

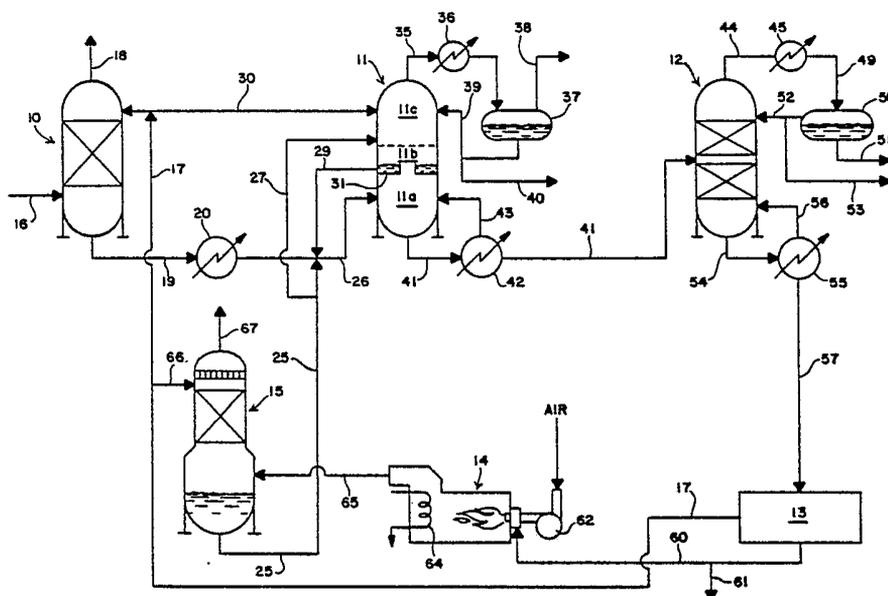


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C01B 17/16	A1	(11) International Publication Number: WO 86/ 02628 (43) International Publication Date: 9 May 1986 (09.05.86)
(21) International Application Number: PCT/US85/02179 (22) International Filing Date: 1 November 1985 (01.11.85) (31) Priority Application Number: 657,809 (32) Priority Date: 4 November 1984 (04.11.84) (33) Priority Country: US (71) Applicant: THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 2199 Addison Street, Berkeley, CA 94270 (US). (72) Inventor: LYNN, Scott ; 2646 San Antonio Drive, Walnut Creek, CA 94598 (US). (74) Agent: GREGG, Edward, B.; Gregg, Caplan & Higgins, 800 Menlo Avenue, Suite 220, Menlo Park, CA 94025 (US).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>

(54) Title: PROCESS FOR REMOVAL OF HYDROGEN SULFIDE FROM GASES**(57) Abstract**

Two stage removal of hydrogen sulfide from a gas. In the first stage solutions of hydrogen sulfide and sulfur dioxide in a solvent react to produce sulfur and water. An excess of hydrogen sulfide is maintained in the first stage resulting in a solution containing sulfur, water and the excess hydrogen sulfide, or resulting in a gas containing the excess hydrogen sulfide. The excess hydrogen sulfide in the solution or in the gas is then treated in a second stage with a solution in the same solvent of sulfur dioxide in excess of or closely equal to that required to react with the hydrogen sulfide. Excess sulfur dioxide in the vapor phase from the second stage may be absorbed in neat solvent. The solvent is selected to have a high solvating power for sulfur dioxide, a lesser but substantial solvating power for hydrogen sulfide and to promote the reaction of hydrogen sulfide with sulfur dioxide. Such gases as natural gas, synthesis gas, and the tail gas of a claus plant may be so treated. By appropriate selection of solvents and/or conditions, accompanying minor components of the gas stream being treated may be removed and recovered if of value, e.g., propane from natural gas, carbon dioxide and water from synthesis gas, etc. The process avoids the need to maintain exact stoichiometric ratios of hydrogen sulfide and sulfur dioxide, it avoids the need to use high flow rates of solvent, a liquid phase capacitance for hydrogen sulfide is provided which dampens the effect of fluctuations in hydrogen sulfide content in the gas stream, etc.



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4 "PROCESS FOR REMOVAL OF HYDROGEN SULFIDE FROM GASES"
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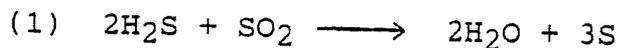
7 BACKGROUND OF THE INVENTION
8

9 1. Field of the Invention
10

11 This invention relates to the removal of hydrogen
12 sulfide from gases.
13

14 2. Description of the Prior Art
15

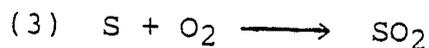
16 One method of removing hydrogen sulfide from a
17 gas, for example from natural gas or from a gas produced in
18 an industrial process, is by absorbing it physically in an
19 organic solvent and then reacting it with a solution of
20 sulfur dioxide in the same solvent in accordance with the
21 following equation:
22



25 The sulfur dioxide may be derived from an outside source,
26 or it may be produced by burning some of the hydrogen
27 sulfide in accordance with the following reaction
28



31 or by burning a part of the sulfur that is produced in
32 Reaction (1) in accordance with the following equation
33



36 A second, related, method of removing hydrogen
37 sulfide from such a gas is by absorbing it chemically in an

- 2 -

1 organic solvent that contains dissolved sulfur dioxide.
2 Reaction (1) then occurs as the hydrogen sulfide is
3 absorbed and may accelerate the absorption process.

4
5 Still a third related method of removing hydrogen
6 sulfide from such a gas is to add sulfur dioxide to the
7 gas and then to contact the gas with an organic solvent.
8 The hydrogen sulfide and sulfur dioxide are absorbed
9 simultaneously and Reaction (1) occurs as absorption takes
10 place.

11
12 In all three of these methods of removing hydrogen
13 sulfide there is only one reaction zone. That zone may or
14 may not correspond with the zone in which gas absorption
15 takes place. Theoretically, if the sulfur dioxide entering
16 the reaction zone is maintained at the exact stoichiometric
17 ratio required by Reaction (1), there will be no excess
18 hydrogen sulfide or sulfur dioxide in the liquid or gas
19 streams leaving the reaction zone. However, it is not
20 possible, as a practical matter, to do this. Among other
21 things either the flow or the hydrogen sulfide content of
22 the gas being treated may vary so that it is necessary to
23 vary the feed of sulfur dioxide to the reaction zone. It
24 is therefore difficult to avoid having residual, unreacted,
25 hydrogen sulfide or sulfur dioxide in either the gas or
26 liquid streams that leave a single reaction zone. The gas
27 stream may then not meet specifications for sulfur
28 species. The presence of hydrogen sulfide or sulfur
29 dioxide may interfere with the recovery of elemental sulfur
30 from the liquid stream. Finally, it may be desired to
31 co-absorb other gas components as well as hydrogen sulfide
32 from the gas stream being treated, and it would then be
33 desirable to recover such gases free of sulfur compounds.
34 Thus all three of the processing methods described above
35 encounter operating problems from unreacted hydrogen
36 sulfide or sulfur dioxide.

37

1 U.S. Patents Nos. 2,881,047; 2,987,379; 3,103,411;
2 3,363,989; 3,953,586 and 4,107,269 and British Patent
3 Publication 2012806, and a paper by Biedermann and Rossarie
4 entitled, "The Solclaus Process: A Direct Sulfur Recovery
5 From Sour Gas" presented at the Cleveland Meeting of The
6 American Institute of Chemical Engineers, August 29 -
7 September 1, 1982, describe various procedures for
8 accomplishing hydrogen sulfide removal by one of the above
9 methods. However, the processes of each of these patents
10 and this publication are lacking in one or more respects
11 with regard to the solution of the problem of adequately
12 removing hydrogen sulfide from gases and converting it to
13 sulfur. For example, U.S. Patent 3,953,586 to Tanimura
14 dissolves hydrogen sulfide from a gas in a solvent such as
15 N-methyl-2-pyrrolidone, then reacts the hydrogen sulfide
16 with sulfur dioxide also dissolved in that solvent. The
17 proportion of hydrogen sulfide and sulfur dioxide in the
18 reactor are such that there is an excess of hydrogen
19 sulfide which leaves in the exiting solution and is removed
20 in a stripper. The hydrogen sulfide removed in the
21 stripper is then burned to produce sulfur dioxide for
22 Reaction (1).

23

24 The Tanimura process requires that one-third of
25 the hydrogen sulfide pass through the reaction zone
26 unreacted, that this excess hydrogen sulfide be stripped
27 from its solvent and burned to produce sulfur dioxide in
28 accordance with Reaction (2), and that the resulting sulfur
29 dioxide be absorbed in the same solvent. This is an
30 energy-intensive process. It also results in the loss of
31 any other gas that is co-absorbed with the hydrogen
32 sulfide.

33

34 Other processes require a precise control over the
35 proportions of hydrogen sulfide and sulfur dioxide in the
36 reaction zone. This is difficult for reasons stated above.

37

1 SUMMARY OF THE INVENTION

2

3 It is an object of the present invention to
4 provide a method of treating a gas containing hydrogen
5 sulfide by a method involving Reaction (1) which avoids
6 or diminishes difficulties which have been encountered
7 heretofore.

8

9 It is a particular object of the invention to
10 provide a method of removing hydrogen sulfide from a gas
11 by means of Reaction (1) which does not depend upon
12 maintaining a stoichiometric ratio of sulfur dioxide to
13 hydrogen sulfide in the reaction zone, which provides a
14 readily managed continuous control of the ratio of
15 reactants and which does not require a large energy input
16 to strip a gas or gases from solution.

17

18 It is a further object of this invention to
19 provide a solvent mixture in which Reaction (1) is very
20 effectively catalyzed by a solvent component of such low
21 volatility and such low concentration that volatile loss of
22 that component is negligible.

23

24 In accordance with the present invention, the
25 difficulties encountered in the prior art are solved by
26 absorbing hydrogen sulfide from a gas in a solvent having
27 the characteristics described below; providing a solution
28 in the same solvent of sulfur dioxide; mixing the two
29 solutions in proportions such that the hydrogen sulfide is
30 in small excess and causing reaction to occur in a first
31 reaction zone; providing a zone of substantial liquid
32 capacitance for hydrogen sulfide to effect a method of
33 damping the fluctuations in hydrogen sulfide concentration
34 in the vapor or liquid streams leaving the first reaction
35 zone; and providing a second reaction zone in which the
36 hydrogen sulfide leaving the first reaction zone reacts
37 substantially to completion according to Reaction (1) with

1 sulfur dioxide solution that has been introduced thereinto.
2 The zone of substantial liquid capacitance for hydrogen
3 sulfide may coincide either with the first reaction zone or
4 with the second reaction zone, or may be separate from
5 both. The hydrogen sulfide leaving the first reaction zone
6 may be transferred directly to the second reaction zone by
7 a stream of vapor or liquid leaving the first reaction zone
8 or, alternatively, may first be stripped from the liquid in
9 which it is dissolved by a vapor stream and then be
10 reabsorbed from that vapor into the liquid in the second
11 reaction zone. The sulfur formed via Reaction (1) in
12 either reaction zone may either remain dissolved in the
13 solvent or precipitate, forming a slurry of crystals in the
14 liquid in the reaction zone. Examples of these methods of
15 employing this invention are illustrated in the following
16 process descriptions.

17
18 BRIEF DESCRIPTION OF THE DRAWINGS

19
20 Certain embodiments of the invention are
21 illustrated by way of example in Figures 1, 2, 3, 4 and 5
22 in which:

23
24 Figure 1 is a flow diagram showing one embodiment
25 of the invention;

26
27 Figure 2 is a similar flow diagram showing an
28 alternative embodiment;

29
30 Figure 3 is a flow diagram of a third embodiment
31 of the invention in which a gas at near-atmospheric
32 pressure that contains hydrogen sulfide such as a Claus
33 process tail gas, is treated;

34
35 Figure 4 is a flow diagram of an embodiment of
36 the invention in which a gas at high pressure, such as
37 synthesis gas, is treated to remove hydrogen sulfide and

1 and also, where present as in synthesis gas, carbon
2 dioxide;

3

4 Figure 5 is a flow diagram similar to Figure 4 but
5 illustrating a modification in which the reaction between
6 hydrogen sulfide and sulfur dioxide is carried out under
7 conditions to cause crystallization of sulfur.

8

9 DETAILED DESCRIPTION OF THE INVENTION

10

11 Referring now to Figure 1 there are shown a
12 hydrogen sulfide absorber 10, a stripper-absorber 11,
13 a solvent dehydrator 12, a sulfur crystallizer 13, a
14 furnace 14, and a sulfur dioxide absorber 15.

15

16 Gas enters absorber 10 through line 16. In the
17 process illustrated it is assumed that this feed gas is
18 natural gas which contains typically about 0.01 to 10
19 percent of hydrogen sulfide and small amounts of water and
20 hydrocarbons higher than methane, chiefly propane and
21 butane. The bulk of the gas is methane and it is desired
22 to remove hydrogen sulfide so that the amount remaining in
23 the treated gas is one part per million or less. In the
24 process illustrated it is also desired to remove water and
25 to separate hydrocarbons higher than ethane. Other feed
26 gases may, if desired, be treated, for example refinery
27 gases from hydrotreating crude oil, synthesis gas obtained
28 from petroleum or coal, and similar hydrogen-sulfide-
29 containing gas streams. Also, the removal of one or
30 more of the minor components such as ethane or higher
31 hydrocarbons may be unnecessary or undesired, but in the
32 case illustrated by Figure 1 it is desired to remove and
33 recover higher hydrocarbons.

34

35 A suitable solvent selected from Table I below
36 enters absorber 10 through line 17. This solvent is
37 selected in accordance with the following criteria: It is

1 a very strong solvent for sulfur dioxide and it has good
2 solvating properties for hydrogen sulfide but less than its
3 solvating property for sulfur dioxide. Solubility of
4 various components of the feed gas in the solvent are as
5 follows: $\text{SO}_2 \gg \text{H}_2\text{S} > \text{COS} > \text{C}_3\text{H}_8$. Further, the solvent
6 is selected to promote Reaction (1). Criteria of the
7 solvent are further elaborated below.

8
9 Suitable contacting equipment such as various
10 commercially available trays or packing may be employed to
11 promote contact between the feed gas and the solvent in
12 absorber 10. The process is conducted so that the gas
13 leaving through line 18 has an acceptably low content of
14 hydrogen sulfide, e.g. one ppm or less.

15
16 The treatment in absorber 10 is at a low
17 temperature, for example 0° to 30°C , in order to favor
18 absorption of hydrogen sulfide in the solvent. The
19 resulting solution leaving through line 19 is heated at
20 20 by indirect heating, for instance by using steam as the
21 heating medium, e.g. to 80° to 120°C sufficient to
22 maintain sulfur in solution. The steam used for this
23 purpose may be generated in the process itself or it may
24 come from an outside source or there may be a mix of the
25 two sources of steam.

26
27 A solution of sulfur dioxide generated as
28 described below joins line 19 through line 25 and the
29 combined streams, suitably mixed as by means of a mixing
30 tee (not shown), pass through a tube 26 which constitutes
31 the first reaction zone where Reaction (1) occurs. In this
32 reaction zone hydrogen sulfide is present in excess.
33 Typical concentrations of hydrogen sulfide and the sulfur
34 dioxide in the reacting stream at the point of mixing and
35 before reaction has occurred are about 0.1 to 10 percent
36 sulfur dioxide and 0.1 to 10 percent hydrogen sulfide.
37 Reaction (1) is exothermic and, since the solvent is

1 selected to promote Reaction (1) the reaction is very
2 rapid and goes to completion within a few seconds and a
3 correspondingly short distance. The proportions in which
4 the two streams are mixed are such that there is a small
5 excess of hydrogen sulfide. This excess hydrogen sulfide
6 is typically such that the solution entering the stripper
7 section 11A of stripper-absorber 11 contains about 0.001 to
8 0.1 percent of hydrogen sulfide. A large fraction of this
9 dissolved hydrogen sulfide is stripped from the solution in
10 the stripper section 11A of the stripper-absorber 11.

11
12 A portion of the sulfur dioxide solution is
13 diverted from stream 25 into line 27 and is introduced into
14 the reactive absorber section 11B of stripper-absorber 11.
15 The proportion so diverted is in excess of that required to
16 react with the excess of hydrogen sulfide introduced into
17 the stripper section 11A of stripper-absorber 11. The
18 reactive absorber section 11B thus forms a second reaction
19 zone, one in which sulfur dioxide is present in excess.
20 This will carry Reaction (1) to completion so that no
21 appreciable quantity of hydrogen sulfide remains and it
22 results in a solution of sulfur in this solvent which also
23 contains much of the sulfur dioxide that enters the
24 stripper-absorber 11 through line 27. The resulting vapor
25 in the top section 11C of stripper-absorber 11, which is
26 completely free of hydrogen sulfide, contains some sulfur
27 dioxide that is absorbed by fresh, neat solvent entering
28 through line 30. The light gases leaving stripper-absorber
29 11 through line 35 are thus substantially free of both
30 hydrogen sulfide and sulfur dioxide.

31
32 The stripper-absorber 11 is shown as having a
33 tray 31 between stripper section 11A and absorber (second
34 reaction) zone 11B. The tray is a chimney type of tray
35 which permits vapor to pass from section 11A into section
36 11B but prevents liquid from flowing from section 11B into
37 section 11A.

1 In the process just described it is relatively
2 easy to maintain a net stoichiometric ratio of sulfur
3 dioxide to hydrogen sulfide. In stripping zone 11A a
4 small excess of hydrogen sulfide is maintained and the
5 amount and fluctuation of this excess in the vapor phase is
6 monitored and used to control the flow of sulfur dioxide
7 solution through line 25 into reaction zone 26. If the
8 concentration of hydrogen sulfide in the vapor in zone 11A
9 becomes too small the rate of flow of sulfur dioxide
10 solution will be diminished whereas if the concentration
11 of hydrogen sulfide becomes too great the rate of flow of
12 sulfur dioxide solution will be increased.

13
14 This procedure precludes the need to maintain a
15 stoichiometric ratio of hydrogen sulfide to sulfur dioxide
16 in reaction zone 26; the amount of hydrogen sulfide in the
17 vapor in zone 11A is easily monitored and need not be
18 maintained at a precise level but may fluctuate between
19 limits; the management of flow of sulfur dioxide solution
20 into reaction zone 26 is easy to accomplish; and the
21 process lends itself to automated control by control
22 equipment that is commercially available. The flow of
23 sulfur dioxide solution through line 27 into reactive
24 absorber section 11B is kept at a constant value. The
25 capacitance for hydrogen sulfide of the solution inventory
26 in this section of the stripper-absorber 11, provided by
27 the excess sulfur dioxide in the solution, effectively
28 dampens the fluctuations in the net flow of hydrogen
29 sulfide.

30
31 Furthermore, since the excess of hydrogen sulfide
32 in line 26 is small, and since the solubility of hydrogen
33 sulfide in the solvent at the elevated temperature in
34 stripper section 11A is relatively small, the flow of
35 stripping vapor needed to strip the excess hydrogen sulfide
36 from solution is not large. In the embodiment of Figure 1
37 propane is a constituent of the feed gas which it is

1 desired to recover separately. The propane vapor generated
2 in stripper section 11A will provide at least a portion of
3 the gas needed to strip hydrogen sulfide from solution.
4 Also the amount of sulfur dioxide in the vapor leaving zone
5 11B is small and the solubility of sulfur dioxide at the
6 temperature in zone 11C is quite high, therefore very
7 little lean solvent need be supplied through line 30. As a
8 result the process is not energy-intensive.

9
10 The effluent gas and vapor from stripper-absorber
11 11 leaves through line 35, is cooled in cooler 36 and the
12 condensate is collected in vessel 37. Gases, chiefly
13 ethane, are vented through line 38. This ethane may be
14 compressed and combined with the methane leaving absorber
15 10, or it may be burned as a fuel or it may be otherwise
16 disposed of. A portion of the condensate is returned to
17 the stripper-absorber 11 as reflux through line 39 and the
18 remainder, chiefly propane, is withdrawn through line 40.
19 This separation of propane provides a useful by-product of
20 the invention.

21
22 The liquid phase is removed from the bottom of
23 stripper-absorber 11 through line 41. This liquid phase
24 may be a homogeneous solution of sulfur, water and higher
25 hydrocarbons in the solvent or it may be a two-phase liquid
26 mixture of such a solution and liquid sulfur. It is heated
27 by steam in heater 42 and a portion of the heated liquid is
28 returned through line 43 to the bottom of stripper-absorber
29 11. Therefore the heater 42 also serves as a reboiler.
30 The liquid phase or phases passing forwardly through line
31 41 enters solvent dehydrator 12 at its mid-portion. Water
32 is evaporated and leaves the solvent dehydrator along with
33 hydrocarbon vapor, chiefly butane vapor, through line 44
34 and is condensed in cooler 45. The condensate passes by
35 line 44 to vessel 50. Two phases are present in vessel 50,
36 namely a lower aqueous phase and an upper hydrocarbon
37 phase. The aqueous phase is removed from the system

1 through line 51. A portion of the hydrocarbon phase is
2 returned to the upper end of the solvent stripper 12
3 through line 52 to serve as reflux and the remainder of
4 the hydrocarbon phase is recovered through line 53 as a
5 by-product.

6
7 The dehydrated solvent leaves the bottom of
8 solvent dehydrator 12 through line 54. A portion of the
9 liquid is vaporized in reboiler 55 and returned to the
10 bottom of solvent dehydrator 12 through line 56 and the
11 remainder of the solvent proceeds by line 57 to sulfur
12 crystallizer 13. Sulfur crystallizer 13 may be of
13 conventional design and mode of operation, for example
14 the solvent may be cooled by means of direct contact
15 with liquid propane refrigerant. This results in the
16 crystallization of sulfur. Suitable equipment (not shown)
17 is employed to separate the solid sulfur from the solvent
18 which is returned by way of line 17 to the top of absorber
19 10 and the top of stripper-absorber 11. One-third of the
20 sulfur proceeds by way of line 60 to furnace 14 and
21 two-thirds is withdrawn from the system through line 61.

22
23 Furnace 14 is supplied with air by compressor 62.
24 The proportion of sulfur diverted to furnace 14 is
25 sufficient to provide the sulfur dioxide needed for
26 Reaction (1). The heat of Reaction (3) is used to generate
27 steam in steam coil 64. This steam may be used in the
28 system. The gas phase (sulfur dioxide, nitrogen, etc.)
29 leaves the furnace by way of line 65 and enters sulfur
30 dioxide absorber 15. This sulfur dioxide is absorbed in a
31 stream of solvent diverted from line 17 through line 66.
32 This step may be conducted so that the stack gas leaving
33 through line 67 contains only a trace of sulfur dioxide.
34 A solution of sulfur dioxide leaves the bottom of sulfur
35 dioxide absorber 15 through line 25 and re-enters the
36 system.

37

1 Referring now to Figure 2 a variant is shown which
2 is applicable to a situation in which it is not necessary
3 to recover gases such as propane and other higher hydro-
4 carbons. An example is the removal of hydrogen sulfide
5 from a raw synthesis gas -- a mixture of hydrogen, carbon
6 monoxide, carbon dioxide, methane and other, very minor
7 components. In this instance the conditions in hydrogen
8 sulfide absorber 10, such as the choice of solvent and the
9 conditions of operation, will be such that only hydrogen
10 sulfide and carbon dioxide are absorbed.

11
12 Most of the units employed in the variant of the
13 Figure 2, namely the hydrogen sulfide absorber 10, the
14 sulfur crystallizer 13, the furnace 14, and the sulfur
15 dioxide absorber 15 remain the same although in certain
16 instances, as will appear from the description below, the
17 mode of operation is different than in Figure 1. Lines and
18 equipment in Figure 2 which are numbered as in Figure 1 are
19 the same. Element 11 functions only as a hydrogen sulfide
20 stripper.

21
22 Inasmuch as lines 27 and 30 are eliminated, the
23 unit 11 will not function as a hydrogen sulfide absorber
24 or reactor; therefore the gas leaving this unit through
25 line 35 will contain a small amount of hydrogen sulfide
26 which, along with other uncondensable gases, principally
27 carbon dioxide, will be separated from water by cooler 36
28 and the water phase will be removed through line 40. The
29 noncondensable gases will leave through line 38 and go to
30 sulfur dioxide absorber 15 which will result in reaction
31 of this small excess of hydrogen sulfide with the sulfur
32 dioxide in the absorber 15. It will therefore be apparent
33 that the sulfur dioxide absorber 15 performs the function
34 of zone 11B in unit 11 in Figure 1, providing both a zone
35 of substantial liquid capacitance for hydrogen sulfide and
36 the second reaction zone for the process.

37

1 Referring now to Figure 3 the application of
2 the present invention to the treatment of a gas at near-
3 atmospheric pressure is illustrated. When hydrogen sulfide
4 is present in such a gas, especially when its concentration
5 is also relatively low, it may not be practical to absorb
6 the hydrogen sulfide physically as an initial step. The
7 solvent flow required might then be excessively high.
8 Alternatively, when hydrogen sulfide is the only component
9 that one wishes to remove from a gas stream, it may be
10 desired to keep the flow of solvent as low as possible to
11 minimize co-absorption of other components. For both of
12 these design conditions the process configuration shown in
13 Figure 3 is a preferred embodiment of this invention. This
14 process configuration is also suitable for treating the
15 tail gas from a Claus process sulfur plant. Such a gas
16 contains sulfur dioxide as well as hydrogen sulfide.

17
18 The Claus process carries out Reaction (1) in the
19 vapor phase by contacting a mixture of hydrogen sulfide and
20 sulfur dioxide in the vapor phase with a solid catalyst.
21 The hydrogen sulfide and sulfur dioxide are employed in
22 stoichiometric ratio; the reaction is carried out at an
23 elevated temperature and results in an equilibrium in which
24 about five percent of the H_2S/SO_2 mixture is unreacted;
25 and this gaseous mixture (the tail gas) requires treatment
26 before it can be vented to the atmosphere. Typically the
27 hydrogen sulfide results from absorbing it from a gas, for
28 example natural gas or a process gas, into an alkaline
29 solution such as an aqueous solution of ethanolamine or
30 sodium carbonate from which it is then stripped by steam
31 and is used in the Claus process.

32
33 The gas to be treated (whether from a Claus plant
34 or from some other source) enters reactor-absorber 84
35 through line 85. The gas stream is usually kept well above
36 the dewpoint of water because of the corrosive nature of
37 the sulfoxy acid compounds that form in liquid water when

1 both hydrogen sulfide and sulfur dioxide are present
2 (Wackenroder's liquid). The gas enters the bottom section
3 84a of absorber 84 which has a reactor section 84b and an
4 upper section 84c. A solution of sulfur dioxide enters the
5 top of section 84b through line 86. Within the reactor
6 section of column 84 hydrogen sulfide reacts with both the
7 sulfur dioxide entering with it through line 85 and with
8 the sulfur dioxide entering with the solvent in line 86.
9 Fresh, neat solvent enters the top of the absorber section
10 84c of column 84 through line 87. Within the absorber
11 section virtually all of the sulfur dioxide remaining in
12 the gas stream is absorbed, reacting with the hydrogen
13 sulfide that is co-absorbed with it. The concentration
14 of hydrogen sulfide in the gas stream leaving the top of
15 column 84 through line 88 is monitored and is kept at a
16 small, approximately constant value by varying the flow of
17 sulfur dioxide solution entering through line 89.

18
19 The liquid stream leaving the reactor section of
20 column 84 contains a small amount of dissolved hydrogen
21 sulfide, which is stripped from the liquid by steam that is
22 introduced through line 90 at the bottom of the stripper
23 section 84a either by direct injection or by boiling water
24 out of the solvent mixture by indirect heat exchange. The
25 liquid stream leaving the bottom of column 84 through line
26 91 is thus substantially free of dissolved hydrogen sulfide
27 and sulfur dioxide, but contains in solution the sulfur
28 that has been formed by reaction. This stream is then
29 sent to a crystallizer for recovery of sulfur as has been
30 previously described.

31
32 The gas stream in line 88 enters the bottom of
33 reactor-absorber column 92. A fixed flow of sulfur dioxide
34 solution enters the top of the reactor section 92a of
35 column 92 through line 93. The sulfur dioxide contained in
36 this stream is in small excess over the hydrogen sulfide
37 contained in the gas stream from line 88, so that

1 substantially all of the hydrogen sulfide is removed from
2 the gas stream as it passes through section 92a of column
3 92. Fresh, neat solvent entering the absorber section 92b
4 of column 92 through line 94 serves to reabsorb any sulfur
5 dioxide that may have been stripped from solution by the
6 gas stream as it passed through the reactor section of
7 column 92. The gas stream leaving column 92 through line
8 95 is thus substantially free of both hydrogen sulfide and
9 sulfur dioxide and may be discharged to the atmosphere.
10 The liquid stream leaving column 92 through line 96
11 contains unreacted sulfur dioxide and is pumped by pump 97
12 to column 84 as previously noted.

13

14 The sulfur dioxide used to form the sulfur dioxide
15 solution that enters through lines 89 and 93 can be
16 produced by burning either hydrogen sulfide or part of the
17 sulfur made in this process. As before, the heat released
18 in the combustion can be used to produce steam.

19

20 As in the previous embodiments of this invention,
21 the process configuration in Figure 3 makes use of two
22 reaction zones, one in which hydrogen sulfide is in excess
23 and one in which sulfur dioxide is in excess. The control
24 of the exact stoichiometry of the reaction is made
25 relatively simple by the capacitance for hydrogen sulfide
26 of solvent containing sulfur dioxide, which allows moderate
27 variations in the hydrogen sulfide content of the tail gas
28 from the Claus plant to occur without upsetting the control
29 of the process.

30

31 In operating the process shown in Figure 3 the gas
32 stream entering through line 85 must contain a ratio of
33 hydrogen sulfide to sulfur dioxide that is substantially
34 greater than 2. This excess hydrogen sulfide can be
35 provided by bypassing part of the hydrogen sulfide around
36 the Claus plant if it proves undesirable to operate the
37 Claus plant with such an excess. However, the process

1 shown in Figure 3 is not limited to the treatment of the
2 tail gas from a Claus plant nor to the treatment of a gas
3 stream containing both hydrogen sulfide and sulfur
4 dioxide. It is suitable as an alternative to the process
5 shown in Figure 1 for treating any gas stream that contains
6 hydrogen sulfide, but is particularly suitable for treating
7 low-pressure gas streams because of the reduced flow of
8 solvent that is required. Furthermore, it will be apparent
9 to those skilled in the art that heating or cooling of some
10 of the streams in Figure 3 may be required in some
11 instances, and that columns 84 and 92 could be consolidated
12 if desired.

13

14 Still another example of a process configuration
15 that utilizes the principles of this invention is shown in
16 Figure 4. The gas to be treated in this example is raw
17 "synthesis gas", a mixture of hydrogen and carbon monoxide
18 that contains carbon dioxide and hydrogen sulfide as
19 undesirable components. The pressure of the gas stream is
20 relatively high, typically at about 40 atmospheres. The
21 gas to be treated enters high-pressure absorber 97 through
22 line 98. Lean solvent enters through line 99 and contacts
23 the gas in absorber 97 countercurrently, absorbing most of
24 the carbon dioxide and substantially all of the hydrogen
25 sulfide from the gas, which leaves absorber 97 through line
26 100. Small amounts of hydrogen and carbon monoxide are
27 co-absorbed in the solvent stream, which leaves absorber 97
28 through line 101. This hydrogen and carbon dioxide are
29 stripped from the solvent in the operation described below
30 and are returned, together with some carbon dioxide and
31 hydrogen sulfide, through line 102.

32

33 A stream of sulfur dioxide dissolved in the
34 solvent is added to the fat solvent in line 101 through
35 line 104. Reaction (1) occurs in line 105 before the
36 combined streams enter stripper 106, where hydrogen and
37 carbon monoxide are stripped from the solvent. The

1 temperature of the stream in line 105 is monitored and
2 heater 103 supplies any heat that is needed to ensure
3 that sulfur does not precipitate. The quantity of sulfur
4 dioxide entering through line 104 is regulated to be about
5 90 to 99 per cent of that required to react with all of
6 the hydrogen sulfide in the stream in line 101. This
7 regulation is accomplished by monitoring the hydrogen
8 sulfide content of the gas leaving stripper 106 through
9 line 102 and keeping it at a relatively low, constant
10 value.

11
12 The stripping vapor in stripper 106 is
13 predominantly carbon dioxide, which is boiled out of
14 solution in line 107 as a result of heat supplied by heater
15 108. The purpose of this stripping vapor is not only to
16 recover hydrogen and carbon monoxide from the solvent but
17 also to homogenize the hydrogen sulfide concentration in
18 the solvent. As the solvent flows through the column,
19 countercurrently to the vapor stream, small fluctuations
20 in the hydrogen sulfide concentration tend to disappear
21 because of the mass transfer and back-mixing that is
22 characteristic in such devices. As a result, the
23 concentration of hydrogen sulfide in the solvent leaving
24 stripper 106 through line 109 will have a relatively
25 constant value that is about one-tenth to one-hundredth
26 that of the stream leaving absorber 97 through line 101.
27 This remaining hydrogen sulfide is eliminated by adding a
28 second regulated stream of sulfur dioxide through line
29 110. Reaction (1) occurs in line 111 before the solvent
30 mixture reaches cooler 112. The sulfur content (either
31 hydrogen sulfide or sulfur dioxide) of the carbon dioxide
32 stream leaving crystallizer 113 through line 114 is
33 negligible. The flow of sulfur dioxide solution through
34 line 110 is regulated to keep the sulfur compound level in
35 line 114 in the low parts-per-million range. It is
36 advantageous to maintain a slight excess of sulfur dioxide
37 in the solvent leaving line 111. Because of its higher

1 solubility, a given excess of sulfur dioxide in the solvent
2 results in substantially less sulfur content of the gas in
3 line 114 than does a similar excess of hydrogen sulfide.
4 However, for this process configuration operation in
5 either mode is feasible. Cooler 112 reduces the solvent
6 temperature to the point of incipient sulfur precipitation.
7 Additional cooling is produced when the dissolved carbon
8 dioxide flashes from solution at the pressure of the
9 crystallizer. The operations of the crystallizer 113,
10 the sulfur furnace and boiler 116, and the sulfur dioxide
11 absorber 117 are similar to those described in the previous
12 examples. Solvent leaves crystallizer 113 through line 118
13 and a portion is diverted to sulfur dioxide absorber 117
14 where it absorbs sulfur dioxide from furnace 116 entering
15 through line 119. A portion of the sulfur leaving
16 crystallizer 113 is diverted through line 115a to
17 furnace 116.

18

19 As in the previous three examples of Figures 1, 2
20 and 3, the process configuration of Figure 4 depends upon
21 having two reaction zones and a method of homogenizing the
22 concentration of the liquid stream passing from the first
23 zone to the second by utilizing the capacitance of the
24 solution for dissolved hydrogen sulfide. The zone of high
25 capacitance in this example is located between the two
26 reaction zones. Again in this example it is essential to
27 have excess hydrogen sulfide in the first reaction zone and
28 advantageous to have excess sulfur dioxide in the second
29 reaction zone. However, in this example it is feasible to
30 operate with a small excess of hydrogen sulfide in the
31 second reaction zone as well.

32

33 Under some circumstances it may be preferable
34 to carry out the reaction between hydrogen sulfide and
35 sulfur dioxide without heating the solution to ensure
36 that the sulfur formed remains dissolved. In this case
37 crystallization will occur simultaneously with reaction.

1 It may also be desirable to carry out the reaction and
2 crystallization with simultaneous cooling, by flashing a
3 dissolved gas. An example of this method of practicing
4 the invention is shown in Figure 5, a modified version of
5 Figure 4.

6
7 In Figure 5, the high-pressure absorber 97 is
8 operated as described with reference to Figure 4, and flow
9 lines and pieces of equipment that remain unchanged bear
10 the same reference numerals as in Figure 4. The rich
11 solvent leaving absorber 97 through line 101 is cooled in
12 exchanger 103 to near the temperature of the cooling water
13 before it enters flash chamber-crystallizer 120. In 120
14 the pressure is reduced to flash carbon dioxide from
15 solution in sufficient quantity to obtain the desired
16 temperature. Sulfur dioxide solution enters 120 through
17 line 104 at a metered rate that is regulated to maintain a
18 constant, small fraction of unreacted hydrogen sulfide in
19 the gas leaving 120 through line 102. This gas is
20 compressed to the pressure of absorber 97 in compressor 121
21 and returned to the bottom of the absorber. The liquid
22 stream leaving flash chamber-crystallizer 120 through line
23 109 contains a slurry of sulfur crystals and a small,
24 nearly constant concentration of unreacted hydrogen
25 sulfide. As in the flowsheet of Figure 4, sulfur dioxide
26 solution is added to this stream through line 110 in nearly
27 exact stoichiometric ratio, as determined by monitoring for
28 traces of unreacted hydrogen sulfide or sulfur dioxide in
29 the sweet carbon dioxide in line 114 that has flashed from
30 solution in crystallizer 113.

31
32 The remainder of the process -- sulfur separation,
33 sulfur burning, and sulfur dioxide absorption -- is
34 unchanged from Figure 4.

35
36 As will be apparent from a comparison of Figures 4
37 and 5, combining flashing, reaction and crystallization in

1 a single operation can reduce energy consumption for this
2 process under some conditions. Operation in this manner is
3 within the scope of this invention since one is still
4 utilizing the high rate of reaction that can be realized
5 even at ambient temperature by the reaction catalysts
6 disclosed herein and is still utilizing the two reaction
7 zones that facilitate control of the overall reaction
8 stoichiometry. The zone of high liquid capacitance for
9 hydrogen sulfide in this example coincides with the first
10 reaction zone. Reactor-crystallizer 120 is a stirred-tank
11 reactor, with well-defined capacitance characteristics.

12

13 Choice of Solvent Components

14

15 The organic solution or solvent should, as stated
16 above, be one in which sulfur dioxide has a high solubility
17 and which has a solvating power for hydrogen sulfide and
18 other concomitants in accordance with the following
19 descending scale: $\text{SO}_2 \gg \text{H}_2\text{S} > \text{COS}$ and mercaptans $> \text{CO}_2$,
20 C_3H_8 .

21

22 The solvating power of the solvent for the major
23 constituents of the gas, for example methane in the case of
24 natural gas, should of course be quite low. Further, the
25 solvent should promote Reaction (1) and it should not form
26 strong chemical complexes with sulfur dioxide or with
27 constituents of the feed gas. Where it is desired to
28 remove water from the feed gas a more polar solvent is
29 indicated. The solvent should have moderate miscibility
30 with water and should be a moderately good solvent for
31 sulfur, for example, capable of dissolving at 25°C one
32 gram per liter or more.

33

34 Where it is desired to absorb propane or other
35 higher hydrocarbons the solvent may be modified by
36 including a less polar component. Solvent mixtures (i.e.,
37 "mixtures" in the sense of two or more liquid components

1 which are in solution as a homogeneous phase) may be
2 employed to advantage to achieve such objects.

3

4 To minimize loss of volatile solvent components
5 in the gas streams being treated it is desirable to use
6 components of low volatility. In most cases liquids with
7 normal boiling points greater than 180°C are preferred.

8

9 In Table I below, there is a list of solvent
10 components by category. Such solvents may be employed
11 individually or in combination of two or more solvents.

12

13

Table I

14

15 (1) Solvent components which have very high
16 solvating power for SO₂

17

18 Dialkyl ethers of polyethylene glycols such as
19 triethylene glycol dimethyl ether, tetraethylene glycol
20 diethyl ether, etc.

21

22 Dialkyl ethers of polypropylene glycols such as
23 tripropylene glycol dimethyl ether, tetrapropylene glycol
24 diethyl ether, etc.

25

26 Monoalkyl ethers of polyethylene glycols such as
27 diethylene glycol monomethyl ether, triethylene glycol
28 monoethyl ether, etc.

29

30 Monoalkyl ethers of polypropylene glycols such as
31 dipropylene glycol monomethyl ether, tripropylene glycol
32 monomethyl ether.

33

34

35

36

37

These glycol ethers have the general formula
 $R_1O-(R-O)_nR_2$ where R is $-CH_2-CH_2-$ or
 $-CH_2-CH(CH_3)-$, n represents the number of alkylene
oxide units, e.g. 3 or 4, R₁ is alkyl (e.g. methyl or

1 ethyl) and R_2 is hydrogen or alkyl.

2

3 Tertiary aromatic amines such as N,N-dimethyl
4 aniline, N-phenyl diethanolamine, etc.

5

6 Trialkyl phosphates such as tributyl phosphate,
7 tripropyl phosphate, etc.

8

9 Tetrahydrothiophene oxide (sulfolane).

10

11 (2) Solvents which are good catalysts for Reaction (1)

12

13 High boiling aromatic compounds containing
14 nitrogen within a ring, such as quinoline, acrolein, the
15 benzyl pyridines and similar compounds.

16

17 Dimethyl aniline.

18

19 bis-Methylene-4,4'-dimethylaminobenzene.

20

21 Trialkyl phosphates such as those in Section (1)
22 above.

23

24 (3) Solvents which are good solvents for sulfur

25

26 N,N-Dimethyl aniline.

27

28 bis-Methylene-4,4'-dimethylaminobenzene.

29

30 Other tertiary aromatic amines such as N,N-diethyl
31 aniline, quinoline and isoquinoline.

32

33 Further considerations in the choice of a solvent
34 are as follows: Reaction (1) is a first order reaction
35 with respect to each of the reactants. Therefore its rate
36 is described by the following equation:

37

1 $R = k_2 [H_2S][SO_2]$
2 in which $R =$ rate of disappearance of SO_2 ,
3 moles/liter-sec.
4 $k_2 =$ reaction rate constant, liter/mole-sec.
5 $[] =$ concentration in moles/liter
6

7 and k_2 is assumed to be a function only of temperature.
8 For use in the process of the present invention a solvent
9 preferably has a value of k_2 at room temperature ($25^\circ C$)
10 of at least 1.0 and preferably of 10 liter/mole-sec. or
11 higher.

12
13 The kinetics of Reaction (1) was determined for a
14 specific solvent composition by carrying out the reaction
15 in the following way: A sample of solvent containing
16 hydrogen sulfide was placed in a calorimeter, together with
17 a thermocouple and a magnetic stirring bar. A sample of
18 solvent containing sulfur dioxide was then added rapidly to
19 the calorimeter while stirring vigorously. The temperature
20 rise that resulted from reaction was followed by recording
21 the potential of the thermocouple as a function of time
22 during the experiment. The change in temperature was used
23 to calculate the change in concentrations of both hydrogen
24 sulfide and sulfur dioxide as the reaction progressed, and
25 this information was used to calculate the value of k_2 in
26 the equation above.

27
28 Experiments of this sort show that quinoline and
29 similar aromatic ring-nitrogen compounds are exceptionally
30 effective catalysts for Reaction (1) and are particularly
31 advantageous in the practice of this invention. As an
32 example, the value of k_2 was determined for mixtures of
33 N,N-dimethyl aniline (DMA) and triethylene glycol dimethyl
34 ether (Triglyme) at $25^\circ C$ as a function of composition.
35 The values were about 1.0 at 1% DMA, 4.0 at 10% DMA, and
36 8.0 at 100% DMA. For a mixture of 1% quinoline in Triglyme
37 the value of k_2 was about 20. In more concentrated

1 solutions of quinoline in Triglyme the values of k_2 were
2 too high to be estimated accurately by this technique.
3 Because of their low volatility and the low concentrations
4 at which they are effective catalysts, quinoline,
5 substituted pyridines such as 4-benzyl pyridine and
6 3-pyridyl carbinol, and similar compounds can be used in
7 the practice of this invention at low cost and with little
8 volatile loss. Their use is thus preferred to the use of
9 DMA, as taught by Urban (U.S. Patent No. 2,987,379), or the
10 use of N-methyl-2-pyrrolidone as taught by Fuchs (U.S.
11 Patent No. 3,103,411) and Tanimura (U.S. Patent No.
12 3,953,586).

13

14

15 A combination of solvents may be preferred, e.g.
16 a mixture of a solvent from Section 1 of Table I for high
17 solvating power for sulfur dioxide and dimethyl aniline for
18 its catalytic and sulfur solvating properties.

19

20

21 It will therefore be apparent that a novel and
22 advantageous method of removing hydrogen sulfide from gases
23 has been provided.

24

25

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WHAT IS CLAIMED IS:

1 1. In a method of continuously treating a gas
stream containing fluctuating amounts of hydrogen sulfide
to remove the hydrogen sulfide by reacting it with sulfur
dioxide in accordance with the reaction



the improvement which comprises

10 (a) providing a solvent having a
high solvating power for sulfur dioxide and a lesser but
substantial solvating power for hydrogen sulfide, such
solvent being one which promotes the reaction of hydrogen
sulfide with sulfur dioxide in accordance with the Reaction
(1) and which does not form a strong chemical complex with
or react chemically with sulfur dioxide

15 (b) absorbing hydrogen sulfide from
such gas stream in such solvent

20 (c) reacting the absorbed hydrogen
sulfide with sulfur dioxide, also dissolved in such
solvent, in a first reaction zone in accordance with the
Reaction (1) and maintaining in said first reaction zone
an excess of hydrogen sulfide over that required for
Reaction (1)

25 (d) reacting excess hydrogen sulfide
from step (c) with sulfur dioxide in a second reaction zone
in solution in such solvent so as to react substantially
all of the excess hydrogen sulfide in accordance with the
Reaction (1)

(e) controlling the input of sulfur dioxide solution to step (c) to maintain the excess of hydrogen sulfide within desired limits and

30 (f) providing a liquid phase capacitance for hydrogen sulfide which dampens the effect of fluctuations in hydrogen sulfide content in the gas stream.

1 2. The improvement of Claim 1 wherein control step (e) includes monitoring the hydrogen sulfide concentration in a gas phase or in a liquid phase separated from the first reaction zone.

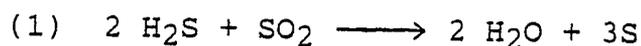
1 3. The improvement of Claim 2 wherein the monitoring step is applied to a gas phase resulting from vaporizing excess hydrogen sulfide from the first reaction zone.

1 4. The improvement of Claim 2 wherein the monitoring step is applied to the liquid reaction mixture resulting from step (c).

1 5. The improvement of Claim 1 wherein the capacitance step (f) is provided by the sulfur dioxide solution employed in step (d).

1 6. The improvement of Claim 1 wherein the capacitance step (f) is provided by continuously mixing the product of step (c) in a tank or other vessel before carrying out step (d).

1 7. A method of reacting hydrogen sulfide with
sulfur dioxide in accordance with the following reaction



5 comprising providing a solvent [defined as in Claim 1]
including at least a catalytic amount of an aromatic ring
nitrogen compound.

1 8. A continuous process of treating a gas to
remove hydrogen sulfide comprising:

5 (a) continuously contacting the gas with a
solvent having a high solvating power for sulfur dioxide
and a lesser but substantial solvating power for hydrogen
sulfide, such solvent being one which promotes the reaction
of hydrogen sulfide with sulfur dioxide to produce water
and sulfur and which does not form a strong chemical
complex with or react chemically with sulfur dioxide,
10 thereby absorbing the hydrogen sulfide in such solvent

 (b) continuously reacting the hydrogen
sulfide in the solution resulting from step (a) with sulfur
dioxide also dissolved in such solvent

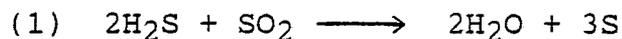
15 (c) maintaining in step (b) a small excess
of hydrogen sulfide, resulting in a solution of sulfur,
water and at least a portion of such excess hydrogen
sulfide in such solvent

20 (d) continuously stripping the solution
resulting from step (c) of hydrogen sulfide, resulting
in a gas phase containing hydrogen sulfide

 (e) continuously reacting the gaseous
hydrogen sulfide resulting from step (d) with sulfur
dioxide in solution in the aforesaid solvent and

25 (f) monitoring the quantity of hydrogen sulfide gas going from step (d) to step (e) and adjusting the input of sulfur dioxide to the process to maintain such excess within certain limits.

1 9. In the method of treating a gas to remove hydrogen sulfide wherein the gas is treated with a liquid solvent to absorb hydrogen sulfide and the resulting solution is contacted with sulfur dioxide to convert the hydrogen sulfide to sulfur and water in accordance with the following reaction



the improvement which comprises:

10 (a) employing as a solvent for absorbing hydrogen sulfide and as a solvent medium for Reaction (1) a liquid having a high solvating power for sulfur dioxide and a lesser but substantial solvating power for hydrogen sulfide, such solvent being one which promotes Reaction (1) and which does not form a strong chemical complex with or
15 react chemically with sulfur dioxide,

(b) absorbing hydrogen sulfide from such gas in such solvent

20 (c) mixing the resulting solution with a solution of sulfur dioxide in the same solvent, said hydrogen sulfide solution and sulfur dioxide solution being mixed in proportions such that there is a small excess of hydrogen sulfide thereby resulting in a liquid reaction mixture containing such small amount of hydrogen sulfide,

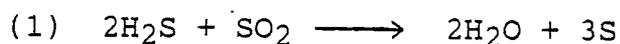
25 (d) separating from the reaction mixture a gas phase containing most of the excess hydrogen sulfide,

(e) contacting such gas phase with a solution in the same solvent of sulfur dioxide in excess of that required for Reaction (1), thereby removing the hydrogen sulfide from the gas phase by Reaction (1) and resulting in a gas phase containing a small amount of sulfur dioxide and

(f) removing such small amount of sulfur dioxide from such gas phase by absorption in a quantity of the same solvent.

10. A method of treating a gas to remove hydrogen sulfide which comprises:

(a) providing a solvent having a high solvating power for sulfur dioxide and a lesser but substantial solvating power for hydrogen sulfide which solvent also serves to promote the following reaction



and which does not form a strong chemical complex with nor react chemically with sulfur dioxide,

(b) contacting such gas with such solvent under conditions to absorb substantially all of the hydrogen sulfide from the gas thereby resulting in a treated gas which is substantially free from hydrogen sulfide and a solution of hydrogen sulfide in the solvent,

(c) providing also a solution of sulfur dioxide in the same solvent,

(d) mixing the aforesaid solutions of hydrogen sulfide and sulfur dioxide in proportions such that the hydrogen sulfide is in small excess of that required by Reaction (1), thereby resulting in a liquid reaction mixture containing dissolved sulfur, and a gas phase containing a small quantity of hydrogen sulfide,

(e) contacting such gas phase with a solution of sulfur dioxide in such solvent in excess of the amount required by Reaction (1), thereby converting substantially all of the hydrogen sulfide to sulfur and water in accordance with Reaction (1).

11. The method of Claim 10 in which the gas phase resulting from step (e) contains sulfur dioxide and is contacted with fresh solvent to absorb the sulfur dioxide.

12. A method of treating a solution of hydrogen sulfide dissolved in a solvent which has a higher solvating power for sulfur dioxide than for hydrogen sulfide, which promotes the reaction of hydrogen sulfide with sulfur dioxide to produce sulfur and water and which does not form a strong chemical complex with nor react chemically with sulfur dioxide, said method comprising

(a) continuously mixing said solution with a solution in the same solvent of sulfur dioxide to cause such reaction to occur and maintaining an excess of hydrogen sulfide in the mixture;

(b) separating from the product of step (a) a vapor phase containing hydrogen sulfide and one or more liquid phases including a solution of sulfur in said solvent; and

(c) continuously contacting the separated vapor phase with a solution of sulfur dioxide in the same solvent in excess of that required stoichiometrically for reaction of the hydrogen sulfide with sulfur dioxide to produce sulfur and water thereby converting the hydrogen sulfide to sulfur and water.

13. The method of Claim 12 wherein a vapor phase is separated from the reaction mixture resulting from step (c), and is continuously contacted with the same solvent to absorb excess sulfur dioxide resulting from step (c).

14. The method of treating a feed gas containing a relatively small but objectionable amount of hydrogen sulfide comprising

(a) providing a solvent which has a high solvating power for sulfur dioxide and a lesser but substantial solvating power for hydrogen sulfide, which promotes the reaction of hydrogen sulfide with sulfur dioxide to produce sulfur and water and which does not form a strong chemical complex or react chemically with sulfur dioxide;

(b) providing a solution of sulfur dioxide in such solvent;

(c) treating the feed gas with such solvent to absorb the hydrogen sulfide and reduce its quantity in the treated gas to the desired amount;

(d) separating the resulting solution of hydrogen sulfide;

20 (e) mixing solutions (b) and (d) in proportions such that the hydrogen sulfide is in excess of that required for reaction with sulfur dioxide to produce sulfur and water, and causing such reaction to go to completion thereby resulting in a solution of sulfur and water in the solvent and a gas phase containing excess hydrogen sulfide;

25 (f) treating such gas phase with some of solution (b) in excess of that required for reaction with hydrogen sulfide to produce sulfur and water, thereby resulting in a solution containing excess sulfur dioxide and a gas phase containing sulfur dioxide; and

30 (g) recycling the solution resulting from step (f) to step (e).

1 15. The method of Claim 14 wherein the gas phase resulting from step (f) is contacted with such solvent to absorb the unabsorbed sulfur dioxide.

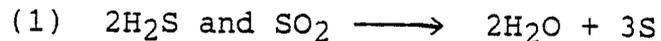
1 16. The method of Claim 15 wherein the unabsorbed gas is cooled to condense a portion thereof while leaving the remainder as a gas phase.

1 17. The method of Claim 16 wherein the feed gas treated in step (c) is natural gas containing at least one of the minor components, water, carbon dioxide and hydrocarbons higher than methane, and the condensation
5 step of Claim 8 effects a separation of one or more of such minor components from one or more of the other of such components.

1 18. The method of Claim 17 wherein the condensate contains propane and such higher hydrocarbons as are present in the feed gas.

1 19. A method of treating a gas containing a
small concentration of hydrogen sulfide which comprises:

5 (a) contacting the gas in a reaction zone
with a solution of sulfur dioxide in a solvent which has a
high solvating power for sulfur dioxide and which promotes
the reaction



10 (b) maintaining in such reaction zone a
small excess of hydrogen sulfide over that required for
Reaction (1), thereby resulting in a solution of sulfur
and water in the solvent and a gas phase containing
hydrogen sulfide,

 (c) removing such solution from the
reaction zone,

15 (d) removing such gas phase from the
reaction zone,

 (e) treating the gas phase so removed with a
solution in the same solvent of sulfur dioxide in excess of
that required for Reaction (1), resulting in a gas phase
20 substantially free of hydrogen sulfide.

1 20. The method of Claim 19 wherein heat is
supplied to the solution resulting from step (b) to
evaporate dissolved hydrogen sulfide and to add it to
the gas phase resulting from step (b).

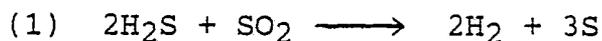
1 21. The method of Claim 19 wherein the gas
introduced into the reaction zone in step (a) contains
both sulfur dioxide and hydrogen sulfide.

1 22. The method of Claim 21 wherein the gas
introduced into the reaction zone in step (a) is the tail
gas of a Claus plant.

1 23. The method of Claim 19 wherein the gas phase
resulting from step (e) is treated with fresh solvent to
absorb sulfur dioxide.

1 24. A process of treating a gas at high
pressure containing carbon monoxide and hydrogen as
major components and hydrogen sulfide and carbon dioxide
as minor components, said method comprising:

5 (a) treating the gas at high pressure with
a solvent having substantial solvating power for hydrogen
sulfide and carbon dioxide and a higher solvating power for
sulfur dioxide and which promotes the reaction



10 such step resulting in a gas substantially free of hydrogen
sulfide and carbon dioxide and a solution in such solvent
of hydrogen sulfide and carbon dioxide,

15 (b) mixing said solution with a solution
in the same solvent of sulfur dioxide and maintaining a
small excess of hydrogen sulfide over that required in
Reaction (1), resulting in a solution containing most of
such excess hydrogen sulfide,

20 (c) mixing the solution resulting from
step (b) with a solution of sulfur dioxide in the same
solvent, thereby reacting the excess hydrogen sulfide
according to Reaction (1) and resulting in a solution of
water and sulfur in such solvent,

(d) separating sulfur, carbon dioxide and water from the product of step (c), and

25 (e) recycling the solution resulting from step (d).

1 25. The process of Claim 24 in which the high pressure gas treated in step (a) is synthesis gas and wherein in step (b) heat is supplied to assist in the evaporation of carbon dioxide and to promote, thereby,
5 the removal of carbon monoxide and hydrogen and to homogenize the hydrogen sulfide in solution.

1 26. The method of Claim 8 wherein the solvent contains an aromatic component containing nitrogen in an aromatic ring.

1 27. The method of Claim 26 wherein said component is selected from the group consisting of quinoline, phenanthridine and substituted pyridines.

1 28. The method of Claim 9 wherein the solvent contains an aromatic component containing nitrogen in an aromatic ring.

1 29. The method of Claim 10 wherein the solvent contains an aromatic component containing nitrogen in an aromatic ring.

1 30. The method of Claim 12 wherein the solvent contains an aromatic component containing nitrogen in an aromatic ring.

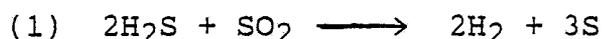
1 31. The method of Claim 14 wherein the solvent contains an aromatic component containing nitrogen in an aromatic ring.

1 32. The method of Claim 19 wherein the solvent
contains an aromatic component containing nitrogen in an
aromatic ring.

1 33. The method of Claim 24 wherein the solvent
contains an aromatic component containing nitrogen in an
aromatic ring.

1 34. In the treatment of a gas containing hydrogen
sulfide and another volatile gaseous component to remove
the same from the gas, the improvement which comprises:

5 (a) treating the gas with a solvent having
substantial solvating power for hydrogen sulfide and said
other gaseous component and a higher solvating power for
sulfur dioxide and which promotes the reaction



10 such step resulting in a gas substantially free of hydrogen
sulfide and said other gaseous component and a solution in
such solvent of hydrogen sulfide and said other gaseous
component,

15 (b) mixing the solution resulting from
step (a) in a reaction zone with a solution of sulfur
dioxide in the same solvent to carry out Reaction (1),

(c) maintaining during step (b) a
temperature such that sulfur formed by Reaction (1)
crystallizes and

20 (d) separating the resulting mixture of
solution of sulfur in the solvent and sulfur crystals from
the reaction zone.

1 35. The improvement of Claim 34 wherein step (c)
is accomplished at least in part by flashing said other
gaseous component from the solution in the reaction zone.

1 36. The improvement of Claim 35 wherein said
other gaseous component is carbon dioxide.

1 37. The improvement of Claim 34 wherein the
solution resulting from step (a) is cooled before it is
introduced into the reaction zone.

1 38. The method of Claim 34 wherein a small excess
of hydrogen sulfide is maintained in the reaction zone
whereby the solution withdrawn in step (d) contains
hydrogen sulfide, and sulfur dioxide in said solvent is
5 mixed with the solution to react with the excess hydrogen
sulfide.

1 39. The improvement of Claim 34 wherein the gas
treated in step (a) is synthesis gas containing hydrogen
and carbon monoxide as the major components.

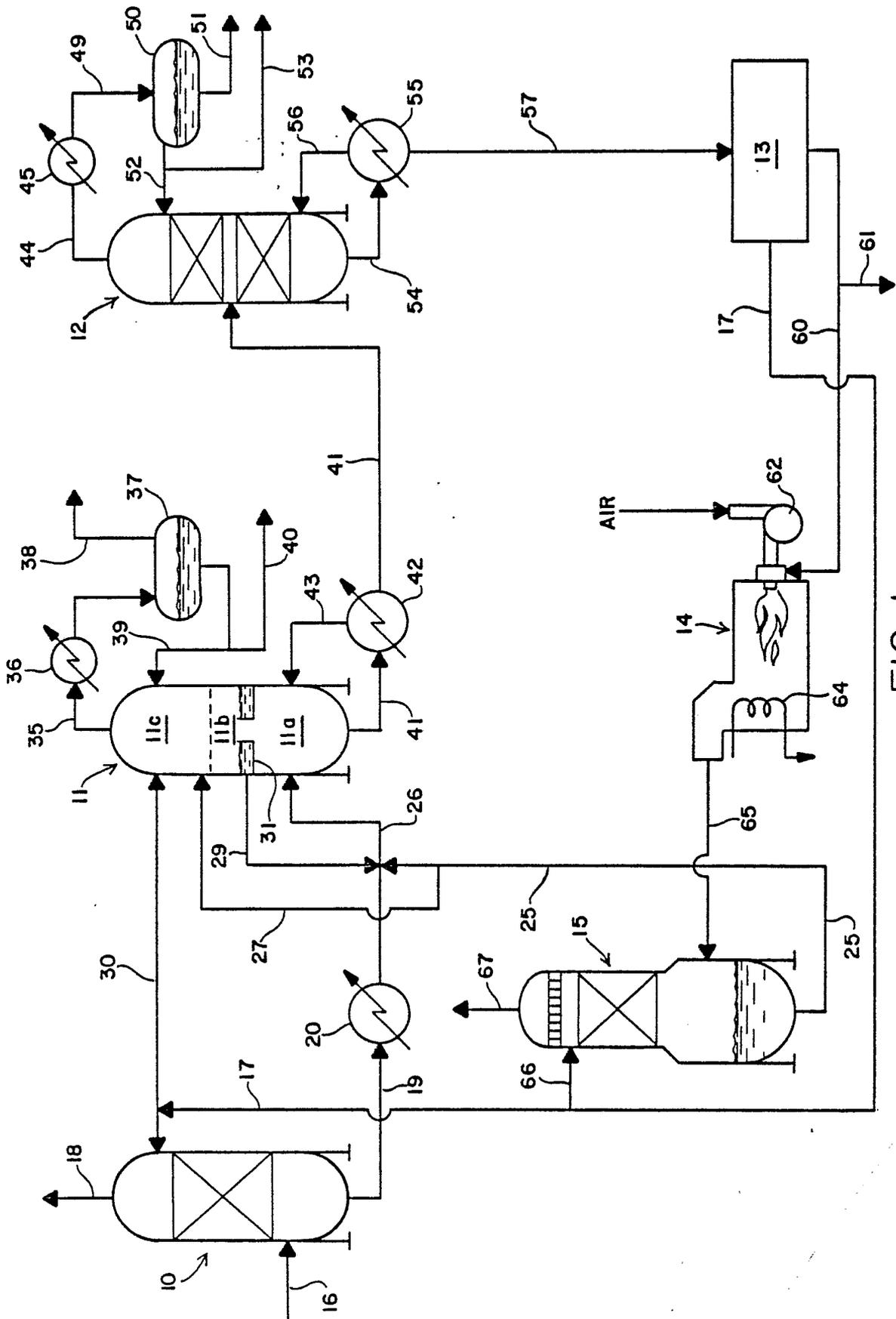


FIG. 1

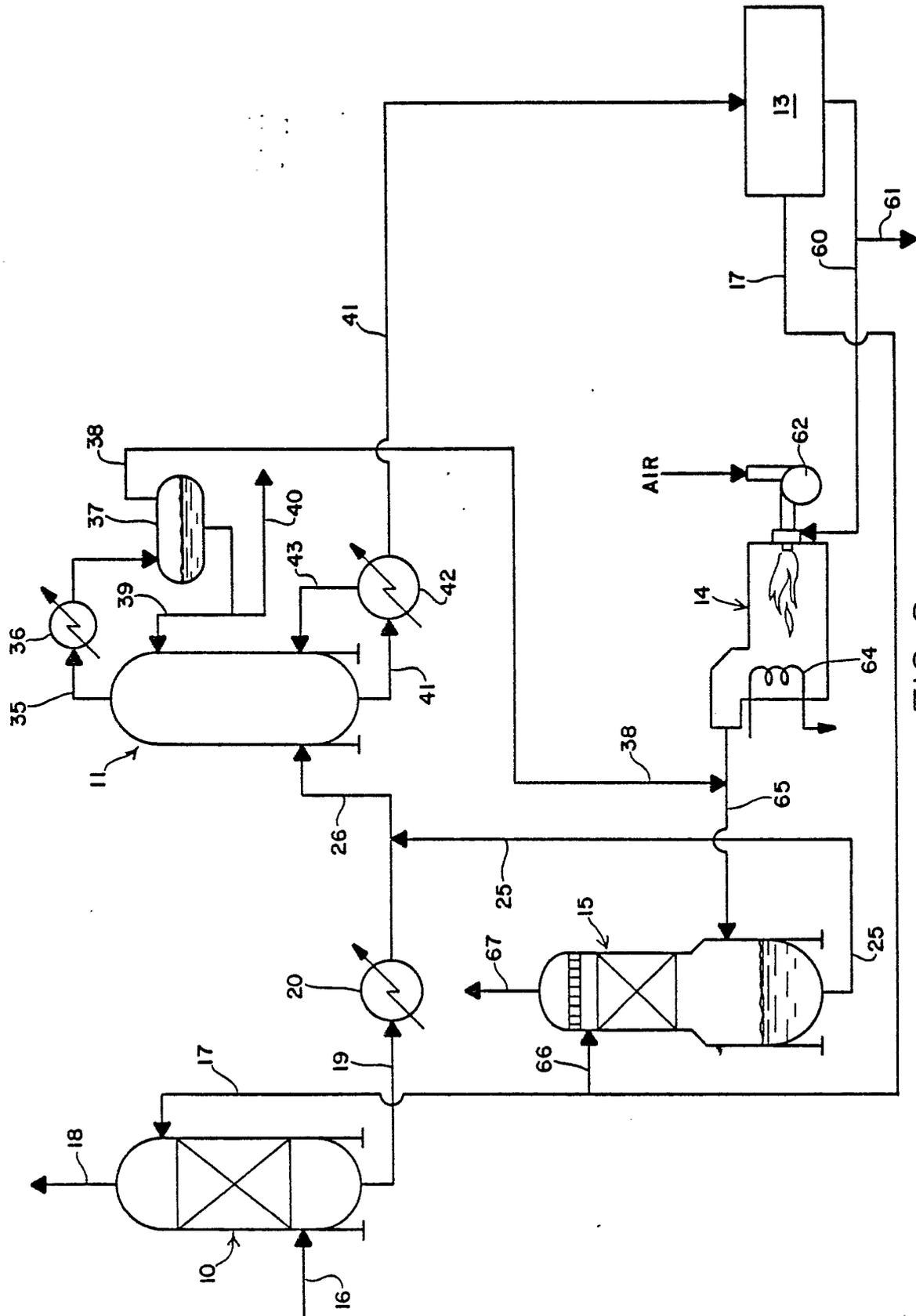


FIG 2

LEAFS AND TWIGS SHEET

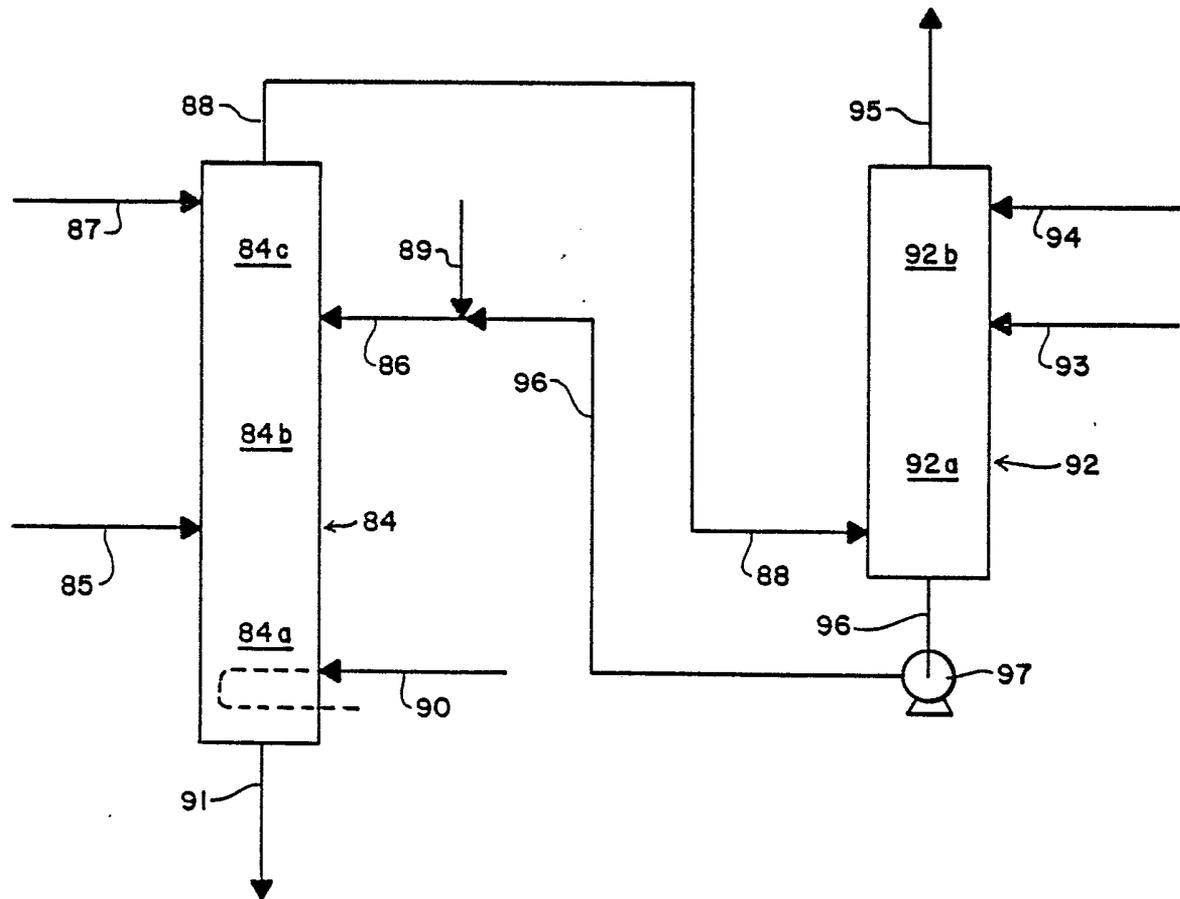


FIG. 3

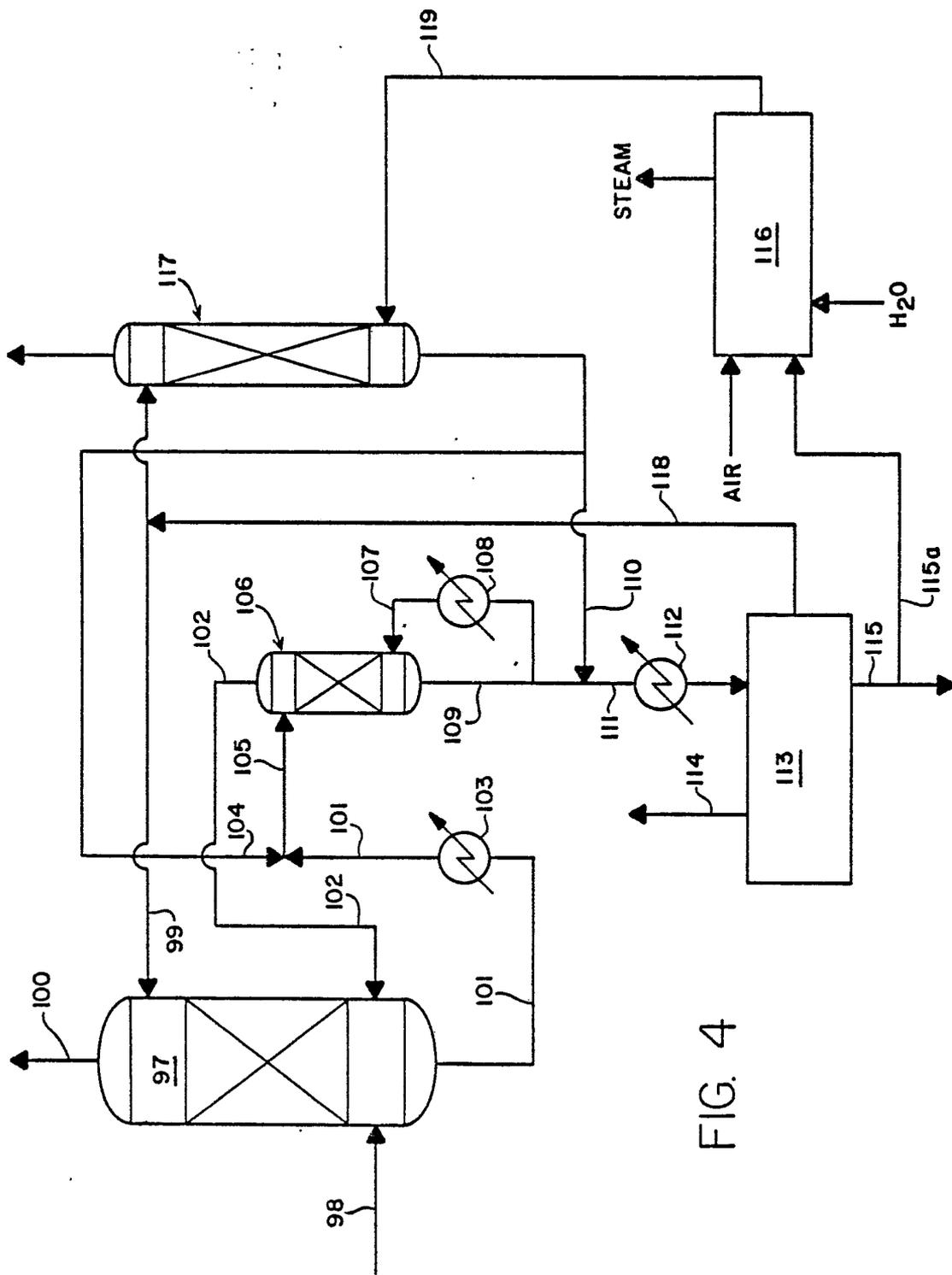


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No **PCT-US85-02179**

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		
INT. CL ⁴ C01B 17/16		
U.S. CL. 423/222		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	423/222, 575, 574L	
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	U.S., A 3103411 PUBLISHED 10 OCTOBER 1963	1-6, 8, 19-23
Y	U.S., A 3363989 PUBLISHED 16 JANUARY 1968	26-33
Y	U.S., A 3875295 PUBLISHED 01 APRIL 1975	17, 18, 25, 35, 36, 39
Y	U.S., A 3882222 PUBLISHED 06 MAY 1975	9-16
Y	U.S., A 3953586 PUBLISHED 27 APRIL 1976	1-39
<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
04 DECEMBER 1985		17 DEC 1985
International Searching Authority ¹		Signature of Authorized Officer ²⁰
ISA/US		L. FREEMAN / <i>John D. Wolf</i>