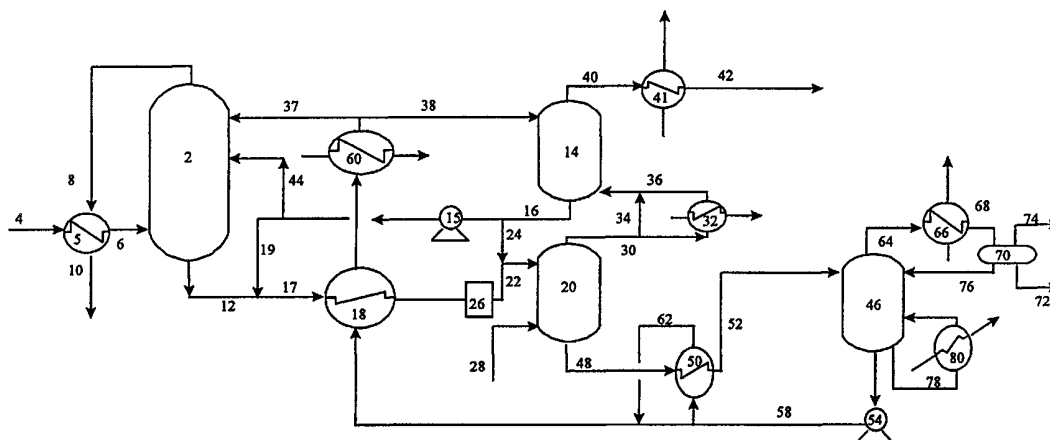




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01B 3/24, 17/04, 17/16, 31/20, C10J 3/00, C10K 1/00, 1/08, F02C 3/00	A1	(11) International Publication Number: WO 99/12847 (43) International Publication Date: 18 March 1999 (18.03.99)
(21) International Application Number: PCT/US98/18939 (22) International Filing Date: 11 September 1998 (11.09.98) (30) Priority Data: 60/058,748 12 September 1997 (12.09.97) US 09/150,846 10 September 1998 (10.09.98) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/150,846 (CON) Filed on 10 September 1998 (10.09.98) (71) Applicant (for all designated States except US): TEXACO DEVELOPMENT CORPORATION [US/US]; 2000 Wetchester Avenue, White Plains, NY 10650 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): JAHNKE, Frederick, C. [US/US]; 2 Winthrop Street, Rye, NY 10580 (US). VOLK, William, P. [US/US]; P.O. Box 4637, Danbury, CT 06813 (US). (74) Agents: RODMAN, Charles, B. et al.; Rodman & Rodman, 7 South Broadway, White Plains, NY 10601 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: REMOVAL OF ACIDIC GASES IN A GASIFICATION POWER SYSTEM WITH PRODUCTION OF HYDROGEN

**(57) Abstract**

This invention is an integrated process which removes acidic gases such as hydrogen sulfide, carbonyl sulfide and carbon dioxide from raw synthesis gas (4). The hydrogen sulfide and carbonyl sulfide is concentrated and separately recovered. The separately recovered carbon dioxide (42) is used as a temperature moderator with the purified syngas (8) in a combustion turbine. The process comprises separating hydrogen sulfide and carbonyl sulfide from a raw synthesis gas (4) by absorption with a liquid solvent (37) in a hydrogen sulfide stripper (2), removing coabsorbed carbon dioxide from the solvent by stripping the solvent (12) with nitrogen (28) in a carbon dioxide stripper (20), separating hydrogen sulfide and carbonyl sulfide from the solvent (48) in a stripper (46) and recovering sulfur from the hydrogen sulfide and carbonyl sulfide. The energy value of the carbon dioxide and its value as a diluent in reducing nitrogen oxides is recovered by using carbon dioxide as a moderator during combustion of the purified syngas in a gas turbine.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

REMOVAL OF ACIDIC GASES IN A GASIFICATION POWER SYSTEM WITH PRODUCTION OF HYDROGEN

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 This invention relates to gasification power generating systems wherein a hydrocarbonaceous fuel is partially oxidized in a gasifier to produce a synthesis gas or syngas which can be used as a fuel in a combustion turbine to produce power, and more specifically to a process for the selective removal of H₂S and COS from the syngas while retaining the values associated with CO₂ and other
10 gases for power production. It also relates to a process for removing CO₂ from the hydrogen content of the syngas.

2. Description of the Prior Art

H₂S and COS are generally removed from the syngas produced by the partial oxidation of a hydrocarbonaceous fuel before the syngas is burned as a
15 high pressure fuel gas in a combustion turbine to drive a generator and produce power. One technique utilizes physical or chemical absorption with a liquid solvent, as disclosed in U.S. Patent No. 5,345,756 to Jahnke et al. In the process of removing the H₂S and COS from the syngas, other acid gases, such as CO₂, are undesirably removed with the H₂S and COS. The retention of CO₂ is
20 desirable because its presence in the high pressure fuel gas generates power when it is expanded in the gas turbine.

Hydrogen is a component of the synthesis gas produced by the partial oxidation of a hydrocarbonaceous fuel. The synthesis gas is purified before use. See U.S. Patent No. 5,152,975 to Fong et al. Procedures for such purification would be more efficient if the CO₂ present in the hydrogen stream could be removed from the hydrogen prior to purification.

To achieve desired SO₂ emission limits, approximately 97% of H₂S + COS must be removed and recovered, typically as elemental sulfur in a Claus plant.

Early attempts to use N₂ to strip coabsorbed CO₂ from physical solvents were either at high pressure, at essentially the same pressure as the H₂S absorption, or at essentially atmospheric pressure. Because the stripping gas requirement increases in direct proportion to pressure, compressing the increased quantity of N₂ to the higher pressure was considered to be practicable only in the case where NH₃ is being produced and the N₂ compression is already required.

A N₂ stripping stage to enrich the Claus plant acid gas feed has been used for some time. In one process, it operates at essentially atmospheric pressure and includes a bottom CO₂ stripping section surmounted by an H₂S reabsorber section. In operation it uses N₂ to strip some CO₂ from the solvent. H₂S in the stripped CO₂ is reabsorbed with an H₂S solvent to give an N₂ plus CO₂ vent stream containing an acceptable amount of about 10 ppm of H₂S. While operation at low pressure minimizes the N₂ stripping gas requirement which is directly proportional to pressure, it increases the solvent flow required to

reabsorb the H_2S which is inversely proportional to operating pressure. Because the reabsorption solvent flow is generally added to the main absorber solvent for regeneration, it increases the regeneration steam requirement. As a result, N_2 stripping at low pressure to obtain a concentrated Claus H_2S stream is
5 unattractive because regeneration solvent flows are excessive and result in prohibitive solvent regeneration steam and refrigeration requirements. Also, the stripped carbon dioxide along with the nitrogen strip gas is vented to the atmosphere and does not contribute to power production in the combustion turbine.

10 A selective acid gas removal process is required to absorb essentially all the H_2S while coabsorbing a minimum amount of CO_2 . Minimum CO_2 removal is required to obtain a concentrated H_2S Claus plant feed to minimize the capital and operating costs of the Claus plant. Co-absorption of CO_2 not only dilutes the Claus H_2S feed, it also decreases the integrated gasification combined cycle
15 (IGCC) power generation thermal efficiency. Since the CO_2 in the high pressure fuel gas generates power when it is expanded in the gas turbine, its removal with the H_2S loses that power generation potential.

The problem is that available acid gas removal processes are not sufficiently selective and co-absorb significant CO_2 . The most selective physical
20 solvents, such as mixed dialkylethers of polyethylene glycol and N methyl pyrrolidone coabsorb over 15% of the CO_2 when solvent flow is set to remove essentially all of the H_2S . This results in a very dilute acid gas which cannot be

processed in a conventional Claus plant. In commercial practice an expensive H_2S selective amine preconcentration is used to increase the Claus feed to 25% H_2S . Even at this concentration the purification is very expensive.

U.S. Patent No. 4,242,108 to Nicholas et al solves the problem of
5 obtaining a concentrated Claus H_2S feed gas by a process utilizing an H_2S absorber, a CO_2 absorber, a H_2S stripper and two CO_2 strippers. The process involves heating the H_2S absorber bottoms solvent and feeding it to a high pressure CO_2 stripping column operating at essentially the same pressure as the H_2S absorber and stripping the coabsorbed CO_2 with a high pressure CO_2 -free
10 inert gas. Nicholas et al notes the possibility of using high pressure N_2 from an air separation unit, however, this disclosure of N_2 use appears limited to NH_3 applications where N_2 has to be compressed and added to the H_2 after acid gas removal to make NH_3 synthesis gas. This application merely routes a portion of the required N_2 through the stripper for beneficial effects and appears limited to
15 situations where CO_2 is rejected from the product gas as in NH_3 synthesis. A major problem with this process is the loss of CO_2 which is vented after being flashed off and the loss of CO_2 and N_2 from the second CO_2 stripper.

U.S. Patent No. 4,568,364 to Galstaun et al discloses the advantage of adding carbon dioxide to a fuel gas for a gas turbine to decrease excess air
20 compression with resultant increase in turbine net power. Also discussed is the advantage in low sulfur coal gasification applications of using nitrogen to strip coabsorbed carbon dioxide from hydrogen sulfide loaded solvent to obtain, after

final hydrogen sulfide stripping, an acceptably concentrated hydrogen sulfide Claus feed gas. Galstaun's process, however, depends on using the selective hydrogen sulfide/carbon dioxide physical solvent acid gas removal system of an adjacent operation producing hydrogen to get the combined advantages of carbon dioxide addition to the fuel gas and the use of nitrogen stripping to obtain a concentrated Claus hydrogen sulfide feed gas. Galstaun imports carbon dioxide into the fuel gas stream by using carbon dioxide loaded solvent from the adjacent hydrogen plant carbon dioxide removal step. Galstaun does not recover coabsorbed carbon dioxide flashed or stripped with nitrogen from the hydrogen sulfide loaded solvent into the fuel gas. Nor does Galstaun recover nitrogen used for stripping into the fuel gas to produce the same advantages in the turbine operation that the carbon dioxide does. Because Galstaun's nitrogen stripper effluent is inevitably contaminated with hydrogen sulfide, it cannot be vented to the atmosphere. Therefore, the gas is sent to the adjacent carbon dioxide stripper where the contained hydrogen sulfide is reabsorbed for recovery.

U.S. Patent Nos. 4,957,515 and 5,240,476, both to Hegarty, offer a solution to the problem of obtaining a concentrated H_2S feed to a Claus unit while retaining the CO_2 content of the syngas as feed to the gas turbine to maximize power recovery. Hegarty uses a small amount of N_2 under pressure to strip coabsorbed CO_2 from the rich physical solvent for recycle to the fuel gas, free of H_2S .

In both Hegarty patents, the H_2S and CO_2 rich solvent from the H_2S absorber bottoms, at about 500 psia, is used to drive a turbine to reduce the pressure to about 90 psia, after which the solvent is stripped of CO_2 using N_2 in a CO_2 stripper operated at 78 psia. The gases from the stripper are recycled while
5 the H_2S laden solvent is sent to an H_2S stripper. In the '476 Hegarty patent the CO_2 rich gases are recompressed and sent directly to the single H_2S absorber. In the '515 Hegarty patent the recompression step is replaced by reabsorption of H_2S in a secondary H_2S absorber. The CO_2 values are absorbed in a solvent and the solvent recycled to the H_2S absorber; the H_2S contaminated nitrogen
10 stripping gas is vented. Nitrogen used in the CO_2 stripper is also vented.

These processes respectively suffer from the energy need to recompress the CO_2 rich recycle to the H_2S absorber from 78 psia to 500 psia and from the venting of N_2 to the atmosphere.

What is needed is a purification process that yields a concentrated H_2S
15 Claus feed, that retains the value of CO_2 , and that does not require excessive pressure changes, or process heating or refrigeration.

SUMMARY OF THE INVENTION

This invention is an integrated process which removes acidic gases such as H_2S , COS and CO_2 from raw synthesis gas. The H_2S and COS is concentrated
20 and separately recovered. The separately recovered CO_2 is used as a moderator with the purified syngas in a combustion turbine. The process comprises

separating H_2S and COS from a raw synthesis gas by absorption with a liquid solvent, removing coabsorbed CO_2 by stripping the solvent with nitrogen, separating the H_2S and COS from the solvent and recovering sulfur from the H_2S and COS . The energy value of the CO_2 and its value as a diluent in reducing
5 NO_x is recovered by using the CO_2 as a moderator during combustion of the purified synthesis gas in a gas turbine.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram showing the removal of H_2S from the synthesis gas product from a gasifier.

10 Figure 2 is a schematic diagram showing improved H_2S gas removal using a high pressure flash drum.

Figure 3 is a schematic diagram showing the removal of H_2S in an integrated acid gas removal unit.

Corresponding reference numbers indicate corresponding parts in each of
15 the figures.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention comprises a process for removing acid gases such as H_2S and COS from synthesis gas before the synthesis gas is burned as a fuel in a combustion turbine to drive a generator and produce power. The H_2S and
20 COS are removed as undesirable contaminants from the synthesis gas while other

acid gases, such as CO_2 are retained in the fuel streams fed to the combustion turbine.

In one embodiment, the CO_2 loss is reduced to a very low level by the use of a solvent for acid gases to remove acid gases from the syngas followed by the
5 use of N_2 at an intermediate pressure of 300 psig, ± 100 psig, preferably 300 psig ± 50 psig, to strip the solvent of absorbed CO_2 .

Clean solvent is regenerated by removal of H_2S by steam reboiling and recycled. The nitrogen stream, containing CO_2 and some H_2S is washed with clean solvent. The H_2S -free stream of nitrogen and CO_2 is utilized in the
10 combustion turbine. The H_2S is sent to a Claus unit for further processing.

This invention also comprises operative steps for removing CO_2 from hydrogen produced by partial oxidation of a hydrocarbonaceous fuel and subsequent shift conversion to form shifted syngas.

In a gasification power system wherein a hydrocarbonaceous fuel is
15 partially oxidized to produce a synthesis gas or syngas from a gasification reactor or gasifier at a pressure of about 1000 psig ± 300 psig, preferably about 1000 psig ± 150 psig, the raw synthesis gas exiting the gasifier primarily comprises H_2 , CO , CO_2 , H_2O , and to a lesser extent N_2 , Ar , H_2S , COS , CH_4 , NH_3 , HCN , HCOOH . Environmental concerns require the removal of H_2S and COS from
20 syngas that will be burned in a combustion turbine.

In removing H_2S and COS from syngas, it is desirable to minimize removal of other acidic gases, such as CO_2 to avoid dilution of the H_2S stream sent to the Claus unit and to maximize the amount of CO_2 sent to the combustion turbine. Increasing the CO_2 to the combustion turbine increases the power
5 produced as the CO_2 is expanded in the combustion turbine and at the same time, minimizes oxides of nitrogen (NO_x) formation by lowering the combustion flame temperature.

This separation is accomplished by sending the syngas to an acid gas recovery unit where it is treated in a first H_2S absorber which uses a liquid
10 solvent for the removal of H_2S . Significant amounts of CO_2 are also removed by the H_2S solvent in the first H_2S absorber, even though the high pressure in the absorber reduces solvent circulation. To recover the CO_2 absorbed in the acid gas solvent, also referred to as the "rich solvent," the rich solvent is heated and the pressure reduced to about 300 psig to desorb the CO_2 .

15 The flashed solvent is sent to a N_2 stripper to remove additional CO_2 . At 300 psig, the desorbed CO_2 and stripping nitrogen can be fed to the combustion turbine without further compression as a diluent to control NO_x and to increase power output. Diluent N_2 is normally produced from an air separation unit for that purpose and is readily available for stripping at the required pressure.

20 Because a small amount of H_2S is stripped with the CO_2 in the N_2 stripper, the stripped H_2S is reabsorbed from the N_2 in a secondary H_2S absorber.

It is to be understood throughout this disclosure that the removal of H₂S also encompasses the removal of COS unless otherwise specified.

In accordance with one embodiment of the present invention, CO₂ removal is reduced to a very low level by the use of N₂ at intermediate pressure
5 to strip the acid gas solvent of absorbed CO₂.

With reference to Fig. 1, a sour unshifted synthesis gas or syngas 4 principally comprising H₂, CO, CO₂ and H₂S at a temperature of 200 °F ± 125 °F, typically 150 °F ± 50 °F, a pressure of 1500 psig ± 1000 psig, typically 1100 psig ± 400 psig, enters heat exchanger 5 where it is cooled to a temperature of
10 about 90°F ± 50 °F, typically 110 °F ± 10 °F, and exits as stream 6. The term “sour” refers to a synthesis gas containing sulfur, whereas the term “sweet” refers to a synthesis gas wherein the sulfur content has been removed.

The cooled unshifted sour syngas stream 6 enters the first H₂S absorber 2 at a pressure of about 1000 psig wherein it contacts a chemical or physical
15 solvent for acid gases, preferably a physical solvent such as methanol and N-methyl pyrrolidone, and most preferably dimethyl ether of polyethylene glycol, available commercially as Selexol® (Union Carbide). The temperatures and pressures shown are based on Selexol® and may vary significantly for other solvents.

20 The sulfur-containing gases such as H₂S and COS are removed. The cleaned, unshifted, sweet syngas 8, at a temperature of about 60 °F to about 130

°F exits H₂S absorber 2 and enters heat exchanger 5 in indirect heat exchange with the sour unshifted syngas 4.

The warmed clean unshifted syngas 10 comprising H₂, CO and some CO₂ at a pressure of about 1000 psig exits heat exchanger 5 and is directed to the combustion turbine (not shown) after being saturated with water, heated and expanded to the proper conditions for combustion in the turbine.

The liquid stream of H₂S rich solvent, including some absorbed CO₂, exits the first H₂S absorber 2 via line 12 and can be optionally combined with recycle solvent 16 exiting the second H₂S absorber 14. The combined solvent 17 is preheated in heat exchanger 18 before entering the CO₂ stripper 20 through line 22. Solvent stream 16 exits the second H₂S absorber 14. A portion or all of the solvent stream represented by line 24 can be separated and combined with the stream 22 of H₂S rich solvent entering the CO₂ stripper 20. A pressure reduction device 26 reduces the pressure to about 300 psig, which are the pressure conditions at which the stripper 20 operates.

CO₂ removal is accomplished by nitrogen stripping. Nitrogen gas stream 28 at a pressure of about 300 psig enters the CO₂ stripper 20 and strips or desorbs the CO₂ and a small amount of H₂S from the solvent before exiting the stripper 20 through line 30.

Because a small amount of H₂S is stripped with the CO₂, the CO₂ and H₂S containing nitrogen stream 30 from the CO₂ stripper 20 is sent to the

second H₂S absorber 14 where the H₂S content is reabsorbed in a solvent. The CO₂ and H₂S containing N₂ stream 30 can be fed directly to the second H₂S absorber 14, or a portion or all of the CO₂ and H₂S containing N₂ stream represented by line 36 can be separated and cooled in heat exchanger 32 and
5 combined with the uncooled portion 34 before entering the second H₂S absorber 14. The second H₂S absorber 14 and the CO₂ stripper 20 operate at the same pressure and can be combined into one vessel.

Solvent 38 enters the secondary H₂S absorber 14 and removes the H₂S from the entering CO₂ and H₂S containing nitrogen stream. Nitrogen stream 40,
10 removed of the H₂S and containing CO₂ exits via line 40, and is passed through heat exchanger 41. The CO₂-rich nitrogen stream exits via line 42 at a pressure of about 300 psig \pm 100 psig, preferably about 300 psig \pm 50 psig, and can be fed to the combustion turbine without further compression as a diluent to control NO_x and increase power output. Diluent N₂ is normally produced from an air
15 separation unit (not shown) for that purpose and is readily available for stripping at the required pressure.

Semi-rich solvent 16 containing H₂S, exits the second H₂S absorber 14 and can be recycled totally or in part to either the first H₂S absorber 2 via line 44, or combined with the solvent 12 exiting the first H₂S absorber 2 to form
20 stream 17, or separated via line 24 and combined with the preheated solvent 22 entering CO₂ stripper 20. Pump 15 increases the pressure of the solvent stream

16 exiting H₂S absorber 14 from about 300 psig to about 1000 psig. All or a portion of the solvent stream enters the first H₂S absorber 2 via line 44 or it can be combined via line 19 with the solvent 12 exiting the first H₂S absorber.

The H₂S-containing solvent 48 exiting the CO₂ stripper 20 is then passed
5 to the H₂S stripper 46. The H₂S-containing solvent 48 is heated in heat exchanger 50 and enters the H₂S stripper 46 via line 52. Because N₂ is only slightly absorbed in the solvent, the N₂ content of the H₂S-containing solvent 52 is minimal. Thus, a highly concentrated H₂S product stream 64 for a Claus or other sulfur processing unit is produced. The solvent 58 stripped of H₂S exits
10 H₂S stripper 46, and after passing through pump 54 and heat exchangers 18 and 60 can be recycled to the first H₂S absorber via line 37 and to the second H₂S absorber via line 38.

The temperature within the CO₂ stripper 20 may be controlled at its optimum level of about 150 °F to about 250 °F by recovering part of the heat
15 from the solvent 58 exiting H₂S stripper 46 and passing through heat exchanger 18. Another option is for all or a portion of solvent stream 58 to pass through heat exchanger 50 in counter-current exchange with the solvent 48 exiting the CO₂ stripper 20, before entering heat exchanger 18.

In H₂S stripper 46 the solvent is reboiled with steam in indirect heat
20 exchanger 80 via line 78 to strip H₂S. The H₂S exits overhead via line 64 where it is cooled in heat exchanger 66 to condense water. The mixed liquid vapor

stream enters separator 70 via line 68 where a portion of the liquid H₂O leaves via line 72 and the H₂S rich product leaves via line 74 to the Claus unit (not shown). A portion of the H₂O is recycled via line 76 to maintain the desired H₂O-solvent balance.

5 Figure 2 shows an alternative configuration for improved gas removal using a high pressure flash drum operating at a pressure of 1000 psig \pm 300 psig, preferably about 1000 psig \pm 150 psig. The solvent is flashed at a temperature of about 150 °F to about 250 °F. This embodiment recovers more CO₂ at higher pressure and will reduce the size of the secondary H₂S absorber 14.

10 In this embodiment solvent 12 with acidic gases exits the first H₂S absorber 2 through the pump 11 and exits heat exchanger 18 as preheated solvent stream 22. Instead of flowing directly to the CO₂ stripper, stream 22 is diverted to a flash drum 82 where about 5% to 25 % of the H₂S and about 10% to 70% of the CO₂ are flashed off. The acid gas depleted solvent flows to the CO₂ stripper
15 20 through line 56. The flashed gases 85 are returned to the first H₂S absorber 2 and combined with the sour unshifted gas 4, after being cooled in exchanger 84 and exiting via line 86.

It is sometimes desired to produce large quantities of hydrogen along with power from a gasification unit. In such instances a portion of the syngas from the
20 gasifier is shifted to hydrogen in a reactor according to the reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. See for example U.S. Patent No. 5,152,975 to Fong et al.,

incorporated herein by reference. The remainder of the syngas is cooled without shifting and, after further processing, sent to a combustion turbine.

The shifted gas is purified by a number of conventional means. One of the most efficient techniques utilized to purify the shifted gas is by means of a pressure swing absorption (PSA) process which removes impurities by use of a pressure change on the adsorbent beds. The shifted gas unfortunately contains a large quantity of CO₂. This is undesirable since the CO₂ reduces the recovery of the hydrogen in the PSA. Furthermore, since CO₂ has no heating value, its presence in the PSA tail gas diminishes the heating value of the tail gas.

Other techniques of H₂ purification, such as methanation, also operate more efficiently when there is full removal of CO₂ from the shifted gas.

For production of power, it is desirable to have CO₂ in the syngas since it helps reduce NO_x formation by lowering the combustion flame temperature and also provides power as it runs through the expander side of the combustion turbine.

A novel and effective technique of accomplishing CO₂ removal and concentration is to combine the use of a physical solvent or other suitable solvent for acid gases to remove the CO₂ from the shifted gas to be fed to the PSA or other purification process while maximizing the content of CO₂ in the syngas used to fuel the combustion turbine.

This is accomplished by combining the above features in the processing steps shown in Figure 3.

Referring to Fig. 3, H₂S and CO₂ depleted shifted gas, consisting primarily of hydrogen, is produced from sour shifted syngas which has been
5 subjected to H₂S removal in shifted gas H₂S absorber 90 and CO₂ removal in CO₂ absorber 104.

The sour shifted gas 109 from the gasifier (not shown) enters shifted gas H₂S absorber 90 through heat exchanger 110 and line 112. The H₂S depleted gas leaves the H₂S absorber 90 via line 114, is combined with solvent stream 116
10 from pump 115 and the CO₂ absorber 104, is cooled in heat exchanger 118 and enters CO₂ absorber 104 via line 120. In CO₂ absorber 104 the syngas 120 is contacted with clean solvent recycle from the sweet CO₂ stripper 100 via pump 101 and line 92 and cooled clean solvent from the H₂S stripper 46 via lines 58 and 121. The H₂S and CO₂ depleted product gas 111, containing mostly
15 hydrogen, is sent to the PSA or other purification procedure via line 122 and heat exchanger 110.

A CO₂ rich nitrogen stream 108 suitable as a diluent feed to the combustion turbine (not shown) is produced from shifted syngas by removing H₂S in a shift gas H₂S absorber 90, followed by solvent absorption of CO₂ in

the H₂S depleted syngas from exit stream 114 in the CO₂ absorber 104 and nitrogen stripping of the CO₂ rich solvent 106 in the sweet CO₂ stripper 100.

A portion 128 of the CO₂ rich solvent 124 exiting the CO₂ absorber 104 is recycled to the first H₂S absorber 2 and a portion 130 is recycled to the shift
5 gas H₂S absorber 90 where it absorbs H₂S.

There are three distinctive features to the combined process.

The first feature takes the CO₂/H₂S-rich solvent from the bottom of the shifted gas H₂S absorber 90 and introduces it via line 88 into the lower part of the first H₂S absorber 2, which is also referred to as unshifted gas H₂S absorber
10 2. Because the unshifted gas has a much lower CO₂ content and partial pressure than the CO₂/H₂S-rich solvent, the unshifted gas H₂S absorber 2 strips the CO₂ from the CO₂/H₂S-rich solvent.

The second feature heats the CO₂/H₂S-rich solvent 12 from the unshifted gas absorber 2 and strips the rich solvent 22 with a sufficient amount of nitrogen
15 or other suitable stripping gas to desorb the CO₂ from the CO₂ stripper 20 operated at about 1000 ± 150 psig. The CO₂/H₂S-rich solvent leaves the first H₂S absorber 2 via pump 11 and line 12, is preheated in heat exchanger 18 and enters the CO₂ stripper 20 via line 22. Nitrogen at about 1000 psig enters line
28. The CO₂ stripper 20 reduces the CO₂ content in the CO₂/H₂S-rich solvent
20 prior to sending the solvent 48 to the H₂S stripper 46 through optional heat

exchanger 50 and line 52. The CO₂ containing nitrogen stream 94 is recycled to the first H₂S absorber 2 through heat exchanger 96 and line 98 where it is combined with the raw, unshifted syngas feed 4 and is ultimately recovered as part of the syngas product 10 passing to the combustion turbine (not shown)

5 wherein the CO₂/N₂ gas mixture functions as a moderator.

The third feature utilizes a CO₂ absorber 104 on the sweet shifted gas 122 which eventually passes to the PSA (not shown) or other H₂ purification process as stream 111. Normally such a CO₂ absorber would rely primarily on pressure differential to regenerate the solvent and vent the CO₂ at atmospheric pressure.

10 However, in this invention the CO₂ rich solvent 106 exiting the CO₂ absorber 104 is directed to the sweet CO₂ stripper 100 where the CO₂ is stripped from the CO₂-rich solvent by N₂ stream 102. The sweet CO₂ stripper pressure is about 300 psig \pm 100 psig, preferably about 300 psig \pm 50 psig.

The CO₂ and N₂ product stream 108 exits from the sweet CO₂ stripper

15 100 and is sent to the combustion turbine (not shown).

Depending upon the quantity of nitrogen available and level of CO₂ desired in the H₂, it may be desirable to enhance the stripping of the CO₂ from the solvent 106 by heating the solvent prior to entering the sweet CO₂ stripper 100 and/or by flashing the stripped solvent 92 at atmospheric pressure after

20 exiting the sweet CO₂ stripper 100.

However, it is preferred that these options not be used since heating requires additional equipment and cooling of the solvent. Flashing at atmospheric pressure vents the CO₂ and makes it unavailable to generate power in the gas turbine. Nevertheless, depending upon economic optimizations, these
5 options may be attractive for specific cases.

This process also has the benefit of producing a concentrated stream 74 of H₂S. The utilization of a CO₂ stripper using nitrogen or some other non-soluble gas, such as H₂, after preheating the rich solvent is extremely effective in minimizing the CO₂ in the gas going to the Claus unit (not shown) to recover the
10 sulfur values. An H₂S purity of greater than 50% can be obtained using this process. This high concentration of H₂S eliminates the need for special handling of the sour gas in the Claus unit and helps reduce the Claus unit size and cost.

A flash drum (not shown) between the sour CO₂ stripper 20 and the H₂S stripper 46 can be used to eliminate additional CO₂ and stripping gas. This can
15 produce an H₂S concentration greater than 95%. However, the relatively small amounts of CO₂ remaining in the solvent after stripping provide a flash gas relatively rich in H₂S and lean in CO₂ and this flash gas requires a compressor to recover the sour gas flashed at the lower pressure along with the CO₂.

Alternatively, a lower pressure sour CO₂ stripper can also be used in
20 place of or in addition to the high pressure (1000 psig) sour CO₂ stripper 20

described in Figure 3. The gas coming from the low pressure stripper is cleaned with a secondary absorber and then routed at about 300 psig \pm 100 psig, preferably about 300 psig \pm 50 psig to the combustion turbine (not shown) as described in Figures 1 and 2. The advantage of having a second sour CO₂ stripper operating at approximately 300 psig is the reduced gas flow which would need to be cleaned in the secondary absorber.

In another embodiment, the high pressure sour CO₂ stripper can be replaced with a flash drum at approximately 1000 \pm 300 psig, preferably about 1000 psig \pm 150 psig followed by an approximately 300 psig \pm 100 psig, preferably about 300 psig \pm 50 psig stripper as shown in Figure 2.

CLAIMS

What is claimed is:

1. A process for the separation, recovery and utilization of acidic gases comprising H_2S , COS and CO_2 contained in a raw synthesis gas produced from the partial oxidation of a hydrocarbonaceous reactant, comprising:

(a) separating the acidic gases from the raw synthesis gas by
5 contacting the synthesis gas with a liquid solvent to selectively absorb and remove at least a portion of the acidic gas from the synthesis gas and produce a purified synthesis gas;

(b) selectively removing CO_2 from the acidic gases contained in the liquid solvent by stripping the liquid solvent with N_2 in a CO_2 stripper to
10 selectively remove the CO_2 and form a gaseous mixture comprising N_2 and CO_2 , and a solvent residue containing H_2S and COS;

(c) purifying the solvent residue containing H_2S and COS to recover the sulfur values.

(d) contacting the gaseous mixture of N_2 and CO_2 with the
15 purified synthesis gas to form a combined N_2/CO_2 -purified synthesis gas mixture; and

(e) combusting the N_2/CO_2 -purified synthesis gas mixture in a combustion turbine wherein the N_2/CO_2 component serves as a moderator during the combustion of said synthesis gas.

2. The process of claim 1, wherein the raw synthesis gas is selected from the group consisting of unshifted synthesis gas, shifted synthesis gas, and separate streams of unshifted synthesis gas and shifted synthesis gas.

3. The process of claim 2, wherein the raw synthesis gas comprises a separate stream of unshifted synthesis gas and a separate stream of shifted synthesis gas.

4. The process of claim 2, wherein the raw unshifted synthesis gas is contacted with a first liquid solvent in a first H₂S absorber to produce a purified unshifted synthesis gas and a first acid-rich solvent containing the COS, H₂S and CO₂ removed from the raw unshifted synthesis gas.

5. The process of claim 4, wherein the first acid-rich solvent is contacted with nitrogen gas in a first CO₂ stripper to form a first acid gas mixture comprising CO₂, N₂ and a small amount of H₂S and COS, and a residual second acid-rich solvent containing the major amount of H₂S and COS present in the first acid-rich solvent.

6. The process of claim 5, wherein the first acid gas mixture is contacted with a second liquid solvent in a second H₂S absorber to selectively remove the COS and H₂S content of the first acid gas mixture and to produce a first gaseous mixture comprising N₂ and CO₂, and a third acid-rich solvent containing the removed H₂S and COS.

7. The process of claim 5, wherein at least a portion of the second acid rich solvent is purified to recover sulfur values.

8. The process of claim 5, wherein at least a portion of the second acid-rich solvent is recycled to the first H₂S absorber.

9. The process of claim 6, wherein at least a portion of the third acid rich solvent is combined with the first acid rich solvent.

10. The process of claim 2, wherein the shifted synthesis gas is contacted with a fourth liquid solvent in a first unshifted gas absorber to produce a treated shifted synthesis gas containing most of the CO₂ and a fourth acid-rich liquid solvent containing H₂S, COS and a minor amount of CO₂.

11. The process of claim 9, wherein the treated shifted synthesis gas is contacted with a fifth liquid solvent in a first CO₂ absorber to remove most of the CO₂ in a first CO₂-rich liquid solvent and to produce a purified shifted synthesis gas.

12. The process of claim 11, wherein the purified shifted synthesis gas is passed to a pressure swing absorption unit.

13. The process of claim 10, where the fourth acid-rich liquid solvent is passed to the first H₂S absorber.

14. The process of claim 11, wherein at least a portion of the first CO₂-rich solvent is passed to a second CO₂ stripper and contacted with nitrogen gas to form a first CO₂-stripped solvent and a second gaseous mixture comprising N₂ and CO₂.

15. The process of claim 14, wherein the second gaseous mixture comprising CO₂ and N₂ is passed to a combustion turbine to serve as a moderator.

16. The process of claim 4, wherein the raw unshifted synthesis gas is processed to remove acid gases at the same time that a raw shifted synthesis gas is processed to remove acid gases.

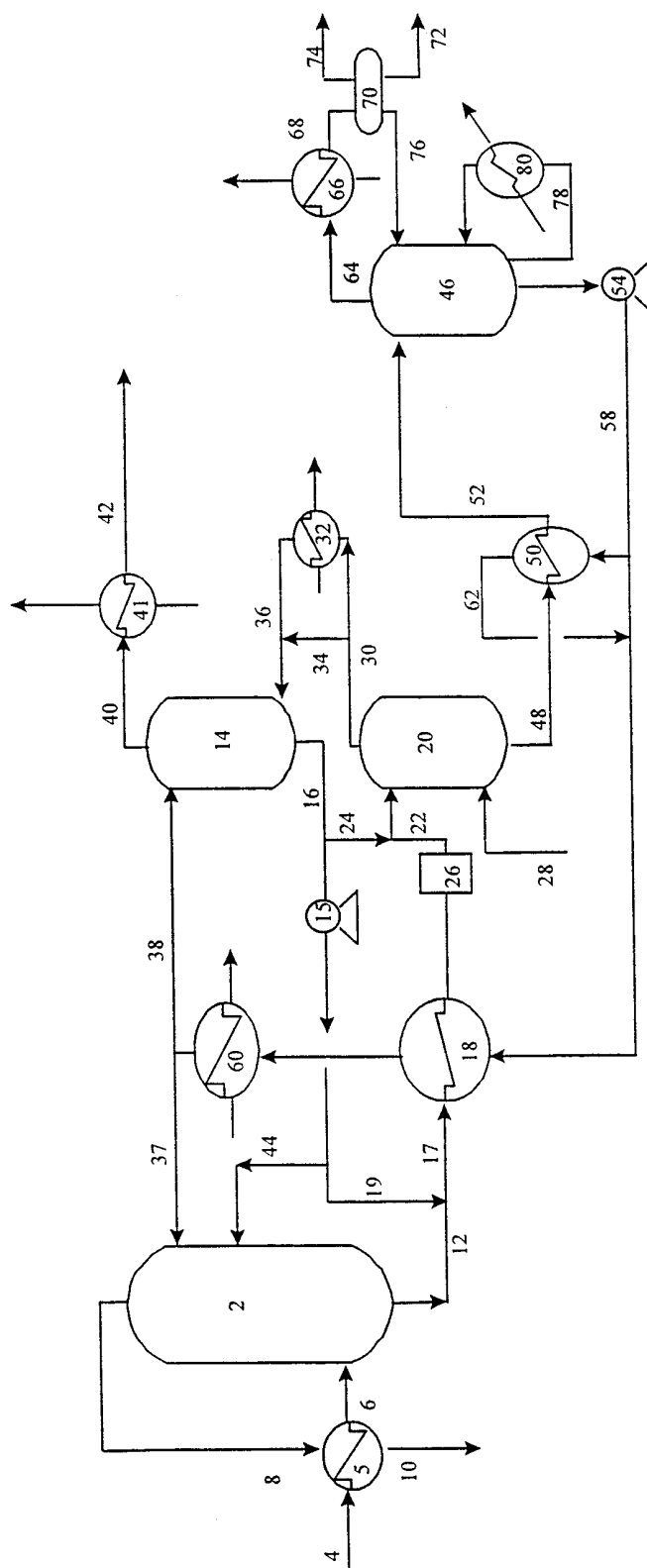


Fig. 1

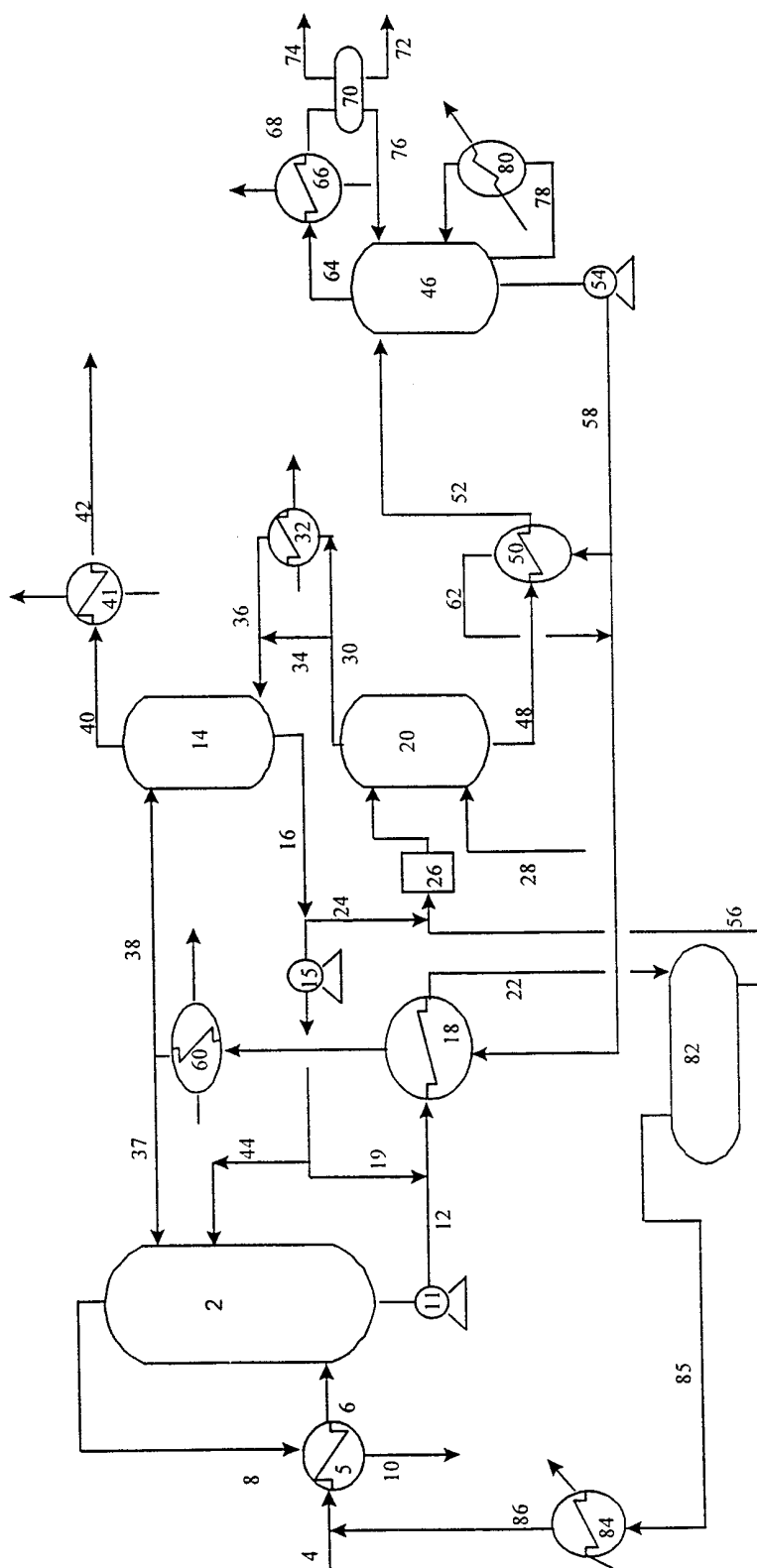


Fig. 2

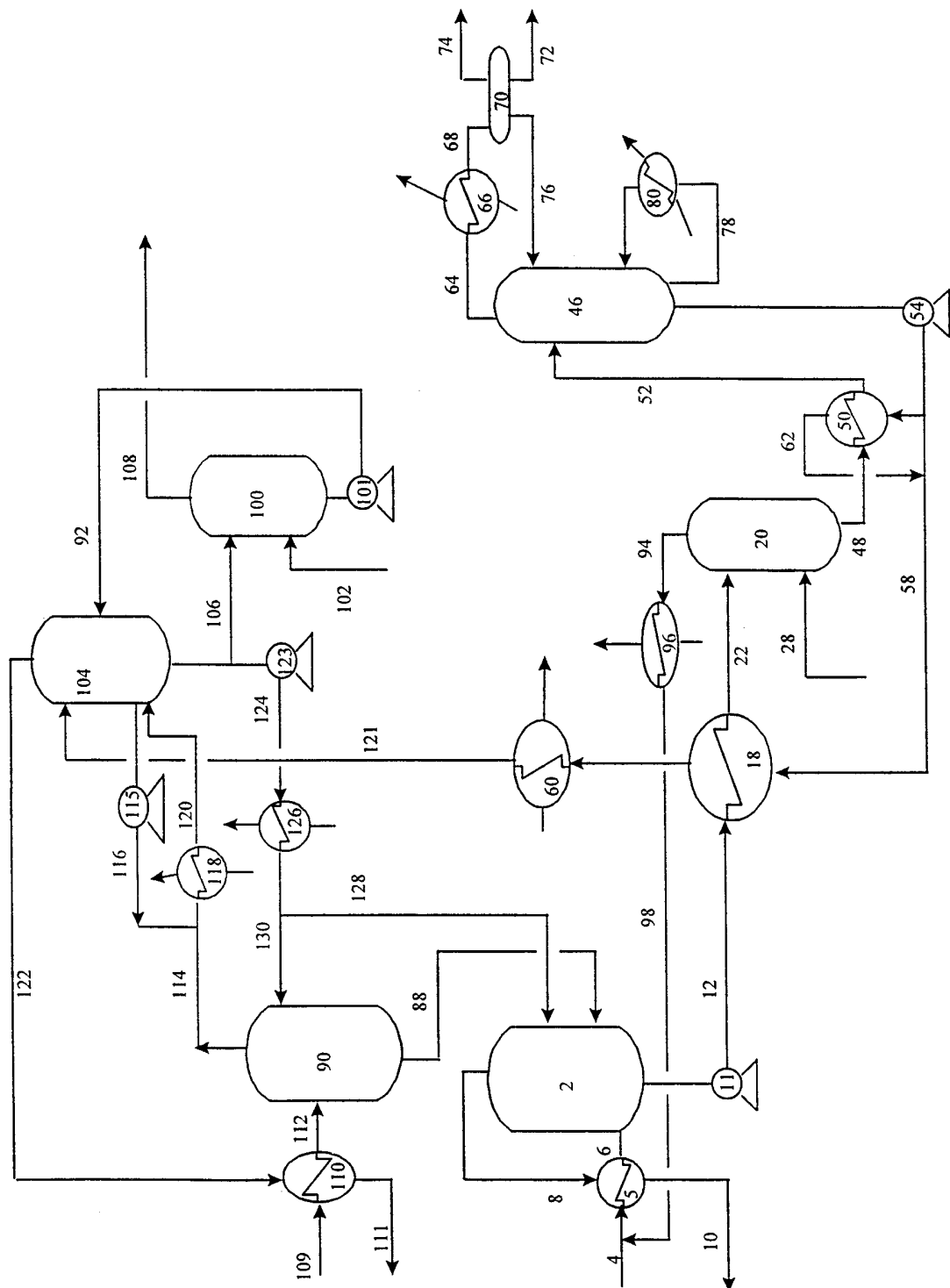


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/18939

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 423/220, 226, 573.1; 48/197R; 60/39.02, 39.12; 95/235, 236

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/220, 226, 573.1; 48/197R; 60/39.02, 39.12; 95/235, 236

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X - Y	US 4,957,515 A (HEGARTY) 18 September 1990, figures 1 and 2 and col. 4 line 48 to col. 6 line 5 and col. 6 lines 51-61.	1, 2, 4, 5, 6, 7 and 8 ----- 1-16
A	US 5,345,756 A (JAHNKE et al.) 13 September 1994, the figure and col. 1 line 38 to col. 2 line 51.	1-16
A	US 5,240,476 A (HEGARTY) 31 August 1993, figure 1 and col. 4 line 46 to col. 6 line 26.	1-16
Y	US 5,152,975 A (FONG et al.) 06 October 1992, figure 2 and col. 2 lines 37-45 and col. 8 line 44 to col. 9 line 52.	3, 10-12 and 16

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*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
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*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
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)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 OCTOBER 1998

Date of mailing of the international search report

11 DEC 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

TIMOTHY C. VANOY

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/18939

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	/ US 4,568,364 A (GALSTAUN et al.) 04 February 1986, figure 1 and col. 6 line 3 to col. 10 line 61.	1-16
A	/ US 4,254,094 A (HEGARTY) 03 March 1981, figure 1 and col. 3 line 12 to col. 6 line 5.	1-16
A	US 4,242,108 A (NICHOLAS et al.) 30 December 1980, figure 1 and col. 2 line 40 to col. 4 line 35.	1-16
A	US 4,202,167 A (SUGGITT et al.) 13 May 1980, figure 1 and col. 3 line 45 to col. 4 line 30.	1-16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/18939

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C01B 3/24, 17/04, 17/16, 31/20; C10J 3/00; C10K 1/00, 1/08; F02C 3/00