethylpropylamino)ethoxyethanol, and 2-(2-isopropylamino)propoxyethanol. One of the preferred amino compounds is tertiarybutylaminoethoxyethano (TBEE).

U.S. Patent 4,405,580 teaches that tertiary amino azabicyclic alcohols such as tropine, pseudotropine, 9-methylgranatanin-3-ol, isoqunuclidine ethanol, trachelanthamidine, 4-hydroxymethylquinuclidine, N-hydroxyethylnortropine, N-hydroxyethyl(9-azabicyclo[3,3,1]nonane, N-hydroxyethoxyethyl(9-azabicyclo-[4.2.1]-nonane, 3-hydroxymethyl-8-methyl-8-azabicyclo[3.2.1]octane, and the like have a high selectivity for H_2S as compared to CO_2 and maintain this selectivity at high H_2S and CO_2 loadings.

U.S. Patent 4,417,075 teaches that di secondary aminoethers and more specifically di(secondary and tertiary alkylaminoalkoxy) alkanes such as 1,2-bis(tertiarybutylaminoethoxy)ethane, bis-(2-isopropylaminopropyl)ether and bis-(tertiarybutylaminoethyl)ether, and the like have a high selectivity for H_2S as compared to CO_2 and maintain this selectivity at high H_2S and CO_2 loadings.

U.S. Patent 4,405,583 teaches that di-severely sterically hindered secondary aminoethers have a high selectivity for H_2S as compared to CO_2 and maintain the selectivity at high H_2S and CO_2 loadings.

The di-severely sterically hindered secondary aminoethers herein are mono- or polyether compounds wherein each amino group has a severely sterically hindered secondary amino moiety.

Representative di-secondary aminoethers include, for example, bis-(tertiary-butylaminoethyl)ether, 1,2-bis-(tertiarybutylaminoethoxy)ethane, 1,2-bis-(tertiarybutylaminoethoxyethoxy)ethane, bis[2-(isopropylamino)-propyl]ether, 1,2-[2-(isopropylamino)-propoxy]-ethane and the like.

U.S. Patent 4,405,582 teaches that diaminoethers have a high selectivity for H_2S as compared to CO_2 and maintain this selectivity at high H_2S and CO_2 loadings.

The diaminoethers herein are mono- or polyether compounds wherein at least one of the two amino groups, and preferably both, is a tertiary amine. The tertiary amine may be acyclic or in the form of an N-heterocycle.

Representative diaminoethers include, for example, 1,2-bis-(N,N-dimethylaminoethoxy)ethane, bis-(N-pyrrolidinylethyl)ether, N-pyrrolidinylethoxyethyl-N,N-diethylamine, 1,2-bis-(pyrrolidinylethoxy)ethane, 1,2-bis-(pyrrolidinylethoxyethoxy)ethane, 1,2-bis-(3-pyrrolidinyl-n-propoxy)ethane, 1,2-bis-(piperidinylethoxy)ethane, 1,3-bis-(piperidinyl-n-propoxy)propane, 1-(pyrrolidinylethoxy)-2-(t-butylaminoethoxy)ethane, 1,2-bis-(azepanylethoxy)ethane, 1-(pyrrolidinylethoxy)-2-(piperidinylethoxy)ethane, 1-(pyrrolidinylethoxy)-2-

[2-(t-butylamino)-propoxy]ethane, 1-(pyrrolidinylethoxy)-2-(2-isopropylamino)propoxyethane, 1-(pyrrolidinylethoxy)-2-(1-methyl-1-ethylpropylaminoethoxy)ethane, 1-(pyrrolidinylethoxy)-2-(t-amylaminoethoxy)ethane, and the like.

U.S. Patent 4,471,138 teaches that severely sterically hindered acyclic secondary aminoether alcohols have a high selectivity for H_2S compared to CO_2 and maintain this selectivity at high H_2S and CO_2 loadings.

Representative severely sterically hindered acyclic secondary aminoether alcohols include tertiarybutylaminoethoxyethanol, 2-(2-tertiarybutylamino)-propoxyethanol, 2-(2-isopropylamino) propoxyethanol, tertiaryamylaminoethoxyethanol, (1-methyl-1-ethylpropylamino)ethoxyethanol.

U.S. Patent 4,618,481 teaches that an absorbent composition comprising a specific ratio of an amine salt and an unreacted alkaline severely hindered amino compound can be used to treat a low pressure gas in an energy efficient manner to produce a treated gas having less than 10 vppm H_2S.

The absorbent composition comprises: (1) at least one severely hindered amino compound having a cumulative $-E_s$ value (Taft's steric hindrance constant) greater than 1.75, and (2) an amine salt, said amine salt being the reaction product of an amine selected from the group consisting of a severely hindered amino compound having a cumulative $-E_s$ value (Taft's steric hindrance constant) greater than 1.75, a tertiary amine and mixtures thereof and a component selected from the group consisting of an acid having at least one pKa of not more than about 7, a decomposable salt of an acid having at least one pKa of not more than about 7, a compound capable of forming an acid having a pKa of not more than about 7 and mixtures thereof, said amine salt and said severely hindered amino compound being present in said absorbent composition in a mole ratio of said amine salt to said severely hindered amino compound of at least about 0.1:1.

U.S. Patent 4,894,178 teaches the use of a mixture of two severely sterically hindered amines for selective removal of H_2S in the presence of CO_2. For example, a mixture of bis-(tertiarybutylaminoethoxy)-ethane (BTEE) and ethoxyethoxyethanol-tertiarybutylamine (EEETB) can be synthesized by the catalytic tertiarybutylamination of trietylene glycol and used in aqueous solution form to selectively separate H_2S from streams containing H_2S and CO_2.

As used throughout the above recitations, by the term "severely sterically hindered" it is meant that the nitrogen atom of the amino moiety is attached to one or more bulky carbon groupings. Typically, the severely sterically hindered amino alcohols have a degree of steric hindrance such that the cumulative $-E_s$ value (Taft's steric hindrance constant) is greater than about 1.75 as calculated from the values given for primary amines in Table V from D.F. DeTar, Journal of Organic Chemistry, 45, 5174(1980), the entire disclosure of which is incorporated herein by reference.

The above recited amino compounds characterized by their high selectivity for H_2S compared to CO_2 and their ability to maintain this selectivity at high H_2S and CO_2 loadings are further characterized by their low volatility and high solubility in water at selective H_2S removal conditions, and most of the compounds are also generally soluble in polar organic solvent systems which may or may not contain water. The term "absorbent solution" as used herein includes but is not limited to solutions wherein the amino compound is dissolved in a solvent selected from water or a physical absorbent or mixtures thereof. Solvents which are physical absorbents (as opposed to the amino compounds which are chemical absorbents) are described, for example, in U.S. Pat. No. 4,112,051, the entire disclosure of which is incorporated herein by reference, and include, e.g., aliphatic acid amides, N-alkylated pyrrolidones, sulfones, sulfoxides, glycols and the mono- and diethers thereof. The preferred physical absorbents herein are sulfones, and most particularly, sulfolane.

The absorbent solution ordinarily has a concentration of amino compound of about 0.1 to 6 moles per liter of the total solution, and preferably 1 to 4 moles per liter, depending primarily on the specific amino compound employed and the solvent system utilized. If the solvent system is a mixture of water and a physical absorbent, the typical effective amount of the physical absorbent employed may vary from 0.1 to 5 moles per liter of total solution, and preferably from 0.5 to 3 moles per liter, depending mainly on the type of amino compound being utilized. The dependence of the concentration of amino compound on the particular compound employed is significant because increasing the concentration of amino compound may reduce the basicity of the absorbent solution, thereby adversely affecting its selectivity for H_2S removal, particularly if the amino compound has a specific aqueous solubility limit which will determine maximum concentration levels within the range given above. It is important, therefore, that the proper concentration level appropriate for each particular amino compound be maintained to insure satisfactory results.

The solution may include a variety of additives typically employed in selective gas removal processes, e.g., antifoaming agents, antioxidants, corrosion inhibitors, and the like. The amount of these additives will typically be in the range that they are effective, i.e., an effective amount.

Also, the amino compounds described herein may be admixed with other amino compounds as a blend preferably with methyldiethanolamine. The mole ratio of the respective amino compounds may vary widely, for example, from 1 to 99 percent of the amino compounds described herein.

U.S. Patent 4,519,991 teaches an improved method for the enrichment of a gas in H_2S comprising selective absorption by a liquid in a primary absorption zone by contacting gas containing H_2S with an absorbent liquid, regeneration of the liquid by heating and/or stripping by an inert gas with liberation of the gases absorbed and recovery of a fraction of the liberated gases, the remainder of the liberated gases being subjected to a second absorption in a secondary absorption zone by a new or regenerated absorbent liquid identical with that utilized in the primary absorption zone, characterized in that the steps of regeneration and secondary absorption are effected in a common operative zone in which there occur simultaneously: introduction of the liquid from the primary absorption, movement of the gases liberated during regeneration for said recovery and for contact with absorbent liquid, flow of the liquid derived from the secondary absorption and discharge from said operative zone of a fraction of the liberated gases enriched in H_2S. A stream containing 85% H_2S is produced.

U.S. Patent 4,085,192 teaches a process for selectively removing H_2S from gaseous mixtures containing H_2S and CO_2. The process involves contacting the gaseous mixture with an H_2S selective aqueous alkanol amine absorbent solution in an absorption column having from 3 to 20 contacting trays, said trays having an average dry tray pressure drop of from about 1.5 to about 5 inches per tray, thereby obtaining a treated gas containing less than 10% of the hydrogen sulfide present in the gaseous feed but more than 50% of the carbon dioxide present in said feed, and a hydrogen sulfide and carbon dioxide enriched-absorbent solution, passing said hydrogen sulfide and carbon dioxide-enriched absorbent solution to a regenerating zone and stripping said absorbent solution to a hydrogen sulfide content which corresponds to an equilibrium loading for a H_2S content having less than 50% of the hydrogen sulfide content of the treated gas, and returning said regenerated absorbent liquid into contact with the hydrogen sulfide and carbon dioxide containing gaseous mixture.

The process can be used to produce a stream of high H_2S concentration from a feed having as little as 5% H_2S and 94% CO_2. The H_2S concentration stream produced is suitable for Claus plant processing.

U.S. Patent 4,356,161 teaches a process for reducing the total sulfur content of a feed gas containing 40-95% CO_2, 0.03 to 20% H_2S and 0.02 to 2% COS. In the process the feed gas is first passed to an absorption column and contacted with an H_2S selective absorbent. The unabsorbed high CO_2-content gas is then routed to a reduction step where it is combined with Claus off-gases and the sulfur compounds are reduced to H_2S. The treated gas is then passed to a second absorption column and the unabsorbed gas is vented to the atmosphere. The H_2S rich solvent from both absorption columns is stripped in a common stripper and the stripped gas is passed to a Claus unit for conversion to elemental sulfur.

U.K. Patent 1,551,692 teaches a process for increasing the H_2S/CO_2 ratio in a gas mixture in order to prepare an acid gas which is a suitable feed to a Claus process. The starting gas is treated in the first absorber with an amine absorbent which removes H_2S selectively. The loaded amine absorbent from the first absorber is combined with a loaded amine absorbent from a second absorber and sent to one common amine regenerator. The second absorber treats a portion of the acid gas liberated in the common regenerator in order to selectively remove H_2S and to produce a treated CO_2 stream. The remainder of the acid gas stream from the regenerator having the desired H_2S/CO_2 ratio is sent to the Claus process. The excess CO_2 which was absorbed in the first absorber is rejected from the second absorber as the treated CO_2 stream. Thus a common amine absorbent which selectively removes H_2S is used in two absorber and one common regenerator in order to enrich the Claus process feed.

Claus-type sulfur recovery units are designed to work on acid gases which contain H_2S to convert the H_2S into elemental sulfur. Acid gas have primarily come from sour water strippers, flue gas desulfurization units and amine regenerators. The conversion of H_2S to elemental sulfur takes place via a combustor and a series of catalytic converters. The elemental sulfur produced is condensed and pumped to storage and the resulting tail gases containing SO_2, CO_2 and inerts is either burned, vented or cleaned further, if environmental regulations require it. The claus tail gases contain inerts because the oxygen used in the Claus combustor is supplied by using air which contains about 80% N_2 by volume.

The Claus process, being a technique to convert H_2S into elemental sulfur, works best on a stream containing a substantial quantity of H_2S. Streams fed to conventional Claus units contain at least about 40% by volume H_2S.

In this conventional Claus unit all of the acid gas is burned in the thermal converter where any of the hydrocarbons are oxidized at 900 to 1200°C to CO_2 and water while one third of the H_2S is converted to SO_2. The H_2S and SO_2 combine to produce sulfur in the subsequent steps. The majority of the sulfur is produced as the gas from the thermal converter is cooled. The remainder of the sulfur is produced over catalyst converters followed by gas coolers/condensers operating at decreasing temperatures. Whenever the acid gas contains less than 40 volume percent H_2S only a portion of the acid gas may be burned to give the desired ratio of H_2S to SO_2. The remainder of the unburned acid gas is bypassed around the thermal converter and recombined with the thermal converter gases before the first catalyst converter. This configuration is typical of a split-flow or fuel burning Claus plant. Because of this configuration any hydrocarbons in the acid gas which bypasses the thermal converter will deactivate the catalysts in the catalytic converters. It is therefore, important to minimize the hydrocarbons in the acid gas feeds which contain less than 40 percent H_2S by volume.

Traditional amine treatment processes produce treated pipeline gas from, for example, natural gas. A relatively sweet natural gas may have a composition of about 0.5% H_2S, 8% CO_2, 1% N_2, and the balance C_1-C_4 hydrocarbons. Amine treatment using MEA, DEA, MDEA etc. at about 1000 psi produces a treated pipeline gas comprising <2% CO_2 <4 wppm H_2S and the balance C_1-C_4 hydrocarbons. A tail gas is recovered from the amine regenerator containing about 2.5% H_2S and 97.5% CO_2 on a dry basis. This acid gas is not appropriate for conversion in a Claus plant, and, because of its high H_2S content is not a candidate for either burning or venting to the atmosphere.

Summary of the Invention

It has been discovered that H_2S lean acid gases consisting essentially of less than about 20% by volume H_2S and the balance CO_2

(no inerts being present) can be upgraded to Claus plant feed by passing the lean acid gas to a selective amine extraction plant employing the severely sterically hindered tertiary amino materials described in U.S. Patents 4,417,075; 4,471,138; 4,405,580; 4,405,581; 4,405,582; 4,405,583; 4,405,585; 4,405,811; 4,483,833; and 4,618,481, preferably the severely sterically hindered tertiary amino materials described in U.S. Patent 4,618,481.

The severely sterically hindered amino material used as adsorbent is selected from the group consisting of di-(secondary and tertiaryalkylaminoalkoxy)alkanes, severely sterically hindered secondary aminoether alcohols, tertiary amino azabicyclic alcohols, severely sterically hindered secondary amino alcohol, diaminoethers wherein at least one amino group is a tertiary amine, di-severely sterically hindered secondary aminoethers, severely sterically hindered tertiary amino alcohols, heterocyclic tertiary aminoalkanols.

An integrated process is disclosed wherein a sour hydrocarbon gas containing from 0.1 to 5% by volume H_2S, 5-15% by volume CO_2 and the balance C_1-C_4 hydrocarbons is treated in a first selective amine extraction unit with a first amine adsorbent which removes both H_2S and CO_2 to produce a treated pipeline gas consisting of <2% CO_2, <4 wppm H_2S and the balance C_1-C_4 hydrocarbons and an acid gas recovered from a first amine regeneration unit consisting essentially of less than 20% by volume H_2S and the balance CO_2. The concentration of H_2S in the acid gas will, of course, be higher than the concentration in the sour hydrocarbon gas feed. The acid gas from said first amine regenerator is fed to a second H_2S selective amine absorber using severely sterically hindered amino materials to produce an enriched acid gas recovered from a second amine regeneration unit consisting of at least 20% H_2S, preferably 20-80% H_2S, the balance being CO_2 and a scrubbed gas consisting essentially of CO_2 and <10 Vppm H_2S, preferably <5 Vppm H_2S, the enriched acid gas going to a Claus or Stretford plant for conversion into elemental sulfur.

The feed sent to the above identified initial amino compound absorber unit may be any sour gas such as tail gas, LNG gas, natural gas, synthesis gas etc. containing about 0.1-5% H_2S, 5-20% CO_2 and the balance inert, i.e. C_1-C_4 hydrocarbon, N_2 etc.

This sour gas stream is sent to a first absorber operating at a pressure of about 0.1 to 1200 psig, preferably 1 to 1000 psig, a temperature of about 60 to 140°F, preferably 80 to 120°F. The sour gas and the amine absorber material are contacted in the absorber zone, preferably countercurrently to produce a treated gas containing very little CO_2 and trace H_2S, typically <2% CO_2 and <4 wppm H_2S. The amine absorbent material is passed to an amine regenerator.

The absorber which is used to first process the initial sour gas feed can employ any of the less selective H_2S amino absorber compounds such as monoethanolamine (MEA), diethanolamine (DEA), depropanolamine (DPA) and hydroxyethoxyethylamine (DGA) or sterically hindered amines which absorb all H_2S and some or all of the CO_2 because the purpose of the first absorber step is to sweeten the gas feed and this is accomplished by removing all H_2S. Other standard absorber compounds include diisopropanolamine (DIPA), methyldiethanolamine (MDEA) and diethylmonoethanolamine (DEAE).

The amine absorbent material from the absorber is passed to an amine regenerator tower where the absorbed H_2S and CO_2 are removed from the amine absorbent. This is accomplished by heating the solvent and stripping it countercurrently with an inert medium such as steam. The amine regenerator can operate at a pressure of 0 to 40 psig preferably 6 to 20 psig and temperatures of 220 to 280°F. The stripped H_2S and CO_2 plus water vapor leave the regenerator and are fed to condensers where the acid gas is cooled and water is condensed. The stripped amine absorbent leaves the bottom of the regenerator and is cooled and recycled to the absorber.

The acid gas liberated from the amino compound contains less than about 20% by volume H_2S and the balance CO_2 with only trace amounts of inerts present.

This H_2S lean acid gas is then passed to the second H_2S selective amino compound absorber vessel and contacted therein with a solution of the H_2S selective amino compound absorbent.

In practicing this invention the selective H_2S absorber employs a severely sterically hindered amine absorbent which may be selected from the following: tertiary butylaminoethoxyethanol (TBEE), 2-(2-tertiarybutylamino)-propoxyethanol, 2-(2-isopropylamino)propoxyethanol, 1,2-bis-(N,N-dimethylaminoethoxy)ethane, bis-(N-pyrrolidinylethyl)ether, N-pyrrolidinylethoxyethyl-N,N-diethylamine, 1,2-bis-(pyrrolidinylethoxy)ethane, 1,2-bis-(pyrrolidinylethoxyethoxy)ethane, 1,2-bis-(3-pyrrolidinyl-n-propoxy)ethane, 1,2-bis-(piperidinylethoxy)-ethane, 1,3-bis-(piperidinyl-n-propoxy)propane, 1-(pyrrolidinylethoxy)-2-(t-butylaminoethoxy)ethane, 1,2-bis-(azepanylethoxy)ethane, 1-(pyrrolidinylethoxy)-2-(piperidinylethoxy)ethane, 1-(pyrrolidinylethoxy)-2-[2-(t-butylamino)-propoxy]ethane, 1-(pyrrolidinylethoxy)-2-(2-isopropylamino)propoxyethane, 1-(pyrrolidinylethoxy)-2-(1-methyl-1--ethylpropylaminoethoxy)ethane, 1-(pyrrolidinylethoxy)-2-(t-amylaminoethoxy)ethane, and the like, N-(3-hydroxypropyl)azetidine, N-hydroxyethylpyrrolidine, N-(3-hydroxypropyl)pyrrolidine, N-(2-hydroxypropyl)-pyrrolidine, N-(4-hydroxy-2-butyl)-pyrrolidine, N-(4-hydroxybutyl) pyrrolidine, N-(hydroxyethoxyethyl)-2,5-dimethylpyrrolidine, N-(3-hydroxypropyl)-2,5-dimethylpyrrolidine, N-(3-hydroxypropyl)piperidine, N-hydroxyethylpiperidine, N-methyl-2-hydroxyethylpiperidine, N-methyl-3-hydroxymethylpiperidine, N-(2-hydroxyethoxyethyl)pyrrolidine, N-2-[(2-hydroxypropoxy)ethyl]-pyrrolidine, N-2-[(2-hydroxypropoxy)-propyl]pyrrolidine, N-(2-hydroxyethoxyethyl)piperidine, N-(3-hydroxy-propyl)-azepane, and the like, tertiarybutylaminoethanol, 2-(isopropylamine)-1-propanol, 3-(tertiarybutylamino)-n-butanol, 2-(tertiarybutylamino)-1-propanol, 3-(tertiarybutylamino)-1-propanol, 3-aza-2,2-dimethyl-1,6-hexanediol, and 2,5-diaza-2,4,4-trimethyl-7-heptanol, N-methyl-N-tertiarybutylaminoethoxyethanol, 2-(N-isopropyl-N-methylamino)propoxyethanol, and 2-aza-2,2,3-trimethyl-1,6-hexanediol, tropine, pseudotropine, 9-methylgranatanin-3-ol, isoquinuclidine ethanol, trachelanthamidine, 4-hydroxymethylquinuclidine, N-hydroxyethylnortropine, N-hydroxyethyl(9-azabicyclo[3.3.1]-nonane), N-hydroxyethoxyethyl(9-azabicyclo[4.2.1]nonane), 3-hydroxymethyl-8-methyl-8-azabicyclo[3.2.1]octane, and the like, bis-(tertiarybutylaminoethyl)ether, 1,2-bis-(tertiarybutylaminoethoxy)-ethane, 1,2-bis-(tertiarybutylaminoethoxyethoxy)ethane, bis[2-(isopropylamino)propyl]ether, 1,2-[2-(isopropylamino)-propoxy]ethane and the like.

The preferred selective severely sterically hindered amine absorbants for use in the selective H_2S absorber comprise at least one severely hindered amino compound having a cumulative $-E_s$ value (Taft's steric hindrance constant) greater than 1.75 and (b) an amine salt, said amine salt being the reaction product of an amine selected from the group consisting of a severely hindered amino compound having a cumulative $-E_s$ value greater than 1.75, a tertiary amine and mixtures thereof and a component selected from the group consisting of an acid having at least one pKa of not more than about 7, a decomposable salt of an acid having at least one pKa of not more than 7, a compound capable of forming an acid having a pKa of not more than about 7 and mixtures thereof, said amine salt and said severely hindered amino compound being present in said adsorbent composition in a mole ratio of said amine salt to said severely hindered amino compound of at least about 0.1:1, preferably about 0.1:1 to 4:1, more preferably about 0.2:1 to 1:1; most preferably about 0.3:1 to 1:1.

In the above preferred selective severely sterically hindered amine absorbent the severely hindered amino compound can be selected from secondary amino ether alcohols such as those disclosed in USP 4,471,138 and di-secondary amino ethers such as those disclosed in USP 4,405,583, and mixtures thereof. Suitable secondary amino ether alcohols include tertiary butyl aminoethoxy ethanol, 2-(2-tertiarybutylamino)-propoxyethanol, tertiaryamylaminoethoxyethanol, (1-methyl-1-ethylpropylamino)ethoxyethanol, 2-2(2-isopropylamino)-propoxyethanol and mixtures thereof. Representative di-secondary amino ethers include bis(tertiarybutylaminoethyl)ether, 1,2-bis-(tertiarybutylaminoethoxy)ethane, bis[2-(isopropylamino)propyl]ether, 1,2-[2-(isopropylamino)propoxt]ethane and the like. A preferred severely hindered amino compound is tertiary butyl aminoethoxyethanol (TBEE). In forming the amine salt suitable acids include inorganic acids such as sulfuric acid sulfurous acid, phosphoric acid, phosphorous acid, pyrophosphoric acid; organic acids such as acetic acid, formic acid, adipic acid, benzoic acid etc. Suitable salts of these acids include the ammonium salts.

The normally gaseous mixture containing from 1-20% H_2S and the balance CO_2 from which the H_2S is to be selectively removed may be brought into intimate contact with the absorbent solution using conventional means, such as a trayed or packed tower with, for example, rings or with sieve plates, or a bubble reactor.

Preferably the absorber vessel should contain from 6 to 12 trays or 12 to 35 feet of packing. The trays or packing should be designed to give adequate gas-liquid contacting and minimum liquid hold-up.

The absorption step is conducted by feeding the normally gaseous mixture into the lower portion of the absorption tower while fresh absorbent solution is fed into the upper region of the tower. The normally gaseous mixture, largely freed from the H_2S, emerges from the upper portion of the tower, and the loaded absorbent solution, which contains the selectively absorbed H_2S, leaves the tower near or at its bottom. Preferably, the inlet temperature of the absorbent solution during the absorption step is in the range of from about 50° to about 210°F., and more preferably from about 75° to about 140°F. Pressures may vary widely; acceptable pressures are between 5 and 2000 psia, preferably 20 to 1000 psia, and more preferably 15 to 400 psia, most preferably 15-20 psia, in the absorber. The contacting takes place under conditions such that the H_2S is selectively absorbed by the solution. The absorption conditions and apparatus are designed so as to minimize the residence time of the liquid in the absorber to reduce CO_2 pickup while at the same time maintaining sufficient residence time of gas mixture with liquid to absorb a maximum amount of the H_2S gas. The amount of liquid required to be circulated to obtain a given degree of H_2S removal will depend on the chemical structure and basicity of the amino compound and on the partial pressure of H_2S in the feed gas.

A typical procedure for the selective H_2S removal phase of the process comprises selectively absorbing H_2S via countercurrent contact of the gaseous mixture containing H_2S and CO_2 with the aqueous solution of the amino compound in a column containing a plurality of trays at a low temperature, e.g., below 45°C., and at a gas velocity of at least about 0.3 ft/sec (based on "active" or aerated tray surface), depending on the operating pressure of the gas, said tray column having fewer than 20 contacting trays, with, e.g., 4-16 trays being typically employed.

The preferred absorber operating in the pressure range of 15 to 30 psia should have from 6 to 12 trays and operate at gas velocities of 2 to 7 ft/sec. (based on "active" tray surface). The preferred absorber operating in the pressure range of 30 psia to 400 psia should have from 4 to 10 trays and operate at gas velocities of 2 to 0.5 ft/sec. If a packed absorber is employed in the above ranges it have about 2 feet of packing per equivalent tray given above.

After contacting the normally gaseous mixture with the absorbent solution, which becomes saturated or partially saturated with H_2S, the solution may be at least partially regenerated in its own dedicated regenerator so that it may be recycled back to the absorber. As with absorption, the regeneration may take place in a single liquid phase. Regeneration or desorption of the acid gases from the absorbent solution may be accomplished by conventional means such as pressure reduction of the solution or increase of temperature to a point at which the absorbed H_2S flashes off, or by passing the solution into a vessel of similar construction to that used in the absorption step, at the upper portion of the vessel, and passing an inert gas such as air or nitrogen or preferably steam upwardly through the vessel. The temperature of the solution during the regeneration step should be in the range from about 50° to about 170°C, and preferably from about 80° to 120°C., and the pressure of the solution on regeneration should range from about 0.5 to about 100 psia, preferably 1 to about 50 psia. The absorbent solution, after being cleansed of at least a portion of the H_2S gas, may be recycled back to the second absorbing vessel. Makeup absorbent may be added as needed.

Suitable ratio of steam to absorbent composition during the regeneration step may range from about 0.4 to about 3.0 pounds of steam per gallon of liquid absorbent circulated to the regeneration zone.

In the preferred regeneration technique, the H_2S rich solution is sent to the regenerator wherein the absorbed components are stripped by the steam which is generated by re-boiling the solution. Pressure in the flash drum and stripper is usually 13 to about 50 psia, preferably 15 to about 30 psia, and the temperature is typically in the range from about 50° to 170°C., preferably about 80° to 130°C. Stripper and flash temperatures will, of course, depend on stripper pressure; thus at about 15 to 30 psia stripper pressures, the temperature will be about 80° to about 130°C during desorption. Heating of the solution to be regenerated may very suitably be effected by means of indirect heating with low-pressure steam or other heat transfer medium. It is also possible, however, to use direct injection steam.

The enriched acid gas stream recovered from the severely sterically hindered amine absorbent regenerator (regenerator 2), having an H_2S content now of about 20% or more is fed to a Claus plant for conversion into elemental sulfur. The enriched acid gas combined with air to supply the oxygen needed for combustion is processed in the Claus plant to produce elemental sulfur, which is recovered, and a tail gas containing SO_2 which is subsequently hydrogenated back to H_2S. This hydrogenated tail gas stream contains about 90% inerts (attributable to the 80% N_2 present in the combustion air), 2% H_2S and 8% CO_2. This gas can be treated with the severely sterically hindered amine absorbent in a separate absorber (third absorber) or can be sent to the second absorber to selectively remove the H_2S. The resulting treated tail gas contains from 1 to 300 vppm H_2S and about 90% of the CO_2 present in the feed tail gas. In the preferred case the treated tail gas contains 1 to 10 vppm H_2S and may be vented. The loaded severely sterically hindered amine absorbent from the third absorber if a dedicated third absorber is used may be combined with the amine absorbent from the enriching absorber (second absorber) and regenerated in a common regenerator. Thus most of the H_2S can be recovered in the Claus unit resulting in very low emissions of sulfur species to the atmosphere.

An example of such process treats a low Btu lean acid gas containing 1% H_2S, 10% CO_2 the balance inerts produced by a FLEXICOKING unit with the amine absorbent at 30 psia. The Claus plant tail gas containing 15% H_2S, 8% CO_2 the balance inerts is also treated with the amine absorbent in a separate absorber at 17 psia. The combined absorbent is regenerated in the single regenerator. The acid gas from the regenerator containing 50% H_2S by volume is fed to a Claus plant. The treated low Btu gas containing less than 20 vppm H_2S is burned in process furnaces while the treated Claus plant tail gas containing less than 10 vppm H_2S is vented.

CLAIMS:

1. A method for reducing H_2S emissions from acid gases produced during the processing of sour hydrocarbon gases containing CO_2 and H_2S, said method comprising contacting the CO_2 and H_2S containing hydrocarbon gas in a first adsorber with a selective adsorbent to remove substantially all the CO_2 and H_2S from the hydrocarbon gas yielding a treated gas of low CO_2 and H_2S content and a lean acid gas containing less than about 20% volume H_2S and the balance essentially CO_2, passing the lean acid gas to an adsorber wherein said lean acid gas is contacted with a selective severely sterically hindered amine adsorbent which selectively removes H_2S from the acid gas stream yielding a tail gas containing essentially pure CO_2 and an H_2S loaded adsorbent, separating the adsorbed H_2S from the adsorbent to produce a stream of enriched H_2S content and a regenerated adsorbent solution which adsorbent solution is recycled to the lean acid gas treatment adsorber and passing the H_2S enriched gas to a Claus process unit for conversion therein of the H_2S into elemental sulfur and a tail gas containing SO_2.

2. The method of claim 1 further comprising the steps of hydrogenating the SO_2 in the tail gas recovered from the Claus or Stretford process unit thereby converting said SO_2 into a stream containing H_2S, CO_2 and inerts and sending this stream to the first adsorber for recycling through the process.

3. The process of claim 1 or 2 wherein the sour hydrocarbon gas contains from 0.1 to 5% H_2S, 5 to 15% CO_2 and the balance being inerts and C_1-C_4 hydrocarbons.

4. The process of claim 1 or 2 wherein the selective severely sterically hindered amine adsorbent comprises (a) at least one severely hindered amino compound having a cumulative $-E_s$ value (Taft's steric hindrance constant) greater than 1.75 and (b) an amine salt, said amine salt being the reaction product of an amine selected from the group consisting of a severely hindered amino compound having a cumulative $-E_s$ value greater than 1.75, a tertiary amine and

mixtures thereof and a component selected from the group consisting of an acid having at least one pKa of not more than about 7, a decomposable salt of an acid having at least one pKa of not more than 7, a compound capable of forming an acid having a pKa of not more than about 7 and mixtures thereof, said amine salt and said severely hindered amino compound being present in said adsorbent composition in a mole ratio of said amine salt to said severely hindered amino compound of at least about 0.1:1.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US91/08940**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): B01D 53/14 C01B 17/04
US CL : 423/228,573.1

II. FIELDS SEARCHED

Minimum Documentation Searched[4]

Classification System	Classification Symbols
U.S.	423/226,228,229,574R,576,573.1

Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched[5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[14]

Category*	Citation of Document,[16] with indication, where appropriate, of the relevant passages[17]	Relevant to Claim No. [18]
Y	US, A, 4,618,481 (HEINZELMANN, ET AL.) 21 OCTOBER 1986 (SEE ENTIRE DOCUMENT).	1-4
Y	CA, A, 1,099,513 (VERLOOP) 21 APRIL 1981 (SEE ENTIRE DOCUMENT).	1-4
Y	US, A, 4,356,161 (MCNAMARA ET AL.) 26 OCTOBER 1982 (SEE ENTIRE DOCUMENT).	1-4
Y/A	US, A, 4,425,317 (ZELLER, ET AL.) 10 JANUARY 1984 (SEE CLAIM 1).	2/1,3,4
A	US, A, 4,001,386 (KLEIN, ET AL.) 04 JANUARY 1977 (SEE COLUMN 1-3).	1-4
A	US, A, 4,519,991 (OLIVEAU, ET AL.) 28 MAY 1985 See entire document.	1-4
A	EP, A, 134,948 (UNION CARBIDE) 27 MARCH 1985 See entire document.	4
A	US, A, 4,085,192 (VAN SCOY) 18 APRIL 1978 See columns 1-3.	1-4

* Special categories of cited documents:[15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search[2] 20 MARCH 1992	Date of Mailing of this International Search Report[2] [illegible]
International Searching Authority[1] ISA/US	Signature of Authorized Officer[20] Ngoc Ho Nguyen CTION PETER T. DIMAURO/DC for

Form PCT/ISA/210 (second sheet)(May 1986) ß