

SELECTIVE SULFUR REMOVAL PROCESS

FIELD OF THE INVENTION

[0001] This invention relates to a process for selectively removing acidic sulfur-containing gases from mixed gas streams.

BACKGROUND OF THE INVENTION

[0002] Natural gas from many gas fields, which is often produced at high pressures, possibly as high as 50 MPa, can contain significant levels of H₂O, H₂S, CO₂, N₂, mercaptans, and/or heavy hydrocarbons that have to be removed to various degrees before the gas can be transported to market. It is preferred that as much of the acid gases H₂S and CO₂ be removed from natural gas as possible to leave methane as the recovered component. Small increases in recovery of this light component can result in significant improvements in process economics and also serve to prevent unwanted resource loss. It is desirable to recover more than 80 vol%, preferably more than 90 vol%, of the methane when detrimental impurities are removed. In many instances effective removal of the H₂S is more important than CO₂ removal as specifications for natural gas transmission pipelines typically limit the H₂S content to be as low as 4 vppm while a more relaxed specification of two to three percent is typically permissible for CO₂. If the contaminant removal process is unselective between these two gases or favorable to CO₂ removal, the treatment will be unnecessarily severe, resulting in increased processing costs. A natural gas treatment process which is selective for H₂S relative to CO₂ is therefore economically attractive.

[0003] Natural gas treating is often carried out using solid sorbents such as activated charcoal, silica gel, activated alumina, or various zeolites. The well-established pressure swing adsorption (PSA) process has been used in this way since about the 1960s. In the PSA process, the solid sorbent is contained in a vessel and adsorbs the contaminant gas species at high pressure and when the design sorption capacity of the sorbent is attained the gas stream is switched to another sorption vessel while the pressure in the first vessel is reduced to desorb the adsorbent component. A stripping step with inert (non-reactive) as or with treated product gas may then follow before the vessel is returned to the sorption portion of the cycle. Variants of the

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conventional PSA (cPSA) process have been developed including the partial pressure swing or displacement purge adsorption (PPSA), rapid cycle pressure swing adsorption (RCPSA), Dual Bed (or Duplex) PSA Process, and rapid cycle partial pressure swing or displacement purge adsorption (RCPPSA) technologies.

[0004] Temperature swing adsorption (TSA) provides an alternative to the pressure swing technology in which the sorbed component is desorbed by an increase in temperature typically achieved by the admission of high temperature gas, *e.g.*, air, to the vessel in the regeneration phase. Rapid cycle thermal swing adsorption (RCTSA) is a variant of the conventional TSA process using short cycles, typically less than two minutes. TSA processes are generally available commercially from a number of technology suppliers, although the state of the art for large scale rapid cycle TSA units is considerably less advanced. Large scale slow (~10 hr) cycle internally heated TSA's have been used in natural gas processing for rigorous dehydration and mercaptan removal. In an internally heated thermal swing adsorption process, the gas or fluid used to heat the contactor directly contacts the adsorbent material. As such, the gas or fluid used to heat the contactor during regeneration can pass through the same channels that the feed gas does during the adsorption step. Externally heated thermal swing adsorption processes employ contactors having a separate set of channels to carry gases or fluids used to heat and cool the contactor so that gases used to heat and cool the contactor do not mix with the adsorbent that contacts the feed gas.

[0005] Other gas streams containing similar contaminants are encountered in various industrial processes, notably in petroleum refining and in petrochemical processes. In petroleum refining, for example, hydrodesulfurization processes utilize separation processes which remove the hydrogen sulfide formed in the process from the circulating stream of hydrogen. Conventionally, amine scrubbers are used for this purpose, using liquid amine sorbents such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), and diisopropylamine (DIPA) in the form of an aqueous solution.

[0006] Conventionally, liquid sorbent systems such as used in hydrogen sulfide scrubbing operate on a closed cycle with separate sorption and regeneration vessels through which the liquid sorbent is continuously circulated in a sorption-regeneration loop in which the sorption is typically carried out at a temperature optimized for

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sorption of the contaminant and the regeneration carried out by stripping, usually by steam at a higher temperature, in the regeneration tower. Inert gas stripping is also potentially useful to remove the sorbed contaminant species.

[0007] The capture of CO₂ by amine species takes place through the formation of carbamate salts for primary and secondary amines, and additionally through the formation of ammonium bicarbonate salts when water is present. When tertiary amines are utilized with water present the formation of carbamate salts which require a proton transfer cannot take place and the reactions are limited to the formation of bicarbonate salts in a reaction sequence which with requires H₂O to be present. In the absence of water, tertiary and other non-protogenic basic nitrogen species do not react with CO₂, as no bicarbonate formation is possible. Hydrogen sulfide (H₂S) is a Brønsted acid, and it reacts with all sufficiently basic amine species, including tertiary or non-protogenic amines, amidines, guanidines, and biguanides through simple acid/base reactions by the transfer of a proton from the H₂S to the amine species to form ammonium sulfide (trisubstituted ammonium sulfide salts in the case of tertiary amines) reversibly, both in the presence and absence of water.

SUMMARY OF THE INVENTION

[0008] We have now devised a cyclic process for the selective sorption of hydrogen sulfide from gas mixtures containing CO₂ and possibly other acid gases including CO₂, SO₂, and other gaseous components such as N₂, mercaptans, and/or heavy hydrocarbons. This process utilizes the selective reaction of H₂S with tertiary and other non-protogenic Lewis bases in non-aqueous systems.

[0009] According to the present invention, the process for selectively separating hydrogen sulfide from a gas mixture including CO₂ comprises contacting the gas mixture under sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound to react the H₂S with the basic compound so that the H₂S is sorbed by the compound. The compound containing the sorbed H₂S can then be subjected to desorption conditions by which the H₂S is desorbed and the sorbent readied for another sorption step in the cycle.

[0010] The basic non-protogenic nitrogenous compound can advantageously be carried on a porous solid sorbent such as those which have conventionally been used

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for gas purification and separation processes, *e.g.*, solid oxides (including mixed oxides) such as alumina, silica, silica-alumina, and/or acidic or non-acidic zeolites. Mesoporous and macroporous materials having a high surface area are preferred.

[0011] The process may be operated on a pressure swing and/or temperature swing between the sorption and desorption portions of the cycle. The present process is amenable to being operated in variants such as partial pressure swing or displacement purge adsorption (PPSA), Dual Bed (or Duplex) PSA with preference given to the rapid cycle variants such as rapid cycle PSA (RCPSA), rapid cycle partial pressure swing or displacement purge adsorption (RCPPSA) technologies, and thermal swing processes with preference being given to rapid cycle temperature swing Adsorption (RCTSA).

[0012] The process is especially useful for selectively separating H_2S from a stream in which H_2S and CO_2 are the major constituents, *e.g.*, a stream resulting from a non-selective separation process in which these two contaminants have been removed in a pre-separation step from a natural gas stream. Pre-separated streams of this type will typically contain at least 50 mol%, for example at least 80 mol% or even at least 90 mol%, combined H_2S and CO_2 . It may also be used to separate H_2S and CO_2 individually from a natural gas stream including both. With a single step separation to remove the H_2S and CO_2 , the incoming gas stream may be treated to sorb the H_2S preferentially to the CO_2 , so as to produce a product natural gas stream depleted in H_2S and an H_2S -containing side stream, *e.g.*, which can be passed to a Claus plant for recovery of sulfur. If the incoming stream is a natural gas stream containing significant quantities of CO_2 to be removed and then used (for example, for re-injection into the producing formation for pressure maintenance), the preferential desorption characteristics of the process may be utilized to form the H_2S -depleted product stream and a CO_2 re-injection stream with a reduced content of H_2S which can be used for re-injection with the potential for accumulation of this contaminant in the producing formation. In this case, the incoming natural gas stream can be treated with the basic nitrogenous adsorbent so that both the H_2S and the CO_2 are sorbed to produce a product natural gas stream in which the levels of both the H_2S and the CO_2 are reduced. The basic nitrogenous compound containing the sorbed H_2S and the CO_2 can then be subjected to a two-stage desorption in which the differential adsorption characteristics of basic nitrogen compound for the two contaminants are effectively

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exploited. In the first step of the desorption, the CO_2 which is less firmly bound than the H_2S , can be preferentially desorbed to form a side stream comprising desorbed CO_2 . Being more firmly bound to the adsorbent, the H_2S can remain bound to the adsorbent at this stage under the conditions selected. The adsorbent still containing the H_2S , can then pass to the second desorption step in which the conditions are selected to favor H_2S desorption. The H_2S desorbed in this step may then be passed to a Claus plant while the other side stream containing the desorbed CO_2 may be re-injected into the producing formation.

[0013] Additionally, the following are incorporated by reference herein in their entirety as being related to this application and for their relevant disclosures: U.S. Patent Application Nos. 61/447,806, 61/447,812, 61/447,824, 61/447,835, 61/447,848, 61/447,869, and 61/447,877, each filed March 1, 2011, as well as the seven U.S. non-provisional applications filed claiming priority thereto. Further, the following are incorporated by reference herein in their entirety as being related to this application and for their relevant disclosures: U.S. Serial Nos. 61/448,117, 61/448,120, 61/448,121, 61/448,123, and 61/448,125, each filed March 1, 2011, 61/594,824 filed February 3, 2012, and the application entitled "Apparatus and Systems having a Rotary Valve Assembly and Swing Adsorption Processes Related Thereto" by Robert F. Tammara *et al.* filed on even date herewith, as well as any PCT applications and U.S. non-provisional applications claiming priority thereto.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIGURE 1 of is a highly simplified schematic of a gas separation unit utilizing a non-aqueous, solid, non-protogenic, basic nitrogenous sorbent system.

[0015] FIGURE 2 shows the H_2S and CO_2 adsorption isotherms for a guanidine base supported on MCM-48.

[0016] FIGURE 3 shows the adsorption isotherms of H_2S and CO_2 on KIT-6 functionalized with a tertiary amino group.

[0017] FIGURE 4 shows the H_2S and CO_2 adsorption isotherms for SBA-15 functionalized with a tertiary amino group.

[0018] FIGURES 5 and 6 show the sorption and desorption cycles, respectively, for the H_2S breakthrough experiment of Example 6.

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[0019] FIGURES 7 and 8 show the sorption and desorption cycles, respectively, for the breakthrough experiment of Example 7.

[0020] FIGURE 9 shows the sorption cycle for the breakthrough experiment of Example 8, where H₂S is sorbed in the presence of water, as compared to the sorption cycle from Example 7, which occurs in the absence of water.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Process Configuration

[0021] A highly simplified schematic of a natural gas purification unit operating in the pressure swing adsorption mode, utilizing a non-aqueous, solid, non-protogenic, basic nitrogenous sorbent system is shown in Figure 1. Ancillary equipment such as compressors, heaters, coolers, pressure reduction valves, and power recovery turbines are not shown, since they are typically conventional. An incoming natural gas stream containing H₂S and CO₂, as well as possibly other contaminants such as N₂, SO₂, mercaptans, and heavier hydrocarbons (C₃₊), can enter the purification unit through line 10 and pass to manifold valve 11 where it is diverted to one of two branch lines 12, 13 that conduct the incoming gas stream in turn according to a controlled cycle to one of two sorption vessels 15, 16. The sorption vessels can contain fixed beds of a solid absorbent material at least a portion of which is selective for the H₂S, as described below. The sorption bed can additionally or alternately contain materials that have selectivity for other species. In one preferred embodiment, the bed can be segmented with an initial portion containing the H₂S-selective sorbent and the final portion containing a CO₂-selective adsorbent. Additionally or alternately, the bed can be constructed as a parallel channel contactor. Examples of preferred bed architectures can include, but are not limited to, those provided in U.S. Patent Nos. 7,959,720, 7,938,886, 7,731,782, and 7,947,120, which are all incorporated herein by reference. After passing through a bed of sorption material in the bed on the sorption phase of the cycle, the purified gas can exit the respective vessel through one of two branch lines and can pass to exhaust manifold valve 17 or 18, and from there to manifold valve 20. Purified gas can leave the unit through line 21, while a portion can be recycled as a purge stream through line 22 in the reverse direction, when the sorbed contaminant H₂S is to be purged from the sorption material in one of the two sorption vessels 15, 16 at

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the end of the sorption phase in the particular vessel. In PSA operations, the bed can advantageously be depressurized before purging, and/or in TSA operations, the bed can advantageously be heated before purging. Purge gas containing the desorbed contaminant can be exhausted from the vessels by way of line 23 and the concentrated contaminants recovered and processed.

[0022] In operation in the PSA mode, the incoming gas can be passed over the selected bed of sorption material for a fixed time controlled by a cycle controller and/or until contaminant breakthrough is indicated by a stream controller in the vessel. At this point, the manifold valves can be actuated to stop the flow of gas into and out of the vessel which has been in the sorption phase and to re-direct it to the other vessel containing freshly purged material. The manifold valves can then be controlled to allow a reduction of pressure in the vessel used for sorption so that the sorbed contaminant(s) can be selectively released from the sorption material into exhaust line 23. Desorption may be assisted, preferably towards/at the end of the pressure reduction phase, by purging with a gas stream comprised of recycle product and/or inert gas such as N₂, admitted by way of line 22 through valve 20. The purge stream may be heated if necessary to facilitate stripping of the sorbed contaminant(s).

[0023] Since the selectivity of the process is typically favored by operation with a non-aqueous sorbent, it can be preferable to maintain the water content of the system at a relatively low level. This, however, is not inconsistent with water in the incoming gas stream at relatively low level, for example, less than 5 mol%, preferably less than 2 mol% or less than 0.1 mol% (less than 1000 ppm), water based on the molar composition of the overall incoming gas stream. If, however, water from the gas stream tends to accumulate in the sorbent, it may be desirable to remove a slip stream of sorbent for removal of the water, *e.g.*, by gas stripping, passing over a dryer, heating, and/or by evaporation under reduced pressure. Embodiments herein can additionally or alternately include drying the incoming feed gas to the system to remove a portion of water therefrom by means of dryers, precipitators, condensers, demisters, coalescers, and/or desiccants prior to subjecting the feed gas to the adsorbent systems described herein.

Sorbent

[0024] The sorbent used in the present process can be a basic, non-protogenic nitrogenous compound. Compounds of this type typically do not, as described above, enter into chemisorption reactions with CO₂ in the absence of water, although they do typically undergo reaction with H₂S. This differential chemical reactivity can be used to selectively separate between the sorbed H₂S and CO₂. The sorbent may be used in liquid form and/or on a porous solid support.

[0025] A wide variety of basic nitrogen-containing compounds may be used as the essential sorbent. If desired, a combination of such compounds may be used. The requirement for the desired selectivity for H₂S adsorption is that the nitrogenous groups be non-protogenic (*i.e.*, incapable of acting as a proton donor). Such nitrogenous groups therefore cannot contain an acidic, dissociable hydrogen atom (such as a primary or secondary amine), which is a prerequisite for the formation of carbamates as a route for the CO₂ chemisorption reaction in the absence of water. It is not generally required that the whole compound be aprotic (though it may), but only that the nitrogen-containing groups in the compound be non-protogenic. Non-protogenic nitrogen species are also typically non-nucleophilic under prevailing reaction conditions. Suitable nitrogenous compounds can include, but are not necessarily limited to, tertiary amines such as triethylamine, triethanolamine (TEA), methyldiethanolamine (MDEA), N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine, as well as non-protogenic nitrogenous bases with cyclic, multicyclic, and acyclic structures, such as imines, heterocyclic imines and amines, amidines (carboxamidines) such as dimethylamidine, guanidines, triazabicyclodecenes, imidazolines, and pyrimidines. Other compounds that can additionally or alternately be used can include the *N,N*-di(lower alkyl)carboxamidines (where lower alkyl is preferably C₁-C₆ alkyl), *N*-methyltetrahydropyrimidine (MTHP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), substituted guanidines of the formula (R¹R²N)(R³R⁴N)C=N-R⁵ (where R¹, R², R³ and R⁴ are preferably lower alkyl (C₁-C₆) and R⁵ is preferably H or lower alkyl (C₁-C₆)) such as 1,1,3,3-tetramethylguanidine and biguanide, as well as combinations thereof. Other substituent groups on these compounds such as higher alkyl, cycloalkyl, aryl, alkenyl, and substituted alkyl and other structures may also be used.

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[0026] In some embodiments, the more highly basic non-protogenic nitrogenous compounds can be preferred, since they are capable of maintaining basic conditions favoring H₂S sorption. For this reason, the bases having a pK_a (acid dissociation constant, as measured or predicted at 25°C in aqueous solution or as measured in another solvent and converted to an aqueous value) of at least 9.0 can be preferred, though higher values of at least 10.0, at least 12.0, or at least 13.0 can be desirable for improved/optimal chemisorption of H₂S. A useful means of making an adequate prediction of the pK_a value of the base may be provided by the ACD/PhysChem Suite (a suite of software tools for the prediction of basic physicochemical properties including pK_a), available from Advanced Chemistry Development, Inc., 110 Yonge Street, Toronto, Ontario, Canada M5C 1T4. Exemplary pK_a values for a limited number compounds (in dimethylsulfoxide) may be found in the Bordwell online pK_a database, <http://www.chem.wisc.edu/areas/reich/pkatable/index.htm>).

Solid Phase Sorbents

[0027] The process may be operated with the basic sorbent in the liquid phase, but preferably can be operated as or can include an adsorption process in which the basic sorbent is supported on a porous, solid support. To operate using a solid phase sorbent, the basic nitrogenous compound, if liquid (as most are), can be supported on a porous, solid support or carrier material, preferably of relatively high surface area. If the basic compound is a solid, it may be dissolved to form a solution which can then be used to impregnate the support material. Supports of this kind are frequently used as the catalysts in catalytic processes such as hydrogenation, hydrotreating, hydrodewaxing, etc. Common support materials can include carbon (activated charcoal) and/or porous solid oxides of metals and metalloids and mixed oxides, including alumina, silica, silica-alumina, magnesia, and zeolites, as well as combinations thereof. Porous solid polymeric materials can additionally or alternately be suitable, provided that they are resistant to the environment in which the sorption reaction is conducted. As the components of the gas stream tend to have relatively small molecular dimensions, the minimum pore size of the support may not in itself be a severely limiting factor, but, when the basic nitrogenous compound is impregnated, the entrances to the pore systems of small and intermediate pore size zeolites (such as zeolite 4A, erionite, ZSM-

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5, ZSM-11, and the like) may become occluded by the (bulky) amine component; for this reason, the smaller pore materials may not be preferred, especially with the bases of relatively larger molecular dimensions. Large pore size zeolites with 12-membered ring systems (such as ZSM-4, faujasites such as zeolite X and the variants of zeolite Y including Y, REY, and USY, and the like) may, however, be suitable depending on the dimensions of the basic nitrogenous compound(s) utilized. Amorphous porous solids with a range of different pore sizes may be utilized in embodiments herein, since some of the pores will have openings large enough to accept the basic component and to also allow sufficient access to the components of the gas stream. Supports containing highly acidic reaction sites, as with the more highly active zeolites, can tend to be more susceptible to fouling reactions upon reaction with the nitrogenous compound and may therefore be generally less preferred in some embodiments than the less acidic supports.

[0028] A preferred class of solid oxide support includes mesoporous and/or macroporous silica materials such as the silica compounds of the M41S series, including MCM-41 (hexagonal), MCM-48 (cubic), and other mesoporous materials such as SBA-1, SBA-2, SBA-3, and SBA-15, as well as the KIT series of mesoporous materials such as KIT-1, KIT-5, and KIT-6. Macroporous silicas and other oxide supports such as the commercial macroporous silicas available as Davisil[®] products may be suitable, *e.g.*, Davisil 634[®] (~6 nm pore size, ~480 m²/g pore volume), Davisil 635[®] (~6 nm, ~480 m²/g), and/or Davisil 644[®] (~15 nm, ~300 m²/g). According to the IUPAC definition, mesoporous materials are those having a pore size of about 2 nm to about 50 nm, and macroporous materials are those having a pore size of over ~50 nm. According to the IUPAC, a mesoporous material can be disordered or ordered in a mesostructure. Preferred mesoporous and macroporous support materials can be characterized by a BET surface area of at least 300 m²/g, *e.g.*, at least 500 m²/g, prior to treatment with the base compound. The M41S materials and their synthesis are described in a number of Mobil patents, including U.S. Patent Nos. 5,102,643, 5,057,296, 5,098,684, and 5,108,725, to which reference is made for a description of them, as well as in the literature in *"The Discovery of ExxonMobil's M41S Family of Mesoporous Molecular Sieves"*, Kresge et al, Studies in Surface Science and Catalysis, 148, Ed. Terasaki, Elsevier bV 2004. SBA-15 is described in *"Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores"*, Dongyuan

Zhao, et al. (1998), *Science* 279 (279). KIT-1 is described in U.S. Patent No. 5,958,368, and other members of the KIT series are known (*see, e.g.*, KIT-6 in *Nanoscale Res Lett.*, 2009 November, 4(11): 1303–1308).

[0029] As shown below, the H₂S/CO₂ selectivity of the material can be adjusted by the judicious choice of the porous support structure; coupled with the potential for controlling the H₂S/CO₂ selectivity by the use of different adsorbent molecules on the support, there is a significant potential for tailoring the selectivity of the adsorbent.

[0030] The basic nitrogenous compound may simply be physically sorbed on the support material (*e.g.*, by impregnation or bonded with or grafted onto it by chemical reaction with the base itself or a precursor or derivative in which a substituent group provides the site for reaction with the support material in order to anchor the sorbent species onto the support). Typically, however, bonding is not required for an effective solid phase sorbent material. Support materials containing reactive surface groups (such as the silanol groups found on zeolites and the M41S silica oxides) are typically capable of reacting with siloxane groups in compounds such as trimethoxysilylpropyl-dimethylamine. An alternative method of fixing more volatile adsorbing species on the support can be by first impregnating the species into the pores of the support and then cross-linking them in place through a reaction that does not involve the basic nitrogenous groups responsible for the sorption reaction in order to render the sorbing species non-volatile under the selected sorption conditions. Grafting or bonding methods are known in the technical literature. The molecular dimensions of the base sorbent can advantageously be selected in accordance with the pore dimensions of the support material, since bulky bases/precursors/derivatives may not be capable of entering pores of limited dimensions. A suitable match of base and support may be determined if necessary by empirical means.

[0031] Solid phase sorbents will normally be operated in fixed beds contained in a suitable vessel and operated in the conventional cyclic manner with two or more beds in a unit with each bed switched between sorption and desorption and, optionally, purging prior to re-entry into the sorption portion of the cycle, as described above briefly with reference to Figure 1. Purging may be carried out with a stream of the purified gas mixture, *i.e.*, a stream of the gas from which the H₂S has been removed in the sorption process. If operated in temperature swing mode, a cooling step will

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intervene at some point between the desorption step and the next absorption step. Alternatively, moving bed or fluidized bed systems may be used; rotating wheel beds are notably useful in rapid cycle sorption systems. All these systems may be operated in their conventional manner when using the present sorbents.

Liquid Phase Sorbents

[0032] If the sorption process is operated with the sorbent in liquid form, either neat or in a non-aqueous solution, the liquid can typically be circulated in a closed loop between a sorption zone (*e.g.*, in one vessel) and a desorption or regeneration zone (*e.g.*, in a separate vessel) in a manner conventional to cyclic amine scrubbing processes. The process may be operated on a pressure swing and/or temperature swing basis. With pressure swing, the partial pressure of H_2S during the sorption step can typically be higher than its partial pressure in the desorption step, with the sorption pressure typically being selected according to the source of the gas stream. With natural gas streams that may emerge from producing formations at pressures up to, say, ~50 MPag, the pressure will normally be reduced, if necessary, to suit processing equipment and the specification pipelining pressure, typically to values in the range of about 1 MPag to about 10 MPag, depending on the pipeline specifications. Pressure in the desorption step can be selected to achieve adequate desorption of the H_2S , with typical natural gas pressures as low as ~1-2 bar for desorption, *e.g.*, when the H_2S is taken to a Claus Plant, although higher desorption pressures can sometimes be preferred, *e.g.*, to reduce/minimize compression costs such as when H_2S is to be re-injected into the producing formation.

[0033] Many of the basic nitrogenous compounds useful as sorbents in the present process can typically be liquids and may generally be used neat as the sorbent material in a liquid phase operation. If necessary or desirable, for example, to preclude the formation of precipitates, the sorbing species may be taken up in a solvent. Water is, of course, excluded as a solvent in order to maintain the required non-aqueous conditions and to preserve the selectivity for sorbing the H_2S . Preferred solvents can generally include those which are themselves non-protogenic, so as to de-emphasize/preclude formation of bicarbonate species and the chemisorption of CO_2 or other species in the gas stream (such as SO_2) and which are not corrosive towards the equipment of the

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processing unit. Solvents such as toluene, DMSO (dimethyl sulfoxide), sulfolane (tetramethylene sulfone), DMF (*N,N*-dimethylformamide), NMP (*N*-methyl-2-pyrrolidone), acetonitrile, HMPA (hexamethylphosphoramide), THF (tetrahydrofuran), ketones such as methyl ethyl ketone (MEK), esters such as ethyl acetate and amyl acetate, halocarbons such as 1,2-dichlorobenzene (ODCB), and the like, and combinations thereof may be found suitable. Preferably, the solvent can have a boiling point of at least 65°C, *e.g.*, at least 70°C, in order to reduce solvent losses in the process. Additionally or alternately, solvents with higher relative boiling points may be desirable in a temperature swing operation, *e.g.*, if the desorption/regeneration is to be carried out at relatively higher temperatures (for instance, with a TSA temperature of at least 100°C, the solvent(s) should typically have a boiling point of at least 100°C, *e.g.*, greater than 110°C). Use of higher boiling point solvents can conserve valuable energy which would otherwise be consumed in solvent vaporization.

[0034] Boiling points for selected solvents herein are tabulated below.

	Boiling Point, °C
Toluene	~110.6
Sulfolane	~285
DMSO	~189
DMF	~153
MEK	~80
Acetonitrile	~81
THF	~66
ODCB	~180.5

[0035] Once the absorbent solution has been formulated, optionally with ingredients such as antioxidants, corrosion inhibitors, and the like, it can be employed in the process.

[0036] When operating with a liquid phase sorbent, the process can be carried out in a two-vessel unit with the liquid sorption medium circulating in a closed loop between a sorption column and a desorption (regeneration) column in a fluidly connected circuit. The sorption column can advantageously be operated in a counter-current flow mode with an stream of the incoming gas passing through an opposite-flowing current of the liquid sorption medium entering at the opposing end of the column. The medium containing the sorbed contaminant can then be passed to the desorption/regeneration column under conditions selected to favor desorption of the sorbed contaminant, *e.g.*, by reduction of pressure and/or increase of temperature. A

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stripping medium such as a non-reactive gas (*e.g.*, N₂ and/or a light hydrocarbon) may be injected to facilitate desorption. Preferably in these embodiments, the sorption medium can be passed in one direction in the desorption column and the desorbed contaminants taken out from one end of the column. The regenerated sorption medium can then be taken out from that one end of the column and recirculated to the proper end of the sorption column for a repeated sorption phase with the incoming gas.

Process Operation

[0037] Apparent selectivity for H₂S sorption can typically be diminished to a certain extent in systems containing both CO₂ and H₂S contaminants, not only by the relative adsorption characteristics of the selected adsorbent material but also by the physical sorption of CO₂ in both liquid and solid systems which becomes more perceivable at higher pressures; generally, the lower the partial pressures of both H₂S and CO₂, the greater the tendency can be toward selectivity for H₂S. With the guanidine base sorbent 1,5,7-triazabicyclo[4.4.0]dec-5-ene, for example, the apparent selectivity towards H₂S is approximately 2.2 at around 1 atm and about 5 at around 0.2 bar. The apparent selectivity is a combination of the selectivity for competitive adsorption on the support and the extremely selective (at least 1,000) adsorption at the functionalized sites that are H₂S-selective. Examples of an H₂S-selective functional site can include tertiary amines and other non-protogenic Lewis acid bases. In a preferred embodiment, the functionalized site H₂S selectivity can be greater than 1,000, for example greater than 10,000 or even greater than 100,000. This extremely large site-specific selectivity can impart one or more unique characteristics to the adsorbent, one of which can include capability for removing trace levels of H₂S in streams with relatively high CO₂ concentrations (which, without being bound by theory, is believed to be due to a substantial lack of competition for the H₂S-selective sites. In some embodiments, the H₂S-selective functionalized adsorbent can be used in a swing adsorption process to produce a product with no more than 4 vppm H₂S from a natural gas feed containing at least 5 mol% CO₂ (*e.g.*, from 5 mol% up to 50 mol%, from 5 mol% to 40 mol%, from 5 mol% to 30 mol%, from 5 mol% to 25 mol%, from 5 mol% to 20 mol%, from 5 mol% to 15 mol%, from 5 mol% to 10 mol%, from 10 mol% up to 50 mol%, from 10 mol% to 40 mol%, from 10 mol% to 30 mol%, from 10 mol% to 25

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mol%, from 10 mol% to 20 mol%, from 10 mol% to 15 mol%, from 15 mol% up to 50 mol%, from 15 mol% to 40 mol%, from 15 mol% to 30 mol%, from 15 mol% to 25 mol%, from 15 mol% to 20 mol%, from 20 mol% up to 50 mol%, from 20 mol% to 40 mol%, from 20 mol% to 30 mol%, from 20 mol% to 25 mol%, from 25 mol% up to 50 mol%, from 25 mol% to 40 mol%, or from 25 mol% to 30 mol%) and from 6 vppm to 10,000 vppm H₂S (e.g., from 8 vppm to 10,000 vppm, from 10 vppm to 10,000 vppm, from 15 vppm to 10,000 vppm, from 20 vppm to 10,000 vppm, from 30 vppm to 10,000 vppm, from 50 vppm to 10,000 vppm, from 100 vppm to 10,000 vppm, from 6 vppm to 5000 vppm, from 8 vppm to 5000 vppm, from 10 vppm to 5000 vppm, from 15 vppm to 5000 vppm, from 20 vppm to 5000 vppm, from 30 vppm to 5000 vppm, from 50 vppm to 5000 vppm, from 100 vppm to 5000 vppm, from 6 vppm to 2000 vppm, from 8 vppm to 2000 vppm, from 10 vppm to 2000 vppm, from 15 vppm to 2000 vppm, from 20 vppm to 2000 vppm, from 30 vppm to 2000 vppm, from 50 vppm to 2000 vppm, from 100 vppm to 2000 vppm, from 6 vppm to 1000 vppm, from 8 vppm to 1000 vppm, from 10 vppm to 1000 vppm, from 15 vppm to 1000 vppm, from 20 vppm to 1000 vppm, from 30 vppm to 1000 vppm, from 50 vppm to 1000 vppm, or from 100 vppm to 1000 vppm). Additionally or alternately, the H₂S-selective functionalized adsorbent can be used in a swing adsorption process to produce a product with no more than 4 vppm H₂S from a natural gas feed containing between 6 vppm and 10,000 vppm H₂S (e.g., from 8 vppm to 10,000 vppm, from 10 vppm to 10,000 vppm, from 15 vppm to 10,000 vppm, from 20 vppm to 10,000 vppm, from 30 vppm to 10,000 vppm, from 50 vppm to 10,000 vppm, from 100 vppm to 10,000 vppm, from 6 vppm to 5000 vppm, from 8 vppm to 5000 vppm, from 10 vppm to 5000 vppm, from 15 vppm to 5000 vppm, from 20 vppm to 5000 vppm, from 30 vppm to 5000 vppm, from 50 vppm to 5000 vppm, from 100 vppm to 5000 vppm, from 6 vppm to 2000 vppm, from 8 vppm to 2000 vppm, from 10 vppm to 2000 vppm, from 15 vppm to 2000 vppm, from 20 vppm to 2000 vppm, from 30 vppm to 2000 vppm, from 50 vppm to 2000 vppm, from 100 vppm to 2000 vppm, from 6 vppm to 1000 vppm, from 8 vppm to 1000 vppm, from 10 vppm to 1000 vppm, from 15 vppm to 1000 vppm, from 20 vppm to 1000 vppm, from 30 vppm to 1000 vppm, from 50 vppm to 1000 vppm, or from 100 vppm to 1000 vppm), while losing less than 5 mol% of the methane in the natural gas feed (e.g., typically less methane than H₂S, but in any event from 4

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ppm to 4.5 mol% CO₂, from 4 ppm to 4 mol%, from 4 ppm to 3.5 mol%, from 4 ppm to 3 mol%, from 4 ppm to 2.5 mol%, from 4 ppm to 2 mol%, from 4 ppm to 1.5 mol%, from 4 ppm to 1 mol%, from 4 ppm to 0.5 mol%, from 4 ppm to 1000 ppm, from 4 ppm to 500 ppm, from 4 ppm to 300 ppm, from 4 ppm to 200 ppm, from 4 ppm to 100 ppm, from 10 ppm to 4.5 mol%, from 10 ppm to 4 mol%, from 10 ppm to 3.5 mol%, from 10 ppm to 3 mol%, from 10 ppm to 2.5 mol%, from 10 ppm to 2 mol%, from 10 ppm to 1.5 mol%, from 10 ppm to 1 mol%, from 10 ppm to 0.5 mol%, from 10 ppm to 1000 ppm, from 10 ppm to 500 ppm, from 10 ppm to 300 ppm, from 10 ppm to 200 ppm, from 10 ppm to 100 ppm, from 50 ppm to 4.5 mol% CO₂, from 50 ppm to 4 mol%, from 50 ppm to 3.5 mol%, from 50 ppm to 3 mol%, from 50 ppm to 2.5 mol%, from 50 ppm to 2 mol%, from 50 ppm to 1.5 mol%, from 50 ppm to 1 mol%, from 50 ppm to 0.5 mol%, from 50 ppm to 1000 ppm, from 50 ppm to 500 ppm, from 50 ppm to 300 ppm, from 50 ppm to 200 ppm, or from 50 ppm to 100 ppm) to the H₂S-rich reject (contaminant) stream.

[0038] To achieve relatively high H₂S selectivity over CO₂, desorption may be carried out in a two step sequence in which the desorption conditions in the first step favor release of the CO₂ physisorbed on the support and those in the second step favor release of the H₂S chemisorbed at the functionalized sites. In a pressure swing operation, this would mean that a reduction of overall pressure such that the CO₂ partial pressure (in a separate vessel for a liquid process) is dropped low enough that its physisorption is disfavored, thus releasing a CO₂ rich stream, followed by the second step where a further pressure swing is used to release an H₂S rich stream. In this manner the physisorption of CO₂, which can potentially lower H₂S selectivity, may be circumvented allowing highly selective removal of H₂S in the presence of CO₂ under relatively higher pressure conditions.

[0039] The process may be operated according to conventional operating procedures appropriate to the process variant in use. It may be operated as a conventional PSA (cPSA) or TSA process, purge desorption (purge with inert gas such as nitrogen, which is not adsorbed), displacement purge (displacement with a competitively adsorbed species), or as a combination of these process variants. It may be operated as one of the rapid cycle variants (cycle time for a complete sorption/desorption cycle less than about two minutes, e.g., less than about one minute),

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including partial pressure swing or displacement purge adsorption (PPSA), rapid cycle pressure swing adsorption (RCPSA), Dual Bed (or Duplex) PSA Process, rapid cycle partial pressure swing, displacement purge adsorption (RCPPSA) technologies, or rapid cycle thermal swing adsorption (RCTSA) with rapid cycle variants using a solid phase sorbent system. Selection of conditions can frequently be dictated by the conditions (*e.g.*, pressure and flow rate of the entering gas stream, proportion and type of contaminants, and desired pressure for the effluent product stream), with the most appropriate conditions selected on an empirical basis.

[0040] Adsorptive kinetic separation processes, apparatuses, and systems, as described above, are useful for development and production of hydrocarbons, such as gas and oil processing. Particularly, the provided processes, apparatuses, and systems can be useful for the rapid, large scale, efficient separation of a variety of target gases from gas mixtures.

[0041] The provided processes, apparatuses, and systems may be used to prepare natural gas products by removing contaminants. The provided processes, apparatuses, and systems can be useful for preparing gaseous feed streams for use in utilities, including separation applications such as dew point control, sweetening/detoxification, corrosion protection/control, dehydration, heating value, conditioning, and purification. Examples of utilities that utilize one or more separation applications can include generation of fuel gas, seal gas, non-potable water, blanket gas, instrument and control gas, refrigerant, inert gas, and hydrocarbon recovery. Exemplary "not to exceed" product (or "target") acid gas removal specifications can include: (a) 2 vol% CO₂, 4 ppm H₂S; (b) 50 ppm CO₂, 4 ppm H₂S; or (c) 1.5 vol% CO₂, 2 ppm H₂S.

[0042] The provided processes, apparatuses, and systems may be used to remove acid gas from hydrocarbon streams. Acid gas removal technology becomes increasingly important as remaining gas reserves exhibit higher concentrations of acid (sour) gas resources. Hydrocarbon feed streams can vary widely in amount of acid gas, such as from several parts per million to 90 vol%. Non-limiting examples of acid gas concentrations from exemplary gas reserves can include concentrations of at least: (a) 1 vol% H₂S, 5 vol% CO₂; (b) 1 vol% H₂S, 15 vol% CO₂; (c) 1 vol% H₂S, 60 vol% CO₂; (d) 15 vol% H₂S, 15 vol% CO₂; or (e) 15 vol% H₂S, 30 vol% CO₂.

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[0043] One or more of the following may be utilized with the processes, apparatuses, and systems provided herein, to prepare a desirable product stream, while maintaining relatively high hydrocarbon recovery:

(a) using one or more kinetic swing adsorption processes, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA), and partial pressure swing or displacement purge adsorption (PPSA), including combinations of these processes; each swing adsorption process may be utilized with rapid cycles, such as using one or more rapid cycle pressure swing adsorption (RC-PDS) units, with one or more rapid cycle temperature swing adsorption (RC-TSA) units or with one or more rapid cycle partial pressure swing adsorption (RC-PPSA) units; exemplary kinetic swing adsorption processes are described in U.S. Patent Application Publication Nos. 2008/0282892, 2008/0282887, 2008/0282886, 2008/0282885, and 2008/0282884, which are each herein incorporated by reference in its entirety;

(b) removing acid gas with RC-TSA using advanced cycles and purges as described in U.S. Provisional Application No. 61/447,858, filed March 1, 2011, as well as the U.S. Patent Application bearing docket number 2011EM060-US2, claiming priority thereto, which are together incorporated by reference herein in their entirety;

(c) using a mesopore filler to reduce the amount of trapped methane in the adsorbent and increase the overall hydrocarbon recovery, as described in U.S. Patent Application Publication Nos. 2008/0282892, 2008/0282885, and 2008/0282886, each of which is herein incorporated by reference in its entirety;

(d) choosing an appropriate adsorbent materials to provide high selectivity and reduce/minimize adsorption (and losses) of methane and other hydrocarbons, such as one or more of the zeolites described in U.S. Patent Application Publication Nos. 2008/0282887 and 2009/0211441, each of which is herein incorporated by reference in its entirety;

(e) depressurizing one or more RC-PSA units in multiple steps to intermediate pressures so that the acid gas exhaust can be captured at a higher average pressure, thereby decreasing the compression required for acid gas injection; pressure levels for the intermediate depressurization steps may be matched to the interstage pressures of the acid gas compressor to optimize the overall compression system;

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(f) using exhaust or recycle streams to minimize processing and hydrocarbon losses, such as using exhaust streams from one or more RC-PSA units as fuel gas instead of re-injecting or venting;

(g) using multiple adsorbent materials in a single bed to remove trace amounts of first contaminants, such as H_2S , before removal of a second contaminant, such as CO_2 ; such segmented beds may provide rigorous acid gas removal down to ppm levels with RC-PSA units with minimal purge flow rates;

(h) using feed compression before one or more RC-PSA units to achieve a desired product purity;

(j) contemporaneous removal of non-acid gas contaminants such as mercaptans, COS, and BTEX; selection processes and materials to accomplish the same;

(k) using structured adsorbents for gas-solid contactors to minimize pressure drop compared to conventional packed beds;

(l) selecting a cycle time and cycle steps based on adsorbent material kinetics; and

(m) using a process and apparatus that uses, among other equipment, two RC-PSA units in series, wherein the first RC-PSA unit cleans a feed stream down to a desired product purity and the second RC-PSA unit cleans the exhaust from the first unit to capture methane and maintain high hydrocarbon recovery; use of this series design may reduce the need for a mesopore filler.

[0044] The processes, apparatuses, and systems provided herein can be useful in large gas treating facilities, such as facilities that process more than five million standard cubic feet per day (MSCFD) of natural gas, for example more than 15 MSCFD, more than 25 MSCFD, more than 50 MSCFD, more than 100 MSCFD, more than 500 MSCFD, more than one billion standard cubic feet per day (BSCFD), or more than two BSCFD.

[0045] Compared to conventional technology, the provided processes, apparatuses, and systems can require lower capital investment, lower operating cost, and/or less physical space, thereby enabling implementation offshore and in remote locations, such as arctic environments. The provided processes, apparatuses, and systems can provide

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the foregoing benefits, while providing high hydrocarbon recovery as compared to conventional technology.

[0046] Additionally or alternately, the invention can comprise one or more of the following embodiments.

[0047] Embodiment 1. A cyclic process for selectively separating H₂S from a feed gas mixture comprising CO₂ and H₂S, which process comprises: a) contacting the feed gas mixture under sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound which reacts with at least a portion of the H₂S in the feed gas mixture; b) sorbing the H₂S into/onto the sorbent; c) subjecting the sorbent to desorption conditions by which at least a portion of the sorbed H₂S is desorbed; and d) retrieving an H₂S-rich product stream that has a higher mol% of H₂S than the feed gas mixture.

[0048] Embodiment 2. A process according to embodiment 1 in which the basic nitrogenous compound comprises a tertiary amine (*e.g.*, triethylamine, triethanolamine, and/or methyldiethanolamine), an amidine, a guanidine, a biguanidine, or a combination thereof.

[0049] Embodiment 3. A process according to embodiment 1 or embodiment 2 in which the basic nitrogenous compound is supported on a porous solid (*e.g.*, a mesoporous and/or macroporous solid oxide such as silica, including MCM-41, MCM-48, SBA-1, SBA-2, SBA-3, SBA-15, KIT-1, KIT-5, KIT-6, and combinations thereof).

[0050] Embodiment 4. A process according to embodiment 3 in which the basic nitrogenous compound is grafted onto the porous solid by chemical reaction.

[0051] Embodiment 5. A process according to any one of the previous embodiments, wherein the sorption and desorption steps are conducted at different temperatures and/or wherein the sorption and desorption steps are conducted at different pressures, such that one or more of (a) the total pressure of the desorption step is lower than the total pressure of the sorption step, (b) the partial pressure of H₂S in the desorption step is less than the partial pressure of H₂S in the sorption step, and (c) the pressure in the sorption step is such as to cause CO₂ to be sorbed from the gas stream in addition to the H₂S.

[0052] Embodiment 6. A process according to any of the previous embodiments in which at least a portion of the sorbed H_2S is desorbed by a non-sorbing inert purge gas and/or by a displacement purge gas.

[0053] Embodiment 7. A process according to any one of the previous embodiments in which desorption is carried out in at least two steps under conditions of different pressure in each step with the pressure of the first desorption step being higher than the pressure of the second desorption step so that most of the CO_2 sorbed in the sorption step is desorbed in the first desorption step and most of the H_2S absorbed in the sorption step is desorbed in the second desorption step.

[0054] Embodiment 8. A process according to any one of the previous embodiments in which the process is operated cyclically between the sorption and desorption conditions with a total cycle time of less than one minute.

[0055] Embodiment 9. A process to any one of the previous embodiments in which the CO_2 and H_2S partial pressures during the sorption step are less than about 1 bar.

[0056] Embodiment 10. A process to any one of the previous embodiments in which the feed gas mixture contains less than 5 mol% water.

[0057] Embodiment 11. A process according to any one of the previous embodiments further comprising a step of retrieving a feed gas product stream that has a lower content of H_2S than in the feed gas mixture, wherein (a) the feed gas mixture contains from about 10 vppm to about 10,000 vppm H_2S and the feed gas product stream contains less than about 4 vppm H_2S and/or (b) the feed gas mixture contains at least 5 mol% CO_2 and the feed gas product stream contains at most 5 mol% less CO_2 than the feed gas mixture.

[0058] Embodiment 12. A cyclic process for selectively separating H_2S from a natural gas feed stream comprising H_2S and CO_2 , which process comprises: (i) contacting the natural gas feed stream under H_2S sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound; (ii) reacting at least a portion of the H_2S in the natural gas feed stream with the sorbent so that the H_2S is absorbed by the sorbent; (iii) retrieving a natural gas product stream; (iv) subjecting the sorbent containing the sorbed H_2S to desorption conditions by which at least a portion of the H_2S in the sorbent is desorbed from the sorbent; (v) retrieving

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an H₂S rich product stream that has a higher mol% of H₂S than the natural gas feed stream; (vi) passing at least a portion of the H₂S-rich product stream to a Claus plant; and (vii) recovering sulfur from the H₂S in the side stream, wherein the natural gas product stream has a lower content of H₂S in mol% than the natural gas feed stream, and wherein optionally a greater mol% of H₂S is sorbed by the basic compound than CO₂ sorbed by the sorbent.

[0059] Embodiment 13. A process according to embodiment 12 wherein (a) the natural gas feed stream contains from about 10 vppm to about 10,000 vppm H₂S and the natural gas product stream contains less than about 4 vppm H₂S and/or (b) the natural gas feed stream contains at least 5 mol% CO₂ and the natural gas product stream contains at most 5 mol% less CO₂ than the natural gas feed stream.

[0060] Embodiment 14. A process according to embodiment 12 or embodiment 13 wherein the sorption and desorption steps are conducted at different temperatures and/or wherein the sorption and desorption steps are conducted at different pressures, such that one or more of (a) the total pressure of the desorption step is lower than the total pressure of the sorption step, (b) the partial pressure of H₂S in the desorption step is less than the partial pressure of H₂S in the sorption step, and (c) the pressure in the sorption step is such as to cause CO₂ to be sorbed from the gas stream in addition to the H₂S.

[0061] Embodiment 15. A cyclic process for separating H₂S and CO₂ from a natural gas feed stream comprising H₂S and CO₂, from a producing formation, which process comprises: (i) contacting the natural gas feed stream under H₂S sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound; (ii) reacting at least a portion of the H₂S and CO₂ in the natural gas feed stream with the sorbent so that the H₂S and the CO₂ are absorbed by the sorbent; (iii) retrieving a natural gas product stream; (iv) subjecting the sorbent containing the sorbed H₂S and CO₂ to first desorption conditions by which a higher mol% of CO₂ is desorbed than H₂S; (v) retrieving a CO₂ rich product stream that has a higher mol% of CO₂ than the natural gas feed stream; (vi) subjecting the sorbent containing the sorbed H₂S and CO₂ to second desorption conditions by which a higher mol% of H₂S is desorbed than CO₂; (vii) retrieving an H₂S-rich product stream that has a higher mol% of H₂S than the natural gas feed stream; and (viii) re-injecting the side stream

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comprising CO₂ into the producing formation, wherein the natural gas product stream has a lower mol% of each H₂S and CO₂ than the natural gas feed stream.

[0062] Embodiment 16. A process according to embodiment 15 further comprising: sending at least a portion of the H₂S-rich stream to a Claus plant; and recovering sulfur from the H₂S-rich stream.

[0063] Embodiment 17. A cyclic process for separating H₂S and CO₂ from a feed gas stream comprising H₂S and CO₂, to produce a first product gas stream comprising H₂S and a second product gas stream comprising CO₂ depleted in H₂S, which process comprises: (i) contacting the feed gas stream under H₂S sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound; (ii) reacting at least a portion of the H₂S and the CO₂ in the feed gas stream with the sorbent so that the H₂S and CO₂ are absorbed by the sorbent; (iii) subjecting the sorbent containing the absorbed H₂S and CO₂ to CO₂ desorption conditions by which a higher mol% of the CO₂ is desorbed than H₂S; (iv) retrieving a CO₂ rich product stream that has a higher mol% of CO₂ than the feed gas stream; (v) subjecting the sorbent containing the absorbed H₂S and CO₂ to H₂S desorption conditions by which a higher mol% of H₂S is desorbed than CO₂; and (vi) retrieving an H₂S rich product stream that has a higher mol% of H₂S than the feed gas stream.

[0064] Embodiment 18. A process according to embodiment 17 in which the CO₂ rich product stream has a lower mol% of H₂S than the feed gas stream and/or in which at least a portion of the H₂S-rich product stream is passed to a Claus plant for the recovery of sulfur.

[0065] Embodiment 19. A process according to embodiment 18 in which the feed gas stream comprises at least a combined total of 50 mol% H₂S and CO₂, wherein the feed gas stream is a pre-separated contaminant stream resulting from the separation of H₂S and CO₂ from a natural gas stream from a producing formation and the CO₂-rich stream is re-injected into the producing formation.

EXAMPLES

Example 1

Synthesis of amine-grafted mesoporous silicas

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[0066] Mesoporous silica supports were prepared according to methods known in the literature or were purchased from commercial sources. Aminosilanes were either purchased from commercial sources or, in the case of the TBD and THP silanes (below), synthesized by the reaction of the cyclic amine with 1-trimethoxysilyl-3-iodopropane.

[0067] Amines were grafted to the mesoporous silica supports by heating an excess of the appropriated amine-silane with the support in toluene at elevated temperature. A typical preparation using MCM-48 is given below.

Synthesis of dimethylaminopropyl-functionalized MCM-48

[0068] MCM-48 was dried at ~200°C in air overnight (~10-16 hours). About 20 g dry MCM-48 was dispersed in ~120 mL toluene and stirred to disperse the solid. About 20 g of (N,N-dimethylaminopropyl)trimethoxysilane (CAS 2530-86-1) was added and the mixture stirred at ~85°C for about 18 hours. The solid was isolated by filtration, washed with toluene, and dried at ~80 °C for about 4 hours.

[0069] The amine reagents used were:

Reagent	CAS #
DMA	(N,N-Dimethylaminopropyl)trimethoxysilane 2530-86-1
TBD	1-(3-trimethoxysilylpropyl)-[1,5,7-triazabicyclo[4.4.0]dec-5-ene]
THP	1-(3-trimethoxysilylpropyl)-[1,4,5,6-tetrahydropyrimidine]

[0070] The amine-grafted silicas were characterized by X-ray diffraction. In all cases the structure of the support was maintained after grafting. Nitrogen isotherms were measured at ~77°K after outgassing at ~100°C to determine BET surface areas and pore volumes. Samples were analyzed for carbon, nitrogen, and ash to determine loading of organic. The loading is quoted in mmol amine/g SiO₂, determined from the %N and %SiO₂ results. CO₂ capacities were measured at ~0.1 bar CO₂ after outgassing at ~120°C in either a gravimetric or volumetric apparatus.

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[0071] The properties of the amine-modified silicas were:

Amine Amount (g)	Support Description	%C	%N	mmol/ g SiO ₂	SA (m ² /g)	PV (cc/g)	CO ₂ @ 0.1 bar (mmol/g)
27	DMA - MCM-48	12.2	2.46	2.21	747	0.603	0.059 0.048
12.36	DMA - SBA-15	8.19	1.75	1.51	428	0.569	
6.1	DMA - KIT-6	8.23	1.89	1.62	363	0.548	
2	TBD- MCM-48	19.3	6.75	2.99	11	0.031	
1.01	TBD - Davisil 634 [®]	10.9	3.56	1.12	154	0.556	
1.89	TBD - MCM-48	19.4	6.67	2.91	17	0.035	
1.5	THP - MCM-48	16.5	5.66	3.15	356	0.241	

[0072] The DMA-functionalized MCM-48 adsorbed very little CO₂ at ambient temperature, comparable to the physisorption for CO₂ shown by ungrafted MCM-48 as the amino group in this material is tertiary and non-protogenic. Without being bound by theory, the low surface area and pore volume of the TBD-functionalized MCM-48 may be attributed to pore blocking by the bulky reactant, implying that the relative dimensions of the modifier could be adjusted in accordance with the pore dimensions of the support material. The retention of pore volume with Davisil 634[®] (surface area ~480 m²/g) demonstrated that even relatively bulky modifiers may be used with appropriately dimensioned support materials.

Example 2

CO₂ Adsorption with protogenic amines

[0073] For comparison, mesoporous supports were modified in the same way as described in Example 1 with two protogenic amines: trimethoxy[3-(methylamino) propyl] silane (MA – CAS 3069-25-8) and 3-(trimethoxysilyl)propylamine (APTS, CAS 13822-56-5). The properties of the modified silicas were then determined as described in Example 1 with the following results:

Amine Amount (g)	Support Description	%C	%N	mmol/ g SiO ₂	SA (m ² /g)	PV (cc/g)	CO ₂ @ ~0.1 bar (mmol/g)
6.12	MA - KIT-6	9.73	2.43	2.11	309	0.456	-
6.53	MA - SBA-15	9.14	2.48	2.19	490	0.676	0.390
13.2	MA - MCM-48	10.7	2.85	2.63	668	0.584	0.373
6.52	APTS - MCM-48	9.27	2.67	2.35	407	0.611	0.470

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[0074] Comparison of the CO₂ adsorption values immediately above shows that the use of non-protogenic amine modification as in Example 1 resulted in significantly decreased affinity for CO₂, compared to the CO₂ adsorption with protic amines (nearly an order of magnitude lower than with the materials of Example 2).

Example 3

[0075] The following adsorption isotherms of H₂S and CO₂ in the guanidine base 1,5,7-triazabicyclo[4.4.0]dec-5-ene(TBD) on an MCM-48 support prepared as described in Example 1, were determined:

1. CO₂ adsorption isotherm taken on the fresh sample (after vacuum desorption at ~120°C).
2. H₂S adsorption isotherm (also after vacuum desorption at ~120°C).
3. A second CO₂ isotherm taken after the H₂S measurements and also after vacuum desorption at ~120°C.
4. To confirm the results of the CO₂ adsorption isotherm on the fresh sample at relatively low pressures, the isotherm was determined on a fresh sample using an Autosorb analyzer at pressures up to ~1 bar.

[0076] The isotherms are shown in Figure 2 and demonstrated that, in the often important pressure region below ~1 barg (pressure in bar gauge), the apparent selectivity of H₂S over CO₂ was significant and that, with increasing pressure, the selectivity increased slowly but progressively to pressures of ~5 barg. The apparent selectivity seen in Figure 2 was believed to be due (without being bound by theory) to a combination of adsorption on the support and the extremely selective H₂S adsorption at the functionalized sites. The lower CO₂ capacity observed in the isotherm for CO₂ after H₂S adsorption may be due (again, without being bound by theory) to the ~120°C desorption not completely removing the H₂S.

Example 4

[0077] Dimethylaminopropyl-functionalized KIT-6 was prepared in the same manner as described in Example 1 using a KIT-6 silica support. The adsorption isotherms of H₂S and CO₂ on the functionalized KIT-6 were determined and are shown in Figure 3.

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1. H₂S adsorption isotherm taken on the fresh sample (after vacuum pretreatment at ~120°C).
2. CO₂ adsorption isotherms taken before H₂S measurements and also after H₂S measurements which were followed by vacuum desorption at ~120°C.
3. H₂S adsorption isotherm repeat after vacuum desorption of H₂S at ~120°C.
4. H₂S adsorption isotherm repeat after vacuum desorption H₂S at ~25°C.
5. H₂S adsorption isotherm repeat after vacuum desorption H₂S at ~120°C.

[0078] The results show that the non-protogenic system was notably more selective for H₂S adsorption than for CO₂. In addition to selectivity for H₂S both at very low as well as higher pressures, this Example shows that approximately 65% of the original H₂S capacity can be regained by using pressure swing desorption conditions only, without applying any temperature swing. No significant change in CO₂ adsorption was seen after the material sorbed H₂S (note closeness of curves designated “No. 2” in Figure 3). These features are highly beneficial for using these amines for H₂S removal.

Example 5

[0079] The adsorption isotherms of H₂S and CO₂ on DMA-functionalized SBA-15 were investigated further using the same methodology to determine the H₂S adsorption isotherm on the fresh sample (after vacuum pretreatment at ~120°C) and the CO₂ adsorption isotherms before and after H₂S measurement.

[0080] The results in Figure 4 show that, despite the fact that the same amine has been attached to the support surface, the material exhibited lower selectivity to H₂S and lower H₂S and CO₂ sorption capacities overall, as compared to KIT-6. The isotherms on this SBA-15 were qualitatively different from both the case of a non-functionalized open silica surface and the same amine grafted on KIT-6 support, with a potential disadvantage that the capacities were relatively lower. This result was unexpected, because the initial SBA-16 and KIT-6 supports had very similar pore structure

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parameters (surface area, pore volume, and pore size) and were given similar amine loadings (in moles of N per gram of the material). Without being bound by theory, it is possible that the differences with KIT-6 can be attributed to the fact that SBA-15 is not only mesoporous but also microporous: SBA-15 is a 1D mesoporous structure with microporous pore walls while KIT-6 has a highly accessible and highly connected three-dimensional structure (3D), which can be beneficial for achieving uniform functionalization and for the resulting sorption properties. Different functional groups can, however, be attached to SBA-15 and other support materials in a different way, which may affect their adsorption properties, notably the H₂S/CO₂ selectivity.

Example 6

[0081] To demonstrate the ability of the adsorbent to remove trace levels of H₂S from streams with high concentrations of CO₂, a breakthrough experiment was constructed. In this experiment, a stream with ~5 mol% CO₂, ~72 ppm H₂S, and the balance methane was flowed through an adsorbent bed containing an H₂S-selective DMA (dimethylaminopropyl) material on KIT-6 adsorbent made according to procedures described in Example 2. For the breakthrough experiment, a ~1/8" tube was packed with ~0.2 grams of the functionalized adsorbent. To condition the adsorbent, the sample was initially pretreated at about 120°C in a flowing helium stream. This pretreatment is not necessarily required but was conducted to simplify interpretation of the breakthrough experiments. Breakthrough experiments were conducted at ~40°C by switching from a helium flow to a feed containing ~5 mol% CO₂, ~72 vppm H₂S, and the balance methane. The feed and helium were flowed through the bed at ~5 cm³/min, and the bed pressure was about 1 bara to about 2 bara (bar absolute). Figure 5 shows the results of the initial breakthrough experiment, as well as a repeat that was conducted after regenerating with a purge and no 120°C pretreatment. It can be seen that the relatively high concentration (~5 mol%) of CO₂ broke through the bed within about the first 120 seconds. When this rise occurred, the CO₂ adsorption front can be said to have passed substantially (entirely) through the bed. The H₂S adsorption front did not break through the bed until about 600 seconds after the start of the experiment. When H₂S broke through the bed, its concentration rose rapidly, showing that the H₂S had a relatively sharp adsorption front in the bed,

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whereas, at times less than about 400 seconds, the H_2S concentration in the effluent was undetectable by gas chromatography methods (less than ~ 1 vppm). This breakthrough experiment validates the concept of an adsorption process to remove H_2S from a relatively high concentration of CO_2 . The bed can be regenerated with either a purge or thermally. In this experiment, the bed was not heated during regeneration and was purged with pure methane with the bed remaining at about 40°C . The time evolution of CO_2 and H_2S coming from the bed is shown in Figure 6. The agreement between the first and second adsorption/desorption cycles are shown in both Figures 5 and 6.

Example 7

[0082] To further demonstrate the ability of the adsorbent to remove trace levels of H_2S from streams with high concentrations of CO_2 , a breakthrough experiment with a different H_2S -selective adsorbent was run. In this experiment, a mass spectrometer was used to assay the composition of the effluent from the bed (in Example 6, compositions were analyzed using gas chromatography). After switching from flowing He, a feed stream containing ~ 5 mol% CO_2 and about 262 vppm H_2S , a relatively small concentration (less than 100 vppm) of COS, and the balance methane, was flowed through an adsorbent bed containing an H_2S -selective adsorbent (in this case, DMA supported on an SBA-15 silica made according to procedures described in Example 2). For the breakthrough experiment, a $\sim 1/8$ " tube was packed with ~ 0.25 grams of the functionalized adsorbent. To condition the adsorbent, the sample was initially pretreated at about 120°C in a flowing helium stream. This pretreatment is not necessarily required but was conducted to simplify interpretation of the breakthrough experiments. Breakthrough experiments were conducted at $\sim 40^\circ\text{C}$ by switching at about 2.5 minutes from the helium flow to the feed containing ~ 5 mol% CO_2 , ~ 262 vppm H_2S , a relatively small concentration (less than 100 vppm) of COS, and the balance methane. The feed and helium were flowed through the bed at ~ 5 cm^3/min , and the bed pressure was about 1 bara to about 2 bara (bar absolute). Figure 7 shows the results of the initial breakthrough experiment. It can be seen that, shortly after the feed begins flowing through the bed, the CO_2 in the effluent from the bed rose to $\sim 100\%$ of the initial CO_2 concentration in the feed (~ 5 mol%). When this rise

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occurred, the CO₂ adsorption front can be said to have passed substantially (entirely) through the bed. The H₂S adsorption front, however, did not break through the bed until about 16 minutes after the start of the experiment, at which point the H₂S concentration gradually rose to ~100% of the initial H₂S concentration in the feed (~262 vppm). At times less than ~16 minutes, the H₂S concentration in the effluent was observed by mass spectrometric methods to be less than about 1 vppm. The regeneration of the bed can be undertaken thermally and/or with a purge. Data showing CO₂ and H₂S effluent concentrations overlaid from four sequential methane purge regenerations at ~40°C following repeated breakthrough experiments is shown in Figure 8 (in which a value of ~100% corresponds to effluent concentrations of ~5 mol% for CO₂ and ~262 vppm for H₂S).

Example 8

[0083] To demonstrate that the H₂S-selective adsorbents can still function in a modest concentration of water, the adsorbent used in the breakthrough experiment of Example 7 was rerun with but about 420 vppm water vapor was added to the feed in place of some of the methane (*i.e.*, ~5 mol% CO₂, ~262 vppm H₂S, less than 100 vppm COS, ~420 vppm water, and the balance methane; same sorbent; same analysis technique). For this breakthrough experiment, a ~1/8" tube was packed with ~0.16 grams of the functionalized adsorbent. To condition the adsorbent, the sample was initially pretreated at about 120°C in a flowing helium stream. This pretreatment is not necessarily required but was conducted to simplify interpretation of the breakthrough experiments. Breakthrough experiments were conducted at ~40°C by switching at about 2.5 minutes from the helium flow to the feed. The feed and helium were flowed through the bed at ~5.4 cm³/min, and the bed pressure was about 1 bara to about 2 bara (bar absolute). Figure 9 shows the results of the breakthrough experiment, overlaid with the results from Example 7. It can be seen in both sets of experimental data that, shortly after the feed begins flowing through the bed, the CO₂ in the effluent from the bed rose to ~100% of the initial CO₂ concentration in the feed (~5 mol%). When this rise occurred, the CO₂ adsorption front can be said to have passed substantially (entirely) through the bed. In the experiment with the water-containing feed, the H₂S adsorption front broke through the bed after about 9 minutes after the start of the

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experiment (as opposed to at about 16 minutes without water in Example 7), at which point the H_2S concentration gradually rose to ~100% of the initial H_2S concentration in the feed (~262 vppm). Without being bound by theory, it is noted that there was a slight difference in the amount of sorbent material and in the flow rate between Example 8 and Example 7, and thus it is possible that the difference in the breakthrough times for the two experiments may be at least partially due to those factors. Before breakthrough, the H_2S concentration in the effluent was observed by mass spectrometric methods to be less than about 1 vppm. Figure 9 shows that water vapor broke through the bed at a later time at which point the H_2O concentration gradually rose to ~100% of the initial water concentration in the feed (~420 vppm). The regeneration of the bed can be undertaken thermally and/or with a purge.

CLAIMS:

1. A cyclic process for selectively separating H_2S from a feed gas mixture comprising CO_2 and H_2S , which process comprises:
 - a) contacting the feed gas mixture under sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound which reacts with at least a portion of the H_2S in the feed gas mixture;
 - b) sorbing the H_2S into/onto the sorbent;
 - c) subjecting the sorbent to desorption conditions by which at least a portion of the sorbed H_2S is desorbed; and
 - d) retrieving an H_2S -rich product stream that has a higher mol% of H_2S than the feed gas mixture.
2. A process according to Claim 1 in which the basic nitrogenous compound comprises a tertiary amine (*e.g.*, triethylamine, triethanolamine, and/or methyldiethanolamine), an amidine, a guanidine, a biguanidine, or a combination thereof.
3. A process according to claim 1 or claim 2 in which the basic nitrogenous compound is supported on a porous solid (*e.g.*, a mesoporous and/or macroporous solid oxide such as silica, including MCM-41, MCM-48, SBA-1, SBA-2, SBA-3, SBA-15, KIT-1, KIT-5, KIT-6, and combinations thereof).
4. A process according to claim 3 in which the basic nitrogenous compound is grafted onto the porous solid by chemical reaction.
5. A process according to any one of the previous claims, wherein the sorption and desorption steps are conducted at different temperatures and/or wherein the sorption and desorption steps are conducted at different pressures, such that one or more of
 - (a) the total pressure of the desorption step is lower than the total pressure of the sorption step,
 - (b) the partial pressure of H_2S in the desorption step is less than the partial pressure of H_2S in the sorption step, and
 - (c) the pressure in the sorption step is such as to cause CO_2 to be sorbed from the gas stream in addition to the H_2S .

6. A process according to any of the previous claims in which at least a portion of the sorbed H_2S is desorbed by a non-sorbing inert purge gas and/or by a displacement purge gas.

7. A process according to any one of the previous claims in which desorption is carried out in at least two steps under conditions of different pressure in each step with the pressure of the first desorption step being higher than the pressure of the second desorption step so that most of the CO_2 sorbed in the sorption step is desorbed in the first desorption step and most of the H_2S absorbed in the sorption step is desorbed in the second desorption step.

8. A process according to any one of the previous claims in which the process is operated cyclically between the sorption and desorption conditions with a total cycle time of less than one minute.

9. A process to any one of the previous claims in which the CO_2 and H_2S partial pressures during the sorption step are less than about 1 bar.

10. A process to any one of the previous claims in which the feed gas mixture contains less than 5 mol% water.

11. A process according to any one of the previous claims further comprising a step of retrieving a feed gas product stream that has a lower content of H_2S than in the feed gas mixture, wherein (a) the feed gas mixture contains from about 10 vppm to about 10,000 vppm H_2S and the feed gas product stream contains less than about 4 vppm H_2S and/or (b) the feed gas mixture contains at least 5 mol% CO_2 and the feed gas product stream contains at most 5 mol% less CO_2 than the feed gas mixture.

12. A cyclic process for selectively separating H_2S from a natural gas feed stream comprising H_2S and CO_2 , which process comprises:

(i) contacting the natural gas feed stream under H_2S sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound;

(ii) reacting at least a portion of the H_2S in the natural gas feed stream with the sorbent so that the H_2S is absorbed by the sorbent;

(iii) retrieving a natural gas product stream;

(iv) subjecting the sorbent containing the sorbed H_2S to desorption conditions by which at least a portion of the H_2S in the sorbent is desorbed from the sorbent;

(v) retrieving an H_2S rich product stream that has a higher mol% of H_2S than the natural gas feed stream;

(vi) passing at least a portion of the H_2S -rich product stream to a Claus plant; and

(vii) recovering sulfur from the H_2S in the side stream, wherein the natural gas product stream has a lower content of H_2S in mol% than the natural gas feed stream, and wherein optionally a greater mol% of H_2S is sorbed by the basic compound than CO_2 sorbed by the sorbent.

13. A process according to claim 12 wherein

(a) the natural gas feed stream contains from about 10 vppm to about 10,000 vppm H_2S and the natural gas product stream contains less than about 4 vppm H_2S and/or

(b) the natural gas feed stream contains at least 5 mol% CO_2 and the natural gas product stream contains at most 5 mol% less CO_2 than the natural gas feed stream.

14. A process according to claim 12 or claim 13 wherein the sorption and desorption steps are conducted at different temperatures and/or wherein the sorption and desorption steps are conducted at different pressures, such that one or more of

(a) the total pressure of the desorption step is lower than the total pressure of the sorption step,

(b) the partial pressure of H_2S in the desorption step is less than the partial pressure of H_2S in the sorption step, and

(c) the pressure in the sorption step is such as to cause CO_2 to be sorbed from the gas stream in addition to the H_2S .

15. A cyclic process for separating H_2S and CO_2 from a natural gas feed stream comprising H_2S and CO_2 , from a producing formation, which process comprises:

(i) contacting the natural gas feed stream under H_2S sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound;

- (ii) reacting at least a portion of the H_2S and CO_2 in the natural gas feed stream with the sorbent so that the H_2S and the CO_2 are absorbed by the sorbent;
- (iii) retrieving a natural gas product stream;
- (iv) subjecting the sorbent containing the sorbed H_2S and CO_2 to first desorption conditions by which a higher mol% of CO_2 is desorbed than H_2S ;
- (v) retrieving a CO_2 rich product stream that has a higher mol% of CO_2 than the natural gas feed stream;
- (vi) subjecting the sorbent containing the sorbed H_2S and CO_2 to second desorption conditions by which a higher mol% of H_2S is desorbed than CO_2 ;
- (vii) retrieving an H_2S -rich product stream that has a higher mol% of H_2S than the natural gas feed stream; and
- (viii) re-injecting the side stream comprising CO_2 into the producing formation, wherein the natural gas product stream has a lower mol% of each H_2S and CO_2 than the natural gas feed stream.

16. A process according to claim 15 further comprising: sending at least a portion of the H_2S -rich stream to a Claus plant; and recovering sulfur from the H_2S -rich stream.

17. A cyclic process for separating H_2S and CO_2 from a feed gas stream comprising H_2S and CO_2 , to produce a first product gas stream comprising H_2S and a second product gas stream comprising CO_2 depleted in H_2S , which process comprises:

- (i) contacting the feed gas stream under H_2S sorption conditions with a non-aqueous sorbent comprising a basic non-protogenic nitrogenous compound;
- (ii) reacting at least a portion of the H_2S and the CO_2 in the feed gas stream with the sorbent so that the H_2S and CO_2 are absorbed by the sorbent;
- (iii) subjecting the sorbent containing the absorbed H_2S and CO_2 to CO_2 desorption conditions by which a higher mol% of the CO_2 is desorbed than H_2S ;
- (iv) retrieving a CO_2 rich product stream that has a higher mol% of CO_2 than the feed gas stream;

(v) subjecting the sorbent containing the absorbed H_2S and CO_2 to H_2S desorption conditions by which a higher mol% of H_2S is desorbed than CO_2 ; and

(vi) retrieving an H_2S rich product stream that has a higher mol% of H_2S than the feed gas stream.

18. A process according to claim 17 in which the CO_2 rich product stream has a lower mol% of H_2S than the feed gas stream and/or in which at least a portion of the H_2S -rich product stream is passed to a Claus plant for the recovery of sulfur.

19. A process according to claim 18 in which the feed gas stream comprises at least a combined total of 50 mol% H_2S and CO_2 , wherein the feed gas stream is a pre-separated contaminant stream resulting from the separation of H_2S and CO_2 from a natural gas stream from a producing formation and the CO_2 -rich stream is re-injected into the producing formation.