

51, is found to be satisfactory for this purpose, since it can be taken directly from the exhaust of exchanger HE-1 at about ambient temperature has sufficiently high specific heat for transfer purposes and is comparatively inert for efficient reactivation.

Summarizing briefly, the refrigeration of adsorber B is transferred for temporary storage to the accumulator S by a carrier stream of reactivating (or transfer) gas that traverses in series relating the adsorber and accumulator, respectively. The start-temperature of the compressed transfer gas can be lowered somewhat if desired, by passing the stream through a water cooler indicated at 52. A blower 50 maintains the transfer gas under sufficient pressure for producing a flow rate that is optimum for efficient heat transfer at the respective units, and that is compatible with the cycle time allowed for reactivation.

The cold accumulator S can be of any suitable type having low resistance to gas flow and large heat storage capacity. In the present instance it comprises a tank that is packed with $\frac{1}{4}$ inch size rocks, and is insulated for cryogenic temperatures. Its function therefore is solely that of heat storage and transfer; i.e. it has neither adsorbing nor absorbing capability.

When refrigeration transfer is completed according to the adsorber temperature reading at T, a heater unit 54 in heat transfer relation to the reactivation line 56 is turned on for providing hot reactivating gas for the adsorber. As shown, the heat can be supplied through valve V-15 from a source of live steam. For setting up the reactivation cycle the accumulator exhaust valve V-8 is closed, the adsorber exhaust valve V-7 is opened for by-passing the accumulator, and the water cooler 52 is turned off. The valves V-10 and V-3B remain open.

The blower 50 now forces a stream of hot reactivation gas by way of valve V-10 and lines 42 and 44 upward through the adsorber B into outlet lines 46 and 48 for exhaust to atmosphere at valve V-7. When the outlet temperature of the adsorber has increased to about 300° F at indicator T, it is held at this point for a preferred time, after which reactivation can be considered complete, subject to cooling down of the adsorber for another on-stream cycle of operation.

In prior practice, cooling of the adsorbers was accomplished in various ways, such as by cooling with a part of the waste nitrogen, otherwise useful for heat transfer purposes. Thus, the work represented by the original adsorber refrigeration was lost to the system, and additional input work was required for restoring the adsorber to its normal low temperature condition. According to the present invention, however, the original adsorber refrigeration stored in the accumulator is retrieved for restoring the adsorber temperature to approximately its normal low level, thereby conserving power represented by the cool-down operation. Since the adsorber units in modern, large capacity air separation plants are necessarily massive, each containing in some instances several tons of adsorbent material, it will be apparent that the cyclic loss of adsorber refrigeration over even a short operating period has heretofore represent a considerable amount of power that must be re-supplied to the system.

Referring again to FIG. 2, cool-down is initiated by again turning on the water cooler 52 (the heater 54

having been turned off) and directing the unheated reactivating gas through the adsorber for exhaust to atmosphere at V-7. The adsorber bed is thereby cooled to about 110° F in readiness for refrigeration re-transfer.

For principal cool-down, the valve V-9 is opened and the valve V-10 is closed, the valves V-8 and V-B remaining closed and the valves V-3-B and V-7 remaining open. In the transfer gas line 57 the water cooler 52 remains on. The water-cooled transfer gas is now blown through valve V-9 into the accumulator and downward therethrough to the adsorber B by way of outlet line 58, check valve CV-13, line 42, check valve CV-6B and line 44. As the now refrigerated transfer gas flows upwardly through the adsorber mass, refrigeration is gradually restored to the mass by heat transfer until the reading at T indicates that the minimum temperature has been reached, i.e., that heat transfer within the accumulator has approached a critical minimum. Since there will be, during transfer and retransfer, certain heat leakage, the comparatively small amount of supplemental or makeup refrigeration required for bringing the adsorber temperature down to about -140° F can economically be supplied by line 38 from the process air line 21, FIG. 1, downstream of the expansion turbine 20, as the stream temperature at this section is in the neighborhood of -200° F. Preferably the supplemental cooling air is valued at V-11 into the transfer line near the lower end of the accumulator at 60. This cold process air, which is continuously bled into the lower or refrigeration receiving end of the accumulator enhances steady-state operation of the system and minimizes interruptions due to thermal unbalance, as could be the case for example, were cold liquid nitrogen periodically fed from a storage tank for make-up refrigeration. This will be apparent by referred to FIG. 2 which indicates the approximate locations of the accumulator refrigeration boundary lines for normal steady-state operation. At the end of refrigeration transfer to the accumulator the refrigeration zone extends, say up to line x, whereas at the end of retransfer it has dropped to line y near the bottom of the accumulator. Thus, uneven addition of make-up refrigeration differing widely in temperature from the zone temperature could change the zone location and upset the thermal balance of the accumulator.

For stabilizing the temperature and preventing freezing of carbon dioxide at the lower end of the accumulator by cold process air from line 38, a small amount of dry air at about 40° F is diverted from the drier outlet, FIG. 1, into line 62 where it passes through a throttling valve V-16 into the accumulator inlet 60, FIG. 2. The temperature of the inlet air is thereby moderated to the extent necessary for preventing freezing of carbon dioxide while providing required make-up refrigeration for adsorber cool-down.

With the reactivated and refrigerated adsorber B now ready for on-stream service, it is put on the line and adsorber A taken out for a similar reactivation and refrigeration transfer cycle by operation of appropriate sectionalizing and control valves diagrammatically indicated in FIG. 2. The inlet line 46 of the adsorber B is connected to the incoming process line 13 by closing valve V-3B and initially opening bleed valve V-2B for gradual pressurization, following which main valve

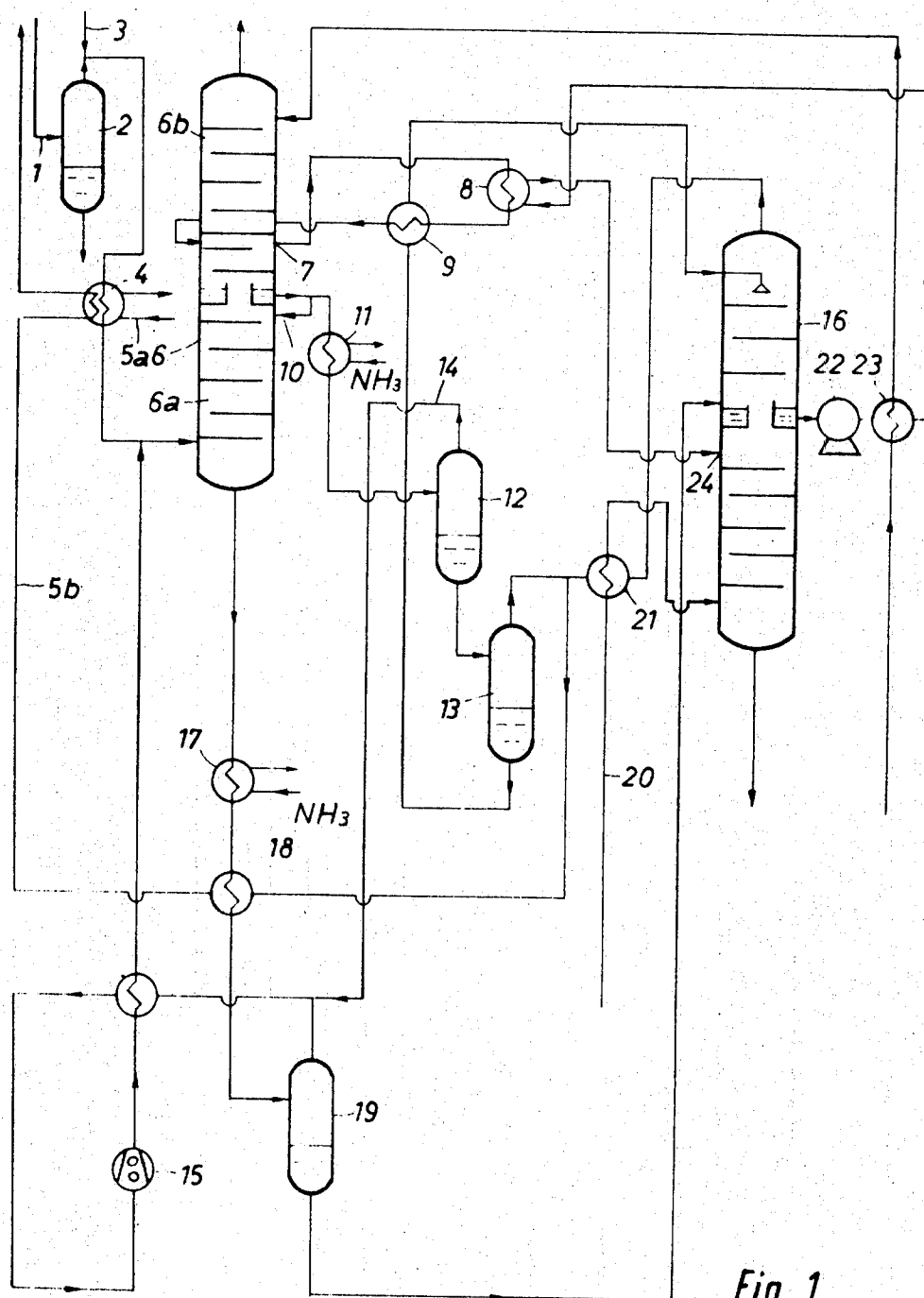


Fig. 1

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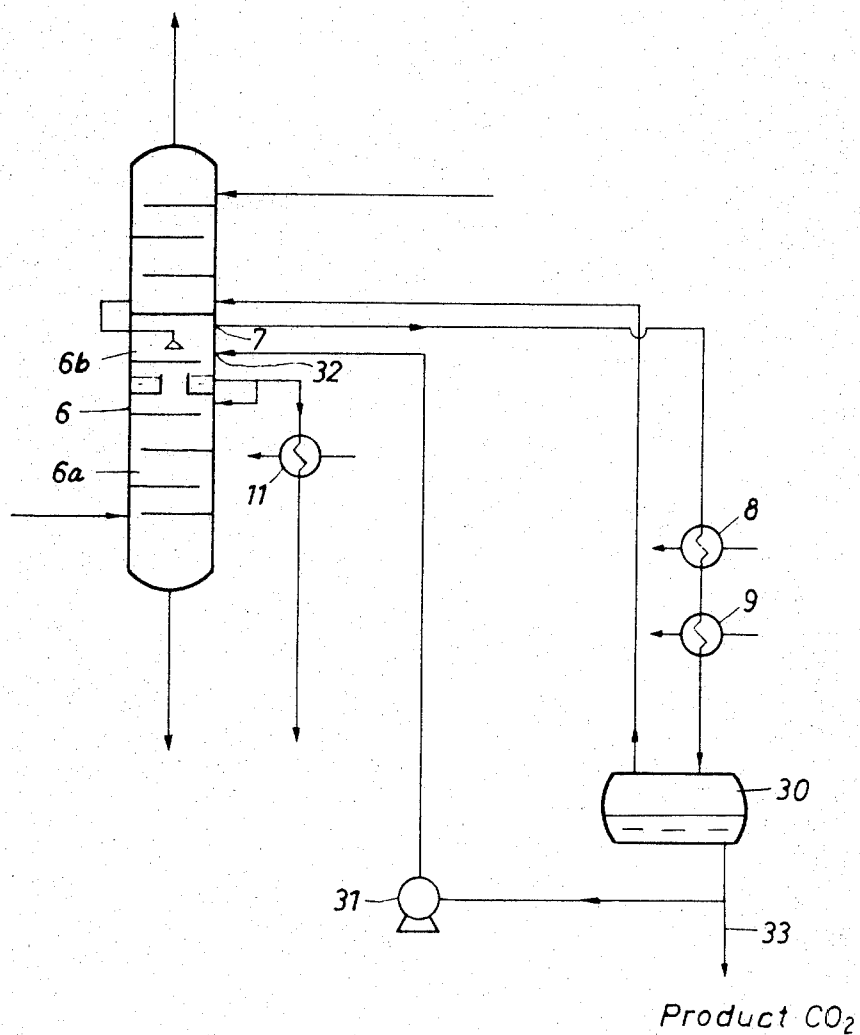


Fig. 2

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PROCESS FOR SELECTIVE ABSORPTION

BACKGROUND OF THE INVENTION

This invention relates to a gas absorption system for the selective removal of at least one component of a gaseous mixture, and in particular to an improvement in such systems wherein the exothermic heat of solution must be dissipated.

In selective gas absorption systems, the scrubbing temperature along the column is dependent on the one hand on the inlet temperature and heat capacity of the process fluids, i.e. the liquid scrubbing agent and the gas, and on the other hand, on the heat of solution of the dissolved gases. If the heat of solution is large as compared to the heat capacity of the process fluids, the scrubbing temperature may rise to such an extent that the solubility of the component to be absorbed will decrease to below workable limits. In such a case, the heat of solution must be removed by one or more cooling techniques.

Part of the cooling necessary for this purpose is conventionally provided by expanding the loaded scrubbing agent to desorb components while simultaneously cooling the solution by evaporative cooling. To utilize the thus-obtained refrigeration values, the resultant cold solution is either fed directly into the column or is heat exchanged indirectly with scrubbing liquid to be fed to the column.

Since it is impossible to completely desorb the solution during the expansion, it is possible to compensate for only a portion of the heat of solution in this manner. This is one of the irreversible refrigeration losses of such processes. Other sources of refrigeration losses are found in imperfect insulation, non-ideal heat exchange and in the thermal equivalent of the pump performance. Because of these refrigeration losses, an external source of refrigeration is required.

One known technique for providing the necessary refrigeration (both from the external refrigeration source as well as the refrigeration recovered by expansion) with the difference between the head and sump temperatures of the scrubbing column remaining the same, is to employ a large amount of scrubbing agent and to pass the same through a cooling stage just once. In this connection, the term "cooling stage" encompasses all types of refrigeration-yielding devices, such as the coolant evaporator and heat exchangers traversed by expansion-cooled solution, which operate at the same temperature level as the bottom of the column from which the scrubbing liquid to be cooled is withdrawn. The coolant evaporator can be disposed in the path of the loaded solution upstream of the expansion vessel or within the column proper in a central section or in the path of the regenerated solvent directly prior to the entrance thereof into the head of the column, i.e., at the point of lowest temperature. It is also conventional to withdraw the scrubbing liquid from a central section of the column and to recycle this liquid via an externally disposed cooling stage.

These processes, which operate with a large amount of scrubbing liquid, exhibit the disadvantage that the quantity of the components remaining in solution during the expansion is very large, and the amount of refrigeration recoverable during the desorption step is correspondingly small. Thereby, the external refrigeration requirements are increased. Furthermore, the

large amount of scrubbing liquid necessitates increased energy requirements for pumping and regenerating same, as well as for increased thermal losses during heat exchange.

If, in this connection, the pure solvent is cooled by the external source of refrigeration, prior to entering the column, i.e. at the lowest temperature level, the cost of refrigeration is increased even further. In contrast thereto, if a coolant evaporator is incorporated into the column, then the necessary heat exchange area is very large, the evaporator is not readily accessible for repair, and in case of any leaks, gas to be scrubbed enters the coolant cycle. Alternatively, when working with a cooling stage disposed externally of the column, it is necessary to provide a pump for handling large amounts of cold saturated solution, and redistributing means for recycling the liquid to the column; additionally, the thermal equivalent of the pump performance must be compensated for by the external source of refrigeration.

Finally, the required refrigeration can be transferred to the scrubbing liquid in a conventional manner by withdrawing the scrubbing liquid several times from several different column plates and conducting this liquid through cooling stages located outside of the column. Though the amount of scrubbing liquid can be kept relatively low by this technique, the other disadvantages described above for the case of a single cooling stage disposed externally of the column are multiplied. Thus, several pumps are required, and the number of conduits to the column, as well as the number of scrubbing distributors are increased.

SUMMARY OF THE INVENTION

As compared to prior systems, it is an object of this invention to provide a novel and improved system for providing the necessary refrigeration values in a selective gas-liquid absorption process in order to compensate for the heat of solution of the dissolved gas.

Upon further study of the specification and appended claims, other objects and advantages of this invention will become apparent. These objects are attained, according to this invention, by withdrawing gaseous mixture to be scrubbed, at least partially, preferably entirely, from a middle section of the scrubbing column, cooling said gaseous mixture and recycling resultant mixture to the scrubbing column. In other words, the gas to be scrubbed is withdrawn from the column along its path through the column, and recycled to the next-higher plate of the column by way of a cooling stage disposed externally of the column.

This technique of providing the cooling to counterbalance the heat of solution exhibits a substantial advantage in that the amount of solvent can be reduced to the minimum necessary amount prescribed by the temperature, pressure, and desired separation of the process. Consequently, by virtue of the minimum amount of scrubbing fluid required in the process, the amount of refrigeration which cannot be recovered during the expansion is also kept to a minimum, which in turn means that the energy requirements for the pumps, the thermal regeneration, and the heat exchange losses are also minimized. At the same time, the investment costs are also relatively low since there is no need for one or more cold pumps, associated con-

duits and distributors; thus, this system is substantially less expensive than the technique based on repeated withdrawals of scrubbing liquid from the column. Finally, the absence of the heat energy associated with the operation of cold pumps means that the refrigeration requirements of the present invention are even further reduced.

In this connection, it is to be noted that the maximum temperature level at which the external refrigeration can be transferred increases with increasing heat capacity of the gaseous mixture. If the heat capacity of the gas mixture is larger than that of the solvent, as can be the case when the absorption is conducted under a high pressure, or when the solubility of the gases to be scrubbed out is very large and the required amount of solvent is accordingly small, the external refrigeration can be supplied at a significantly higher temperature than would be the case in the conventional system wherein the scrubbing liquid is cooled. Under such conditions, the present invention offers an exceptionally significant economic advantage over prior art processes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a preferred comprehensive embodiment of the invention wherein all the components of the gas withdrawn from the intermediate section for cooling purposes are recycled to the column.

FIG. 2 is a modification of FIG. 1, showing only certain parts of FIG. 1, but wherein it is possible to recycle less than all the components of the cooled gaseous mixture.

DETAILED DISCUSSION OF THE INVENTION

The present invention is applicable to all types of systems wherein a liquid solvent is employed to scrub out one or more components from a gaseous mixture. It has special pertinence moreover to absorption process wherein the scrubbing liquid must not exceed a temperature of 40°C, preferably not higher than 0° C. Examples of such systems include but are not limited to those disclosed in U.S. Pat. No. 2,863,527; Further: CO₂ and/or H₂S from converter gas, steam reforming gas, partial oxidation gas, with methanol; benzene or C₇₋₁₂-hydrocarbons from natural gas, coke oven gas, crackgas, refinery gas with toluene or xylene; acetylene from C₂-mixture with acetone.

A preferred embodiment of this invention resides in cooling the gaseous mixture into the condensation zone of at least one component to be absorbed. The advantage of this mode of operation is that the heat of solution is removed at least partially in the form of heat of condensation. This means that the temperature difference necessary for the transfer of a specific amount of cold is reduced, i.e., that the refrigeration can be produced at a higher temperature, resulting in a thermodynamically more efficient system.

In case the gaseous mixture to be cooled, which is withdrawn from the washing column, is not saturated in the component to be condensed, then the formation of condensate is suitably achieved by bringing the gaseous mixture, by means of heat exchange, to the dew point temperature, then further cooling under condensate formation, and finally again heating the condensate-

free gaseous mixture by heat exchange with itself to such an extent that it can be recycled to the scrubbing column. This process is of advantage when the condensed component is to be discharged in the liquid phase. For since at this point of the process other impurities contained in the raw gas, which exhibit a better solubility, have already been absorbed by the solvent, the condensate is obtained in a very pure form.

A particularly advantageous aspect of the embodiment operating with the condensation of one gaseous component resides in withdrawing the gaseous mixture from the scrubbing column at a point where the partial pressure of this component is so high that, during the transfer of only the amount of refrigeration necessary for the removal of the heat of solution, condensation occurs, so that the gaseous mixture is subsequently recycled into the scrubbing column in a condition wherein it is saturated in condensed components. Thus, the temperature level at which the heat of solution is to be removed is increased to above the value applicable to processes involving pure gas cooling with no condensation. This is also of importance in those cases wherein the gaseous mixture exhibits a lower heat capacity than the solvent, because in this case the external refrigeration source can be operated at a higher temperature level than those known processes operating with cooling of the scrubbing liquid.

Another advantageous and highly unusual modification of this invention provides that the liquid condensed out of the gaseous mixture is also, at least in part, recycled to the column. This technique is especially beneficial when a preliminary absorption step takes place prior to the scrubbing stage operated in accordance with the invention, wherein a more soluble component is to be removed beforehand by means of the same solvent. In this manner, solvent substantially saturated with the component of lower solubility is employed to absorb the component of higher solubility. Thus, in this case, only the heat of solution of the component having a higher solubility need be removed. In the section of the column where the components to be absorbed are reintroduced as a condensate, the heat of mixing between the solvent and the condensate is so minor that it can be ignored.

When the condensate is recycled, it is especially advantageous to reintroduce the liquid phase, together with the gaseous mixture, by gravity flow. Under these conditions, a cold pump is completely obviated. However, it can also be advantageous to collect the condensate in a separator and pump it back into the column at least partially. In this case, it is merely necessary to provide a cold pump designed for a small amount of liquid.

Preferably, the gaseous mixture withdrawn from the column is cooled by heat exchange with solution cooled by desorption. The irreversible refrigeration losses are suitably compensated for by cooling an amount of liquid intended for heat exchange with a gaseous mixture, this being done by external refrigeration, and preferably prior to desorption.

The apparatus for conducting the process of this invention comprises a conduit extending from a middle level or section of the column from the gaseous space above a column plate, which conduit is connected to a cooling stage and is connected to the column above the next-higher plate. By middle level, it is generally meant

anywhere from the plate 60 to 85 from the top, preferably 65 to 70 from the top in a column having 100 plates as a basis. In this connection, the cooling stage is preferably arranged at a height that allows the condensates to pass back into the column under their own gravity. However, it can also be advantageous to insert a separator after the cooling stage and to place this separator in communication with the column by way of a conduit provided with pump for the liquid phase, and a conduit for the gas phase. In this instance, it is also advantageous to branch off a conduit for liquid CO₂-product from the separator.

DETAILED DESCRIPTION OF THE DRAWINGS

Referring now to the drawings, they are to be understood as preferred specific comprehensive embodiments of the invention and are not to be construed as limiting the invention as described by the appended claims. For example, the following description will refer to one specific gas composition and one scrubbing agent (solvent), but it is readily apparent that many others can be employed.

All atmospheres are absolute unless otherwise indicated.

The crude gas to be processed has the following composition:

H ₂	61%
N ₂ , CO, Ar, CH ₄	4%
CO ₂	34.5%
H ₂ S	0.5%

The crude gas is fed to the plant via conduit 1 at a pressure of about 76 atmospheres. In the separator 2, aqueous condensate is collected. Through conduit 3, methanol is sprayed into the gaseous mixture in order to prevent the formation of ice in the following parts of the apparatus. The raw gas is then passed into the heat exchanger 4 wherein it is cooled against cold separation products, namely against the hydrogen-nitrogen mixture (N₂ + 3H₂) arriving through conduit 5a from a liquid nitrogen scrubbing stage disposed thereafter (the latter is not shown but is conventional in the production of ammonia synthesis gas — Kirk-Othmer Encyclopedia of Chemical Technology), and against CO₂-enriched gaseous mixture from conduit 5b.

At a temperature of about -10° C., the raw gas is introduced into the H₂S absorption stage 6a of the scrubbing column 6, and brought into contact with CO₂-saturated methanol at that point in order to absorb the hydrogen sulfide.

The H₂S-free gas now passes into the CO₂-absorption stage 6b wherein part of the CO₂-content is absorbed by an increased quantity of methanol. Just above point 7 there is a partition plate, which prevents gas from further passing upwards and liquid from further flowing downward. At that point 7, where the gaseous mixture exhibits a temperature of -20° C., and a partial pressure of CO₂ of about 25 atmospheres, it is withdrawn from the column and cooled to -45° C. in the cooling stage comprising heat exchangers 8 and 9. During this step, the major portion of CO₂ condenses out. Both heat exchangers are placed at such a height that the condensate flows back to the column, together with the gaseous mixture, by gravity flow. The cooled gas then returns to the upper part of the CO₂ absorption stage 6b

at a point just above that partition plate. An external bypass carries liquid from the upper part of stage 6b to the topmost tray of the lower part of that stage. In the upper section of the column, pure solvent is passed countercurrently to the gaseous mixture. The gaseous mixture leaves the head of column 6 at a temperature of -60° C. and with a residual content of 1 ppm H₂S and 20 ppm CO₂.

The solution which leaves the CO₂-absorption stage 6b and is almost saturated in CO₂ is divided. One partial stream, preferably about 20 to 50 percent, is recycled to the column section 6a via conduit 10. The second stream is cooled, in heat exchanger 11, to -30° C. by an ammonia refrigerating machine and then expanded, first into the separator 12 at 25 atmospheres and then into the separator 13 at about 2 atmospheres. A hydrogen-enriched gaseous mixture emerges from the separator 12 by way of conduit 14, and is then recycled into the raw gas via compressor 15. In this manner, the hydrogen losses are reduced. The solution exiting from the separator 13, already mostly freed of CO₂, now flows through the heat exchanger 9 and at that point transfers its refrigeration values (obtained during the desorption) to the gaseous mixture. The thus-warmed solution is introduced to the head of the desorption column 16, operating at about 2 atmospheres.

A middle section of column 16 is supplied with H₂S-loaded solution discharged from the sump of the absorption column 6 at about -10° C. This latter solution is first cooled in heat exchanger 17 to -30° C. by an external source of refrigeration, and then further cooled in heat exchanger 18 by CO₂-enriched gas and finally by expansion to a pressure of 25 atmospheres, and is separated in separator 19 from the hydrogen-enriched gas liberated during this procedure. In order to increase the hydrogen yield, this gas is likewise admixed to the raw gas by way of compressor 15.

The solution leaving the separator 19, after a further expansion to the pressure of the desorption column 16, exhibits a temperature of about -60° C., and is fed to column 16 in this condition.

Nitrogen gas is fed through conduit 20 via heat exchanger 21 into the bottom of column 16 to serve as the stripping gas. A large portion of the dissolved CO₂ as well as some H₂S are thereby liberated from the solutions in column 16. Owing to the H₂S-free solution introduced to the head of column 16, said solution being derived from the CO₂-absorption stage 6b, the H₂S entrained by the rising gaseous stream is absorbed so that there can be withdrawn from column 16, as the head product, an H₂S-free CO₂ diluted with nitrogen. This CO₂ cools the stripping gas in heat exchanger 21 and is finally discharged from the plant together with the CO₂ leaving separator 13, via heat exchangers 18 and 4.

Owing to the desorption of the scrubbing liquid, the latter is cooled to about -65° C. The liquid is withdrawn from column 16 by pump 22, and is passed to heat exchanger 23 where it cools the pure methanol coming from the warm regeneration step. The desorbed liquid is then passed to heat exchanger 8 where it cools the gaseous mixture withdrawn from the column section 6b, and is finally reintroduced into the column 16 at 24. From the sump of column 16, an H₂S-containing solution which is substantially free of CO₂ is withdrawn and fed to the warm regeneration stage.

In FIG. 2, only that portion of the process is illustrated which differs from the process of FIG. 1. Identical components bear the same reference numerals. The gaseous mixture is withdrawn from the column 6 at 7, cooled in heat exchangers 8 and 9 to such an extent that the CO₂ is partially condensed, and thereafter recycled to column 6 by way of the separator 30. The liquid CO₂ collected in 30 is recycled into the column at 32 by way of pump 31. The advantage of this modification of the process resides in that a portion of the CO₂ separated in 30 can be withdrawn as product via conduit 33.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Consequently, such changes and modifications are properly, equitably, and intended to be, within the full range of equivalence of the following claims.

What is claimed is:

1. A process for the removal of at least one component from a gaseous mixture by selective gas-liquid absorption in a liquid polar organic solvent, said component having an exothermic heat of solution in said liquid solvent, said process comprising the steps of:
 - a. passing a gaseous mixture consisting essentially of at least one component selected from the group consisting of CO₂ and H₂S and at least one member selected from the group consisting of H₂, N₂, CO, Ar and CH₄ into the bottom zone of an absorption column having top, middle and bottom zones wherein the middle zone is located between the 60-85 plates from the top of said column, based on 100 plates in the column;
 - b. scrubbing said gaseous mixture by passing a liquid polar organic solvent into the top zone of said absorption column to selectively absorb at least a portion of said component from the remainder of said gaseous mixture, whereby said solvent is heated by said exothermic heat of solution;
 - c. withdrawing partially absorbed gaseous mixture in the gas phase from the middle zone of said column, thereby separating said scrubbed gaseous mixture from said liquid polar organic solvent and the com-

- ponent absorbed therein;
- d. cooling the withdrawn gaseous mixture externally of said column to counterbalance said heat of solution;
- e. recycling at least a portion of cooled gaseous mixture to the middle zone of said absorption column; and
- f. scrubbing said recycled, cooled gaseous mixture with said liquid polar organic solvent to complete said absorption.
2. A process as defined by claim 1 wherein said cooling in step (d) is conducted in indirect heat exchange with cold desorbed solvent.
3. A process as defined by claim 1 wherein said gaseous mixture in step (d) is cooled to below the dew point of said at least one component to be removed by absorption to form a liquid phase of said at least one component, whereby at least a portion of the exothermic heat of solution of said component in said solvent is removed externally of the column as heat of condensation.
4. A process as defined by claim 3 wherein all of said liquid phase and all of resultant cooled gaseous phase are recycled to said absorption column.
5. A process as defined by claim 3 wherein at least a portion of said liquid phase and all of resultant cooled gaseous phase are recycled to said absorption column.
6. A process as defined by claim 4 wherein said liquid phase and gaseous mixture are recycled to said absorption column by gravity flow.
7. A process according to claim 3 wherein the gaseous mixture is withdrawn from the scrubbing column at a point where the partial pressure of the component to be condensed is sufficiently high that during the transfer of only that amount of refrigeration necessary to counterbalance the heat of solution, condensation takes place.
8. A process as defined by claim 2 wherein said cold desorbed solvent heat exchange medium is first cooled by external refrigeration prior to desorption and then indirectly heat exchanged with said withdrawn gaseous mixture.
9. A process according to claim 1, wherein said liquid polar organic solvent is methanol.

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