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Nieh

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[54] TREATMENT OF GAS STREAMS FOR REMOVAL OF ACID GASES

[75] Inventor: **Edward C. Y. Nieh,** Austin, Tex.
[73] Assignee: **Texaco Inc.,** White Plains, N.Y.
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[51] **Int. Cl.**⁴ **C01B 17/16**
[52] **U.S. Cl.** **423/228;** 55/68; 423/229
[58] **Field of Search** 55/68, 73; 423/228, 423/229

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,622,267	11/1971	Bartholome	23/2 R
4,096,085	6/1978	Holoman et al.	425/229 X
4,336,233	6/1982	Appl et al.	423/238
4,483,834	11/1984	Wood	423/228
4,537,753	8/1985	Wagner et al.	423/228
4,575,455	3/1986	Miller	423/228

OTHER PUBLICATIONS

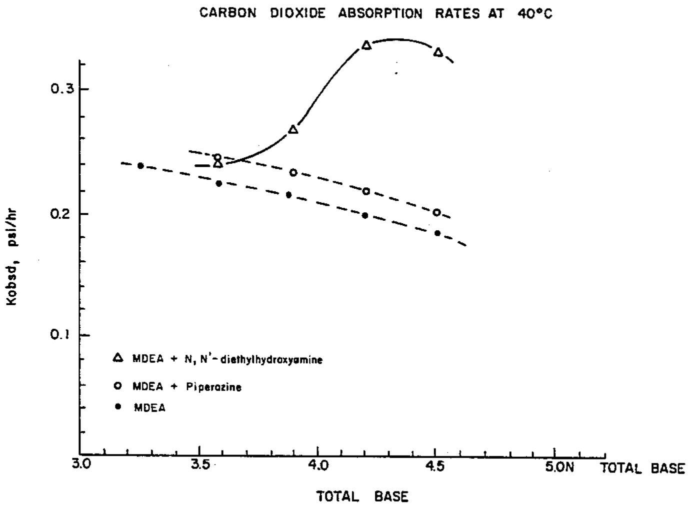
"Reaction of Acid Gases with Mixtures of Amines", Chakravarty et al., Chemical & Engineering Science, vol. 39, #12, pp. 1753-1757, 1984, printed in Great Britain.

Primary Examiner—Charles Hart
Attorney, Agent, or Firm—Jack H. Park; Kenneth R. Priem

[57] ABSTRACT

Improvements are provided in accordance with the present invention by a continuous process for the treating of a gas stream containing acid gas components wherein the gas stream is counter currently contacted in an absorption zone with an aqueous solution of a mixture of N-methyldiethanolamine with N,N-diethyl hydroxylamine to thereby provide for acid gas (e.g., CO_2) absorption.

5 Claims, 2 Drawing Figures



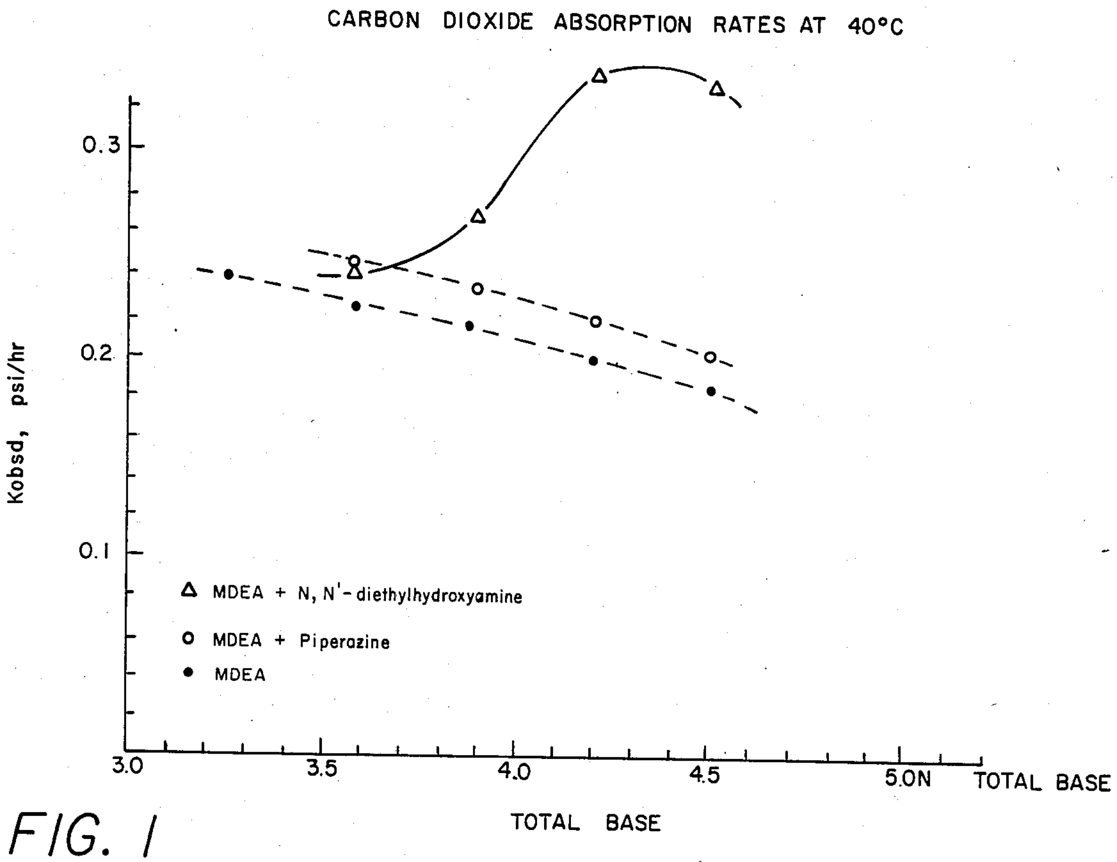
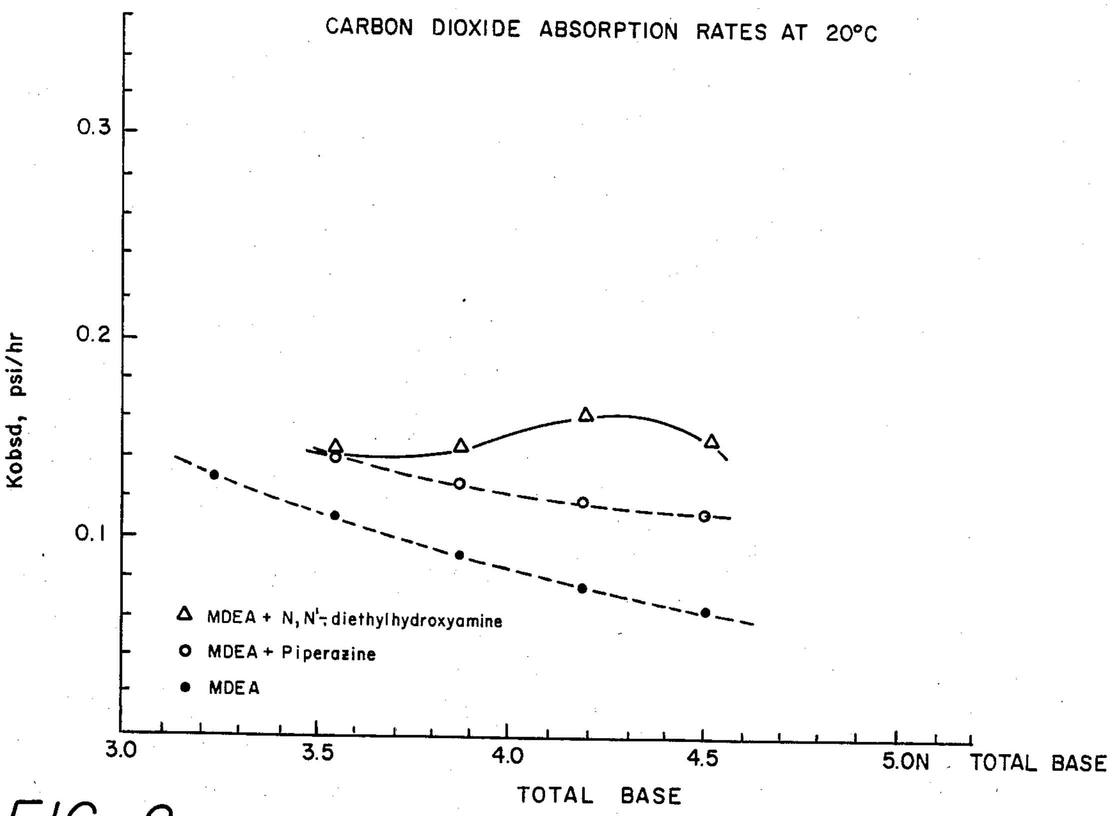

CARBON DIOXIDE ABSORPTION RATES AT 40°C
Kobsd, psi/hr
0.3
0.2
0.1
△ MDEA + N, N'-diethylhydroxyamine
○ MDEA + Piperazine
● MDEA
3.0
3.5
4.0
4.5
5.0N
TOTAL BASE
TOTAL BASE

FIG. 1


CARBON DIOXIDE ABSORPTION RATES AT 20°C
Kobsd, psi/hr
0.3
0.2
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△ MDEA + N, N'-diethylhydroxyamine
○ MDEA + Piperazine
● MDEA
3.0
3.5
4.0
4.5
5.0N
TOTAL BASE
TOTAL BASE

FIG. 2

TREATMENT OF GAS STREAMS FOR REMOVAL OF ACID GASES

TECHNICAL FIELD OF THE INVENTION

This invention relates to a method for the bulk removal of acid gases such as CO_2, H_2S, etc. from a gas stream by absorption. More particularly, this invention is directed to a method wherein a gas stream, such as a synthesis gas stream, a natural gas stream comprising normally gaseous hydrocarbons, etc., is counter currently contacted in an absorption zone with a treating agent consisting essentially of an aqueous solution of N-methyldiethanolamine and N,N-diethyl hydroxylamine to provide a gas stream containing a significantly reduced concentration of acid gas and to provide a rich absorption stream of treating agent containing acid gases absorbed from the gas stream and wherein the rich solution is depressured in order to flash at least a portion of the absorbed acid gases from the rich solution for recovery and to thereby provide a lean solution of N-methyldiethanolamine and N,N-diethyl hydroxylamine for recycle to the absorption zone.

DESCRIPTION OF THE PRIOR ART

Appl et al. U.S. Pat. No. 4,336,233 discloses a process for the removal of CO_2 and/or H_2S from a gas stream by scrubbing the gas stream with an aqueous solution of methyldiethanolamine and piperazine.

French Pat. No. 2,100,475 is directed to a process for the selective absorption of sulfur-containing gases, especially sulfur dioxide and hydrogen sulfide. The patentees propose the use of a solvent for selective absorption which is a mixture of water with at least one nitrogen compound and, optionally, a polyoxyalkylene glycol or a monoalkyl ether of a polyoxyalkylene glycol. The patentees propose to use, as the nitrogen compound, materials such as alkoxylated amines (e.g., diethanolamine, N-methyldiethanolamine, etc.), alkoxylated alkylene polyamines (e.g., tetrahydroxyethylethylene diamine), nitrogen-containing heterocyclic compounds such as hydroxyethoxyethyl-morpholine, dihydroxyethyl-piperazine, hydroxyethylpiperidine, hydroxyethylpyrrole, hydroxyethylacetidine), etc.

H. D. Frazier, et al., in an article entitled "Selective Absorption of Hydrogen Sulfide from Gas Streams", *Industrial and Engineering Chemistry,* November, 1950, pgs. 2288–2292, disclose a selective process for the removal of hydrogen sulfide from a gas stream containing both hydrogen sulfide and carbon dioxide through the use of a solvent comprising an aqueous solution of N-methyldiethanolamine and diethylene glycol.

F. C. Vidaurri et al., in a paper presented at the 1977 Gas Conditioning Conference, disclose the use of N-methyldiethanolamine for the purification of ethane.

The relative solubilities of hydrogen sulfide and carbon dioxide in aqueous solutions of N-methyldiethanolamine is reported in an article by Fang-Yuan Joe et al. entitled "Solubility of H_2S and CO_2 in Aqueous Methyldiethanolamine Solutions" (*Ind. Eng. Chem. Process Des. Dev.,* Volume 21, No. 4, 1982, pgs. 539–544).

The use of "Sterically Hindered Amines for CO_2 Removal from Gases" has been disclosed by Sartori et al. (*Ind. Eng. Chem. Fundam.,* 1983, 22, 239–249).

An article entitled "Purified CO_2 with a Low-Energy Process" (Meissner, *Energy Progress,* Volume 4, No. 1, March 1984, pgs. 17–21) describes a cyclic process for removing hydrogen sulfide from carbon dioxide streams to be used for enhanced crude oil recovery wherein the gas treating agent that is used is an aqueous solution of N-methyldiethanolamine with triethanolamine. A novel feature of the process described by Meissner is the regeneration of the rich solvent treating solution by flashing rather than by steam stripping.

The kinetics of the reaction of CO_2 with methyldiethanolamine is discussed by Barth et al. in an article entitled "Kinetics and Mechanisms of the Reactions of Carbon Dioxide with Alkanolamine: A Discussion Concerning the Cases of MDEA and DEA" (Chemical Engineering Science, Vol. 39 #12, pp. 1753–1757, 1984; printed in Great Britain).

A study of the use of blended amines, specifically N-methyldiethanolamine and monoethanolamine, is described in an article by Chakravaity et al. entitled "Reaction of Acid Gases with Mixtures of Amines" (Chemical and Engineering Science, Vol. 39, #12, pp. 1753–1757, 1984; printed in Great Britain).

The use of N-methyldiethanolamine in a continuous gas treating process involving counter current extraction of acid gases is disclosed in some detail in an article by Roland E. Meissner, III, presented at the 34th Annual Gas Conditioning Process and entitled "Reducing Gas Treating Plant Capital and Operating Costs".

DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a graph showing carbon dioxide absorption rates at 20° C. for the mixture of MDEA with N,N'-diethylhydroxyamine of the present invention in comparison with MDEA and mixtures of MDEA with piperazine, and

FIG. 2 is a similar graph showing carbon dioxide absorption rates at 40° C.

BACKGROUND OF THE INVENTION

Many gas streams such as natural gas streams comprising normally gaseous hydrocarbons such as methane, ethane, propane, etc., synthesis gas streams, etc., are contaminated with sulfur-containing acid gases such as carbon dioxide, hydrogen sulfide, sulfur dioxide, mercaptans, etc. It is important to remove the acid gas impurities from such gas streams in order to enhance their utility and also to avoid environmental pollution. A commonly used method for removing acid gases is a solvent extraction process wherein a lean solvent which has absorption capacity for one or more of the acid gas contaminants is brought into counter current contact with a gas stream to be treated on a continuous basis in an absorption zone. The at least partially purified gas stream is discharged from the absorption zone for further processing or venting to the atmosphere while the solvent, rich in absorbed gases, is discharged from the absorption zone to a regeneration zone where the acid gases are removed from the rich solvent solution to thereby provide a lean solution of solvent for recycle to the absorption zone and a stream of desorbed sulfur-containing contaminants. Such a process is shown, for example in Appl et al. U.S. Pat. No. 4,336,233.

The desorbed stream of carbon dioxide can be used, for example, for enhanced oil recovery.

A wide variety of solvents have been proposed for processes of this nature, such as sulpholanes, alkanolamines, heterocyclic nitrogen-containing compounds such as piperazines and morpholines, etc. The particular solvent that is used in a particular situation is normally selected on the basis of the nature of the gas stream, the degree of contamination of the gas stream to be treated, the pressure of the gas stream and the downstream processing of the gas stream.

Aqueous N-methyl diethanolamine (MDEA) is a preferred gas treating agent for the bulk removal of carbon dioxide from natural gas, associative gas derived from carbon dioxide flooding, coke-oven gases and synthesis gases of any origin. The primary advantage of the MDEA based absorbent stems from the fact that aqueous MDEA can absorb as much as one mole of carbon dioxide per mole of amine whereas common amino-alcohols such as monoethanolamine, diethanolamine, hydroxyethoxyethylamine and diisopropanolamine can absorb not much beyond 0.5 mole/mole of amine. Furthermore, under a high carbon dioxide loading condition, the aqueous MDEA absorbent can be regenerated by adiabatic flashing when pressure is reduced. These features contribute to the overall energy efficiency of gas treating processes based on aqueous MDEA.

The energy efficiency and equipment costs of gas treating processes can be further improved if the total amine concentration of the absorbent can be increased. A factor limiting how much MDEA concentration can be increased is that at a certain point any further increase in MDEA concentration will result in a counter-productive absorption rate decrease. The prior art discloses that morpholine, monomethyl ethanolamine and piperazines can be used to increase the total base in the MDEA based absorbent.

Although the results that have heretofore been obtained with N-methyldiethanolamine have been encouraging, they have not been entirely satisfactory and there is a need for improvement.

SUMMARY OF THE INVENTION

Improvements are provided in accordance with the present invention by a continuous process for the treating of a gas stream contaminated with acid gases wherein the gas stream is counter currently contacted in an absorption zone with an aqueous solution of N-methyldiethanolamine and N,N-diethylhydroxylamine to thereby provide for acid gas (e.g., CO_2) absorption. The gas stream which is thus treated, can be discharged from the absorption zone as a gas stream substantially depleted of acid gas for further downstream processing while the rich concentrated aqueous solution of a mixture of N-methyldiethanolamine with the N,N-diethyl hydroxylamine can be discharged from the absorption zone for regeneration, all in accordance with known procedures.

In accordance with the preferred embodiment of the present invention, the desorption is accomplished by reducing the pressure on the rich concentrated solution of MDEA and the N,N-diethyl hydroxylamine whereby the absorbed acid gas will flash from the solution to at least partially purify the same. One, or preferably a plurality of stages of flashing are incorporated in order to at least partially purify the concentrated aqueous solution of MDEA and the N,N-diethyl hydroxylamine so that it can be recycled to the absorption zone.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The starting materials for the preparation of the gas treating solution of the present invention are water, N-methyldiethanolamine and N,N-diethyl hydroxylamine.

The N-methyldiethanolamine will suitably be used in an amount such that the aqueous gas treating solution contains from about 40 wt. % to about 60 wt. % of N-methyldiethanolamine. A lesser amount of N,N-diethyl hydroxylamine may suitably be used such that the aqueous gas treating solution contains from about 5 wt. % to about 15 wt. % of the N,N-diethyl hydroxylamine.

When the gas stream to be treated contains a significant amount of CO_2, a preferred treating solution will consist essentially of an aqueous solution of N-methyldiethanolamine and N,N-diethyl hydroxylamine in order to attain an enhanced rate of removal of the CO_2.

Treating conditions in the absorption zone may include, for example, a temperature of about 10° to about 70° C. and a pressure of about atmospheric to about 2000 psig.

The equipment to be used in the practice of the present invention may be of any suitable conventional construction, as disclosed for example, in the prior art mentioned above.

EXAMPLE OF PRACTICE OF THE PREFERRED PROCESS OF THE PRESENT INVENTION

By way of example, a feed gas may be derived from a natural gas well consisting essentially of hydrocarbons (e.g., methane) and contaminated with from about 30 to 50 wt. % of CO_2.

The gas may be fed to an absorption tower of conventional construction at a rate of about 200 cubic meters per hour.

At the same time a lean aqueous solution of N-methyldiethanolamine and N,N-diethyl hydroxylamine containing about 50 wt. % of N-methyldiethanolamine and about 5 wt. % of N,N-diethyl hydroxylamine may be charged to the top of the absorption tower at a temperature of about 50° C.

As a consequence, the gas fed to the absorption tower will be significantly purified such that the treated gas leaving the absorption zone will contain not more than about 2 wt. % of CO_2.

EXAMPLES

The invention will be further illustrated by the following specific examples which are given by way of illustration and not as limitations on the scope of this invention.

Example 1

In order to demonstrate the efficacy of the present invention, for the selective removal of carbon dioxide, a number of experiments were performed in a specially designed apparatus.

The apparatus comprised a thermostated autoclave equipped with gauges, a pressure transducer, Validyne model CD23 and an adjustable speed stirrer containing 250 ml of the absorbing agent to be tested and was stirred at 450 rpm rate and evacuated to 24 inches of Hg vacuum. A sample of carbon dioxide, 3785 ml at 67 psig. was allowed to expand at reaction temperature into the thermostated vapor space of the evaporated autoclave while minimizing the disturbance of the vapor liquid interface. The absorption rate was then determined from the subsequent pressure drop which results from carbon dioxide being absorbed into the test solution. The pressure drop was recorded on a strip chart recorder. The observed first order rate constant was calculated by the method of Guggenheim (E. A. Guggenheim, *Phil. Mag.*, 1, 538 (1926)) from the pressure time plot covering four to five half lives of the reaction. The results of Examples 1-26 are listed in Tables I and II and are further illustrated in graphical form in FIG. **1** and FIG. **2**.

TABLE I

Carbon Dioxide Absorption Rates at 40° C.[a]

Example	Additive	Grams	N	Total[b] Base N	Kobsd psi/hr	Half Life, Hours
1	None	—	—	3.26	0.237	2.92
2	MDEA	9.2	0.31	3.57	0.227	3.05
3	MDEA	18.4	0.62	3.88	0.217	3.19
4	MDEA	27.6	0.93	4.19	0.201	3.45
5	MDEA	36.8	1.24	4.50	0.179	3.87
6	Piperazine	3.3	0.31	3.57	0.244	2.84
7	Piperazine	6.6	0.62	3.88	0.239	2.90
8	Piperazine	9.9	0.93	4.19	0.218	3.18
9	Piperazine	13.2	1.24	4.50	0.206	3.36
10	N,N—diethyl hydroxylamine	6.9	0.31	3.57	0.236	2.94
11	N,N—diethyl hydroxylamine	13.8	0.62	3.88	0.261	2.65
12	N,N—diethyl hydroxylamine	20.7	0.93	4.19	0.354	1.96
13	N,N—diethyl hydroxylamine	27.6	1.24	4.50	0.352	1.97

[a] Experiments were carried out using 3.26 N aqueous MDEA promoted with additive as noted in the table.

[b] Total base is the sum of normality of additive and the normality of MDEA.

TABLE II[a]

Carbon Dioxide Absorption Rates at 20° C.

Example	Additive	Grams	N	Total[b] Base N	Kobsd psi/hr	Half Life, Hours
14	None	—	—	3.26	0.132	5.25
15	MDEA	9.2	0.31	3.57	0.111	6.24
16	MDEA	18.4	0.62	3.88	0.093	7.41
17	MDEA	27.6	0.93	4.19	0.081	8.56
18	MDEA	36.8	1.24	4.50	0.069	10.04
19	Piperazine	3.3	0.31	3.57	0.144	4.81
20	Piperazine	6.6	0.62	3.88	0.133	5.29
21	Pierazine	9.9	0.93	4.19	0.121	5.72
22	Piperazine	13.2	1.24	4.50	0.118	5.87
23	N,N—diethyl hydroxylamine	6.9	0.31	3.57	0.131	5.27
24	N,N—diethyl hydroxylamine	13.8	0.62	3.88	0.133	5.20
25	N,N—diethyl hydroxylamine	20.7	0.93	4.19	0.164	4.21
26	N,N—diethyl hydroxylamine	27.6	1.24	4.50	0.151	4.59

[a] Experiments were carried out using 3.26 N aqueous MDEA promoted with additive as noted in the table.

[b] Total base is the sum of normality of additive and the normality of MDEA.

Note from Tables I and II, and more particularly from FIG. **1** and FIG. **2**, that N,N'-diethyl hydroxylamine was effective for the absorption of CO_2. Thus, at a total base below about 4, the mixture of N,N'-diethyl hydroxylamine with MDEA had about the same effectiveness as the mixture of piperazine with MDEA.

However, it has been surprisingly discovered in accordance with the present invention that the mixture of N,N'-diethyl hydroxylamine and MDEA of the present invention was strikingly superior than the mixture of piperazine with MDEA. Thus, there was a progressive decline of Kobsd for MDEA alone and in admixture with piperazine, but a significant and unexpected increase in Kobsd for the mixture of N,N'-diethyl hydroxylamine of the present invention.

What is claimed is:

1. A method for the purification of a stream of gas comprising a normally gaseous hydrocarbon or synthesis gas contaminated with acid gases which comprises the steps of:

countercurrently contacting said gas stream in an absorption zone with a treating agent to thereby remove a substantial portion of the acid contaminants from said hydrocarbon gas stream by absorption into said treating agent, discharging an at least partially purified hydrocarbon gas stream from said absorption zone, and discharging said treating agent enriched with absorbed acid gas components from said absorption zone, said treating agent consisting essentially of an aqueous solution of from about 40 to about 60 wt. % of N-methyldiethanolamine and from about 5 to about 15 wt. % of N,N-diethyl hydroxylamine.

2. A method as in claim **1**, wherein the conditions utilized in said absorption zone include a temperature within the range of about 10° to about 70° C. and a pressure of from about atmospheric to about 2000 psig.

3. A method as in claim **1** wherein the sum of the normality of the N-methyldiethanolamine and the normality of the N,N'-diethyl hydroxylamine in said aqueous solution is about 4 or more.

4. A method for the purification of a stream of gas comprising a normally gaseous hydrocarbon or synthesis gas contaminated with acid gases, including carbon dioxide, which comprises the steps of:

countercurrently contacting said gas stream in an absorption zone with a treating agent to thereby remove a substantial portion of the carbon dioxide contaminants from said hydrcarbon gas stream by absorption into said treating agent, discharging an at least partially purified hydrocarbon gas stream from said absorption zone, and discharging said treating agent enriched with absorbed carbon dioxide from said absorption zone, said treating agent consisting of an aqeouous solution of from about 40 to about 60 wt. % of N-methyldiethanolamine and from about 5 to about 15 wt. % of N,N'-diethyl hydroxylamine.

5. A method as in claim **4** wherein the sum of the normality of the N-methyldiethanolamine and the normality of the N,N'-diethyl hydroxylamine in said aqueous solution is about 4 or more.

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