2-26-2019

Method of Increasing Mass Transfer Rate of Acid Gas Scrubbing Solvents

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US010213734B2

(12) **United States Patent**
Remias et al.

(10) **Patent No.: US 10,213,734 B2**
(45) **Date of Patent: Feb. 26, 2019**

(54) **METHOD OF INCREASING MASS TRANSFER RATE OF ACID GAS SCRUBBING SOLVENTS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 217 days.

(21) Appl. No.: **15/221,100**

(22) Filed: **Jul. 27, 2016**

(65) **Prior Publication Data**

US 2016/0361683 A1 Dec. 15, 2016

Related U.S. Application Data

(62) Division of application No. 13/853,292, filed on Mar. 29, 2013, now Pat. No. 9,409,125.

(51) **Int. Cl.**

B01D 53/14	(2006.01)
B01D 53/86	(2006.01)
C07F 9/54	(2006.01)
C07F 15/06	(2006.01)
C07F 3/00	(2006.01)
B01J 31/02	(2006.01)
C07F 3/06	(2006.01)

(52) **U.S. Cl.**

CPC ***B01D 53/1493*** (2013.01); ***B01D 53/1475*** (2013.01); ***B01D 53/8671*** (2013.01); ***B01D 53/8681*** (2013.01); ***B01J 31/0271*** (2013.01); ***C07F 3/003*** (2013.01); ***C07F 3/06*** (2013.01); ***C07F 9/5456*** (2013.01); ***C07F 9/5463*** (2013.01); ***C07F 15/065*** (2013.01); *B01D 2252/20421* (2013.01); *B01D 2252/20431* (2013.01); *B01D 2252/20442* (2013.01); *B01D 2252/20447* (2013.01); *B01D 2252/20452* (2013.01); *B01D 2252/20484* (2013.01); *B01D 2252/20489* (2013.01); *B01D 2252/602* (2013.01); *B01D 2255/70* (2013.01); *B01D 2256/245* (2013.01); *B01D 2257/504* (2013.01); *Y02C 10/06* (2013.01); *Y02P 20/152* (2015.11)

(58) **Field of Classification Search**

None

See application file for complete search history.

(56) **References Cited**

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* cited by examiner

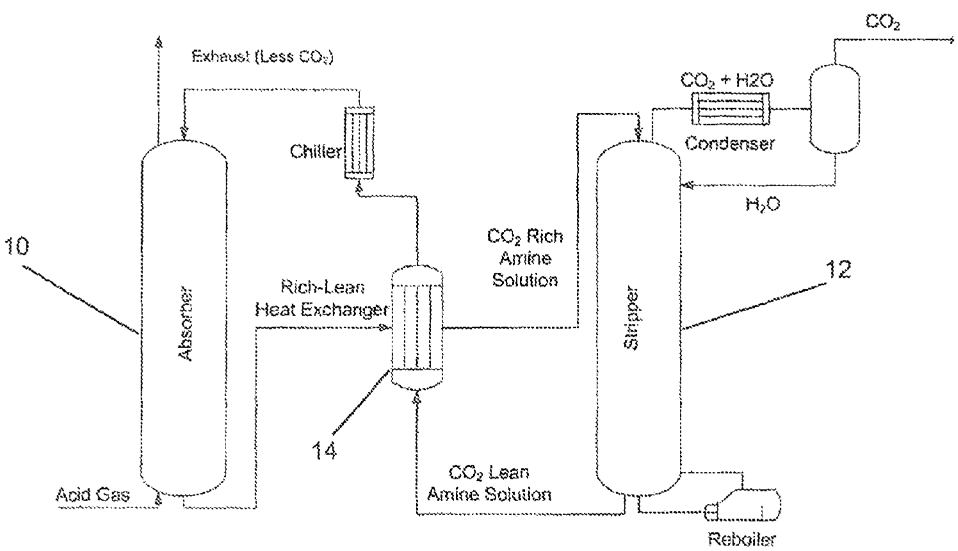
Primary Examiner — Anita Nassiri-Motlagh

(74) *Attorney, Agent, or Firm* — King & Schickli, PLLC

(57) **ABSTRACT**

A method of increasing the overall mass transfer rate of acid gas scrubbing solids is disclosed. Various catalyst compounds for that purpose are also disclosed.

12 Claims, 6 Drawing Sheets



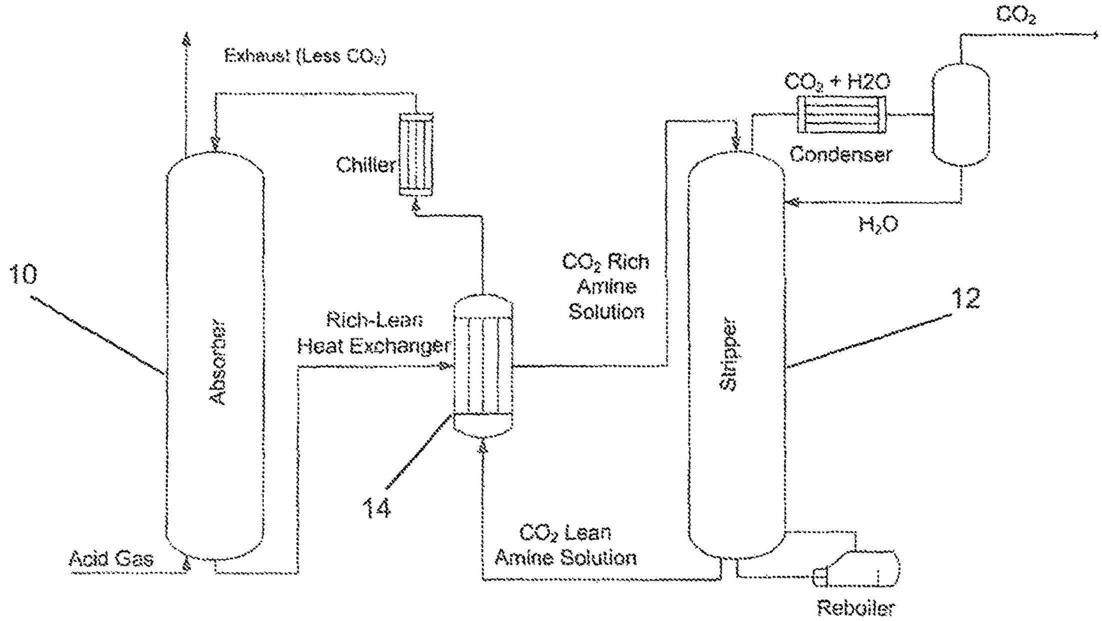
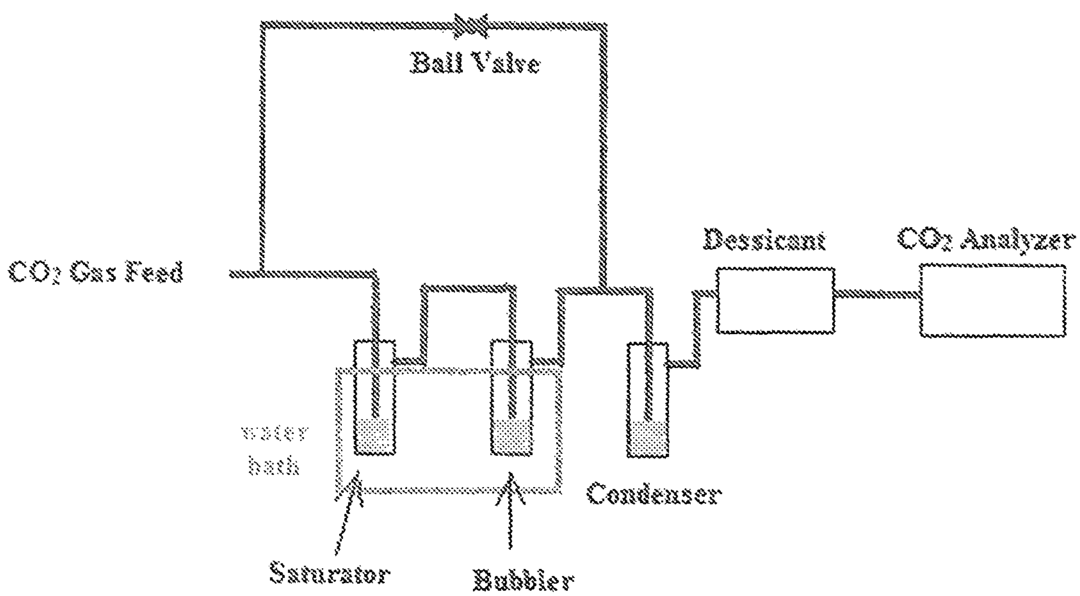
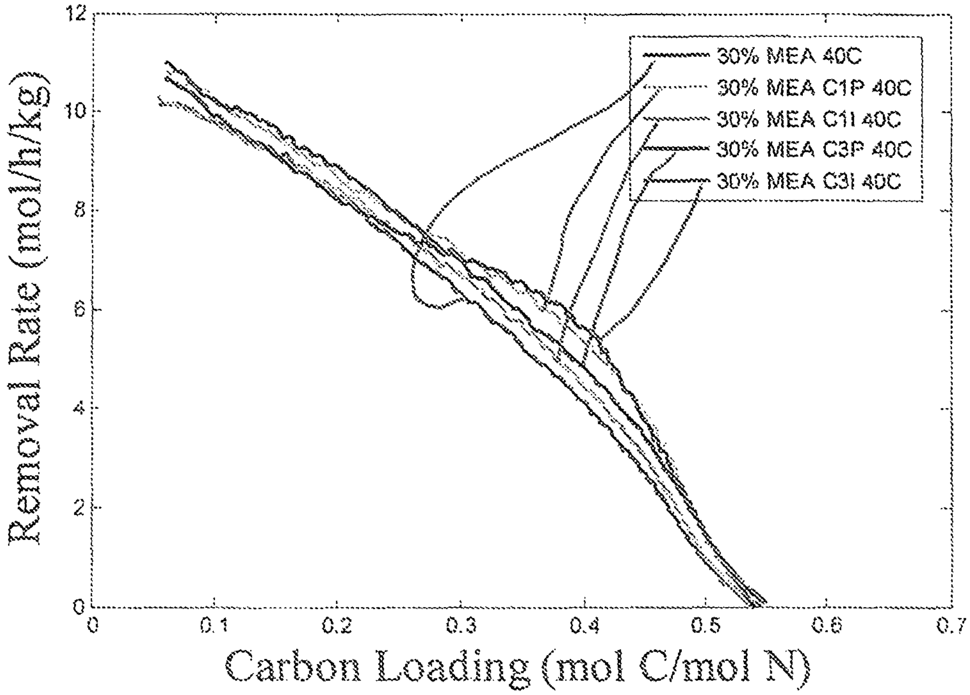

CO2
Exhaust (Less CO2)
CO2 + H2O
Chiller
Condenser
H2O
10
CO2 Rich
Amine
Solution
Rich-Lean
Heat Exchanger
12
Absorber
Stripper
14
CO2 Lean
Amine Solution
Acid Gas
Reboiler

FIG. 1



Ball Valve
CO2 Gas Feed
Dessicant
CO2 Analyzer
water bath
Condenser
Saturator
Bubbler

FIG. 2



30% MEA 40C
30% MEA C1P 40C
30% MEA C1I 40C
30% MEA C3P 40C
30% MEA C3I 40C
Removal Rate (mol/h/kg)
Carbon Loading (mol C/mol N)
0
2
4
6
8
10
12
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7

FIG. 3

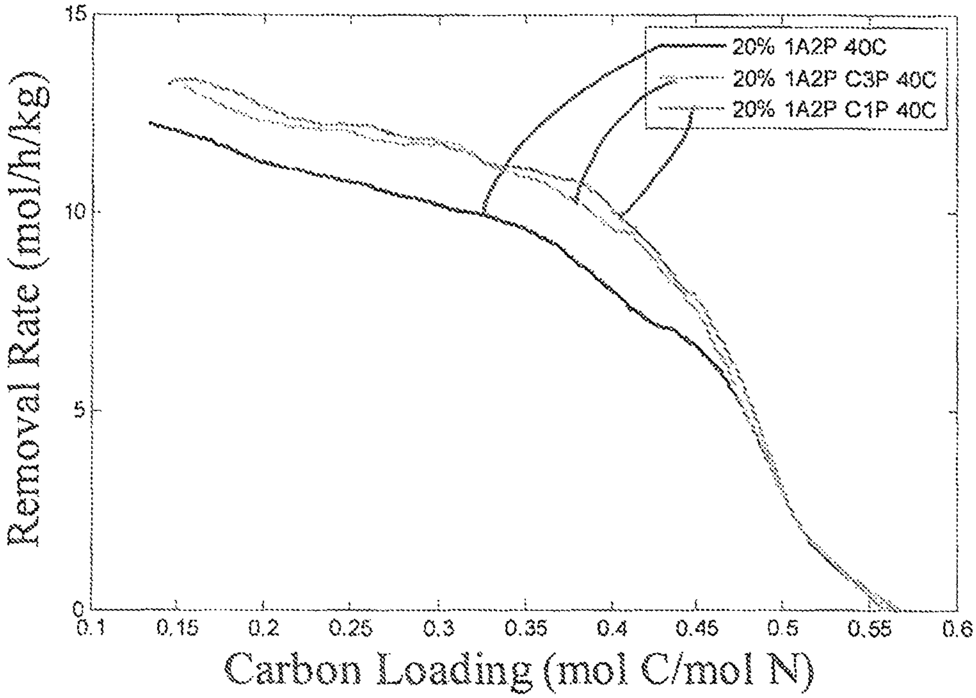

15
10
5
0
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
Removal Rate (mol/h/kg)
Carbon Loading (mol C/mol N)
20% 1A2P 40C
20% 1A2P C3P 40C
20% 1A2P C1P 40C

FIG. 4

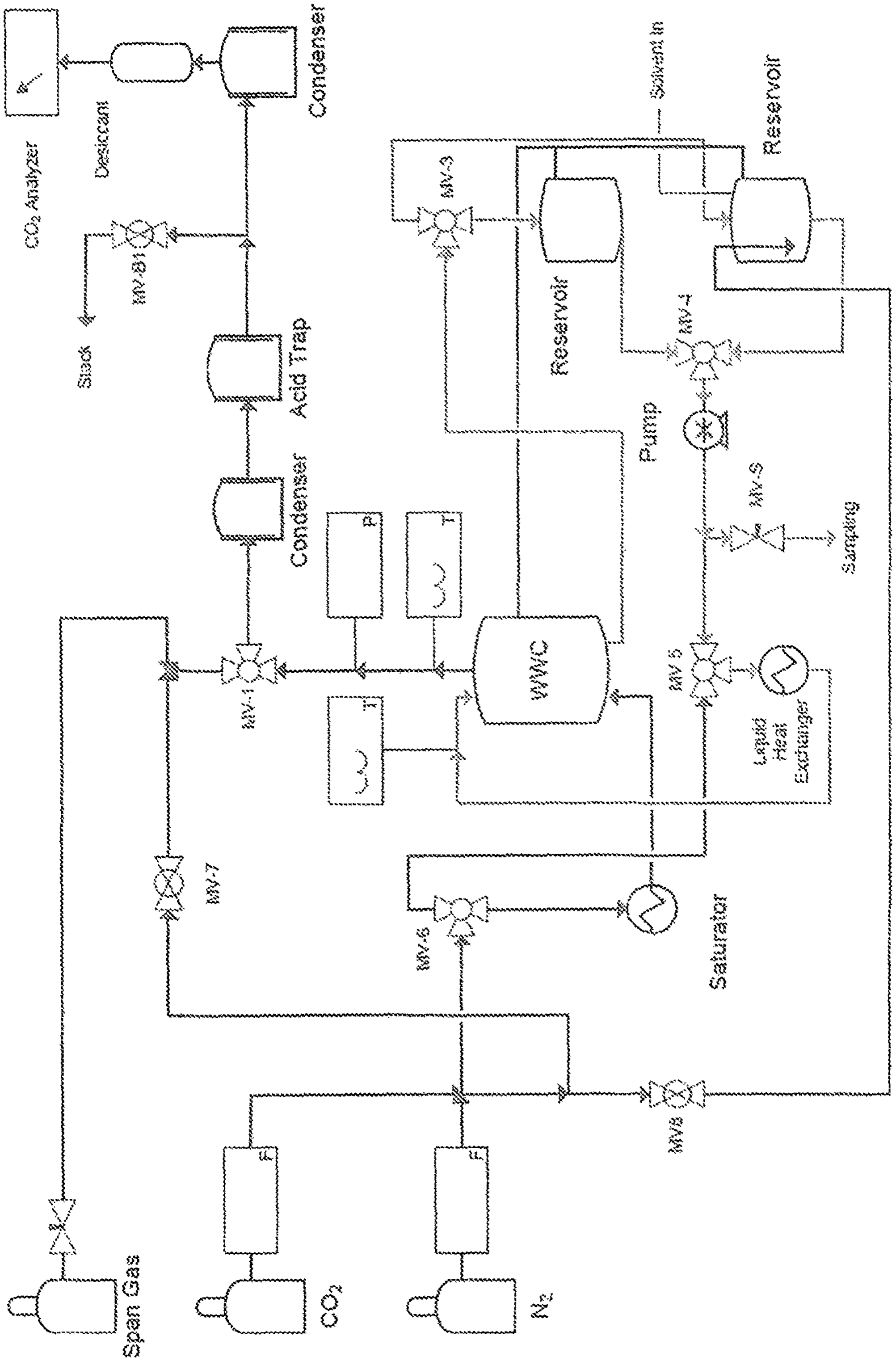

Span Gas
CO_2
N_2
F
F
MV-7
MV-6
Saturator
MV8
MV-1
P
T
T
WWC
Condenser
Acid Trap
Condenser
Desiccant
CO_2 Analyzer
MV-B1
Stack
MV-3
Reservoir
Reservoir
Solvent In
MV-4
Pump
MV-S
Sampling
MV 5
Liquid Heat Exchanger

FIG. 5

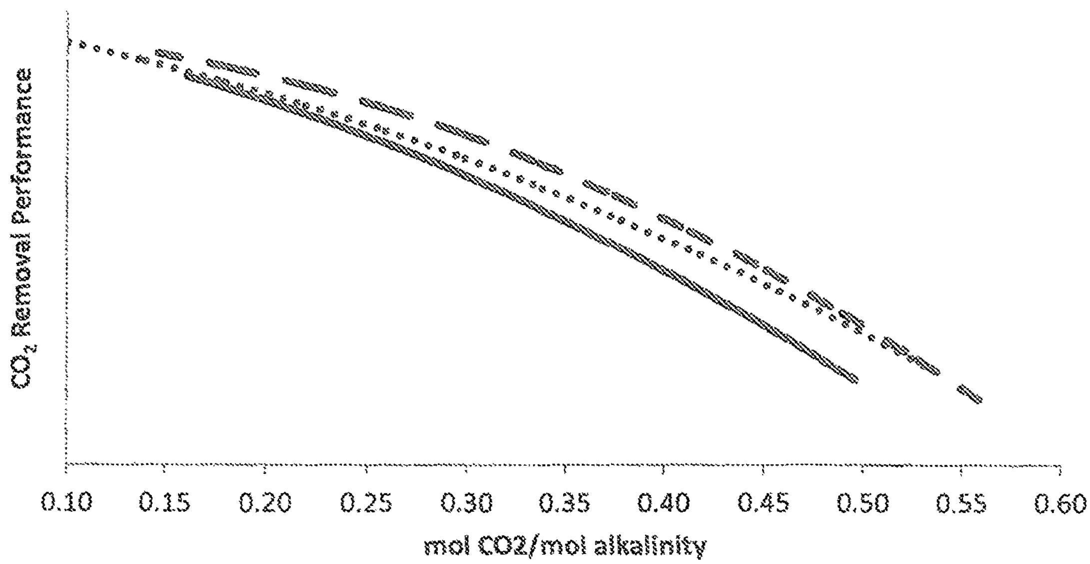

CO2 Removal Performance
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
mol CO2/mol alkalinity

FIG. 6

METHOD OF INCREASING MASS TRANSFER RATE OF ACID GAS SCRUBBING SOLVENTS

This application is a division of U.S. patent application Ser. No. 13/853,292 filed 29 Mar. 2013, now U.S. Pat. No. 9,409,125.

TECHNICAL FIELD

The present invention relates generally to various methods of increasing the overall mass transfer rate of acid gas scrubbing solvents utilizing various catalysts compounds.

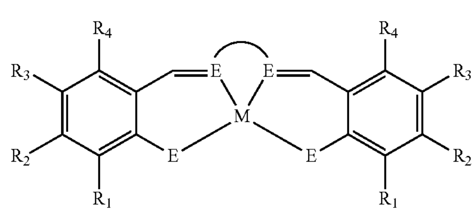
BACKGROUND

The cleanup of acid gasses or sour gas, such as CO_2 in particular, from natural gas and in oil refining has been an extensively practiced technology. The industrial removal of CO_2 from natural gas dates back to the 1930's. In the 21st century, due to the potential impact of anthropogenic CO_2 emissions on the climate, post-combustion CO_2 capture has gained tremendous attention. While several technologies exist for the removal of acid gasses one of the most commonly employed practices is the use of aqueous amines. Of these amines, tertiary amines are often used for natural gas applications due to their low energy of regeneration. For post-combustion CO_2 capture applications primary and secondary amines tend to be in part favored by their faster rate at the low CO_2 driving force condition. Regardless of the application, the mass transfer rate in the absorber column dictates the size of the column (capital cost) used and, consequently, has a substantial impact on the overall process cost. An overall process depicting a thermal swing process is presented in FIG. **1**. An aqueous amine solution is circulated between the absorber **10** and stripper **12**. The gas, containing CO_2, enters the bottom of the absorber where it contacts the aqueous amine absorbent removing it from the gas stream. The liquid solution, CO_2 rich amine solution, is then passed through a heat exchanger **14** to improve efficiency before being heated to a higher temperature in the stripper **12**. The stripper **12** removes the CO_2 as a gas from the amine solution to produce a lean, or CO_2 deficient solution. The lean solution is returned to the absorber **10** by way of the heat exchanger **14** to repeat the process.

In order to minimize system capital (absorber cost) it is important to maximize the overall mass transfer rate for the scrubber system as there is a direct correlation between the two. This invention relates to methods for this purpose as well as to catalyst compounds useful in those methods.

SUMMARY

A method is provided for increasing the overall mass transfer rate of acid gas scrubbing solvents. The method comprises adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent wherein that catalyst compound has a chemical formula:



where:

(a) M is any group VII B through XII B element;

(b) E is any combination of N, O, S having a net 2^- charge per individual ligand;

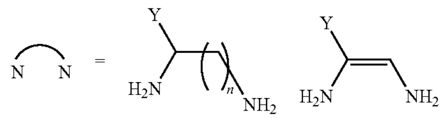
(c) $R_{1,2,4}$=—H, —COOH, —$[OCH_2CH_2]_n$—OR_9, CH_3, amine, amide, phosphate, —OH, —R_5OH, —$[SO_3]^-$;

(d) R_3=—H, —COOH, —$[OCH_2CH_2]_n$—OR_9, amine, amide, phosphate, —OH, —R_5OH, —$[SO_3]^-$, —$[(CH_2)_n Q]^+[A]^-$;

(e) R_5=C_1-C_5 alkyl; (f) A=monovalent anion: Cl, Br, I, F, PF_6, BF_4, acetate, trifluoroacetate, ClO_4, NO_3;

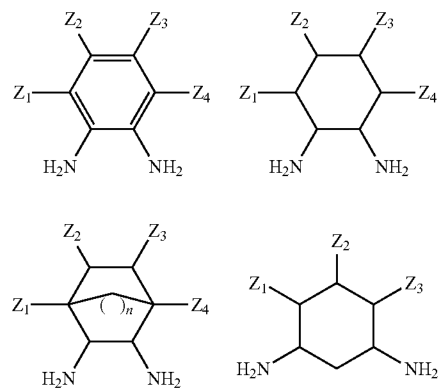
(g) Q=monovalent cation: PX_3 where X=alkyl, cyclic alkyl, aryl, O-alkyl, O-aryl, $N(R_6)_3$ where R_6=alkyl, cyclic alkyl, N-heterocyclic ring, imidazole;

(h)

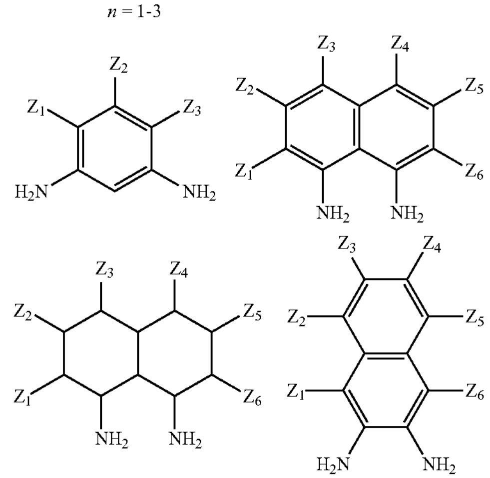


where Y=—H, —COOH, —R_7OOH (R_7=alkyl ranging from 2-10 carbons);

—$[OCH_2CH_2CH_2]_n$—OR_9; —OH; —SO_3; —NO_2; amine, amide; or



n = 1-3



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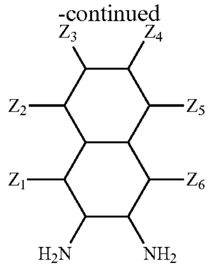
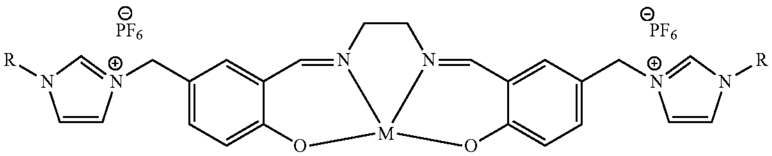


where Z_{1-6}=—H, any alkyl, —COOH, —R_8OOH (R_8=alkyl ranging from 2-10 carbons), —$[OCH_2CH_2]_n$—OR_9; OH; SO_3; NO_2; amine, amide; and

(i) where n=1 to 10; and

(j) R_9=H or alkyl.

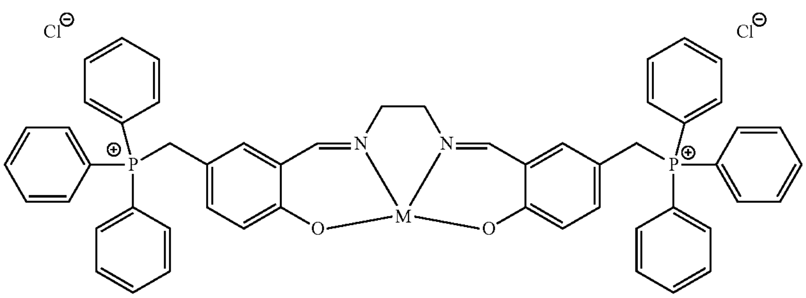
In one possible embodiment the catalyst compound has a chemical formula:



where R=any alkyl

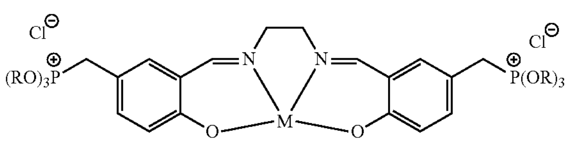
M=Co, Zn.

In another possible embodiment the catalyst compound has a chemical formula:



where M=Co, Zn.

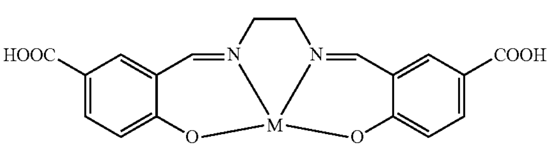
In another possible embodiment the catalyst compound has a chemical formula:



where M=Co, Zn

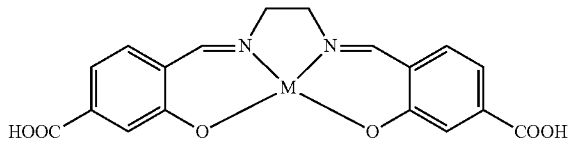
R=any alkyl.

In still another possible embodiment the catalyst compound has a chemical formula:



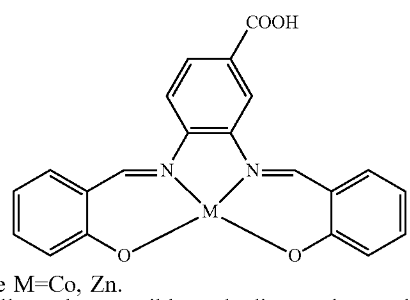
where M=Co, Zn.

In yet another possible embodiment the catalyst compound has a chemical formula:



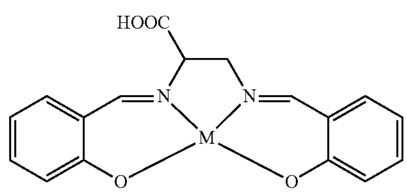
where M=Co, Zn.

In yet another possible embodiment the catalyst compound has a chemical formula:



where M=Co, Zn.

In still another possible embodiment the catalyst compound has a chemical formula:



where M=Co, Zn.

In any of the embodiments the acid gas scrubbing solvent includes an amine or a mixture of amines. In one possible embodiment the acid gas scrubbing solvent includes a mixture of (a) a promoter amine and (b) a tertiary amine.

In one possible embodiment the acid gas scrubbing solvent includes chemical compounds selected from a group including but not limited to, monoethanolamine (MEA), 1-amino-2-propanol (1A2P), 3-amino-1-propanol, 2-amino-1-propanol, 2-amino-1-butanol, 1-amino-2-butanol, 3-amino-2-butanol, 2-(methylamino)ethanonol (MAE), 2-(ethylamino)ethanol, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxypiperadine, 2-piperidineethanol, N-aminoethylpierazine (AEP), aminopropylmorpholine, 4-aminopiperidine, 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), diisopropanolamine (DIPA), glycine, alanine, β-alannine, sarcosine, ethylene diamine (EDA), 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, 1,6-hexanediamine, methyldiethanolamine (MDEA), triethanolamine (TEA), dimethylethanolamine (DMEA), N,N,N',N'-tetramethyl-1,8-naphthalenediamine, diethylmonoethanolamine, dipropylmonoethanolamine, 1,4-dimethylpiperazine, N N,N',N'-tetramethyl-1,6-hexanediamine, N,N,N'N'-tetrakis (2-hydroxyethyl)ethylenediamine, N,N,N',N',N"-pentamethyldiethylenetriamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylpropane-1,3-diamine, N,N,N',N'-tetramethylbutane-1,4-diamine, N,N,N',N'-tetramethyl-1,5-pentanediamine, alkali carbonate, and mixtures thereof.

Further the catalyst compound is provided at a concentration of between about 0.05 mM and about 100 mM.

Various catalyst compounds are also claimed.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

The accompanying drawings incorporated herein and forming a part of the specification, illustrate several aspects of the present method and together with the description serve to explain certain principles thereof. In the drawings:

FIG. **1** is a schematical illustration of a process for removing acid gas from a fluid stream utilizing solvent and thermal swing regeneration.

FIG. **2** is a schematical illustration of a simple CO_2 bubbling apparatus used for catalyst testing.

FIG. **3** is a graphical illustration of removal rate versus carbon loading for various catalysts used with 30 wt % MEA at 40° C.

FIG. **4** is a graphical illustration of removal rate versus carbon loading for various catalysts in 20% 1-amino-2-propanol solvent with 13% CO_2 at 40° C.

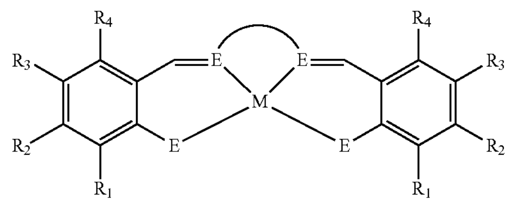
FIG. **5** is a schematical illustration of a wetted wall column (WWC) apparatus used in testing the catalysts.

FIG. **6** is a graphical comparison of CO_2 overall mass transfer as measured on a wetted wall column for 30 wt % MEA at 40° C. with catalyst CAER—CIP and CAER—C3I.

DETAILED DESCRIPTION

This document relates generally to methods of increasing overall mass transfer rate of acid gas scrubbing solvents as well as to novel transition metal monomer complexes incorporating a single transition metal atom.

The method may be broadly described as comprising adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent. The catalyst compound has a chemical formula:



where:

(a) M is any group VII B through XII B element;

(b) E is any combination of N, O, S having a net 2^- charge per individual ligand;

(c) $R_{1,\ 2,\ 4}$=—H, —COOH, —$[OCH_2CH_2]_n$—OR_9, amine, amide, phosphate, —OH, —R_5OH, —$[SO_3]^-$;

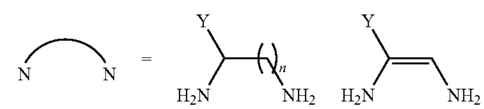
(d) R_3=—H, —COOH, —$[OCH_2CH_2]_n$—OR_9, amine, amide, phosphate, —OH, —R_5OH, R_5OH, —$[SO_3]^-$, —$[(CH_2)_n\ Q]^+[A]^-$;

(e) R_5=C_1-C_5 alkyl;

(f) A=monovalent anion: Cl, Br, I, F, PF_6, BF_4, acetate, trifluoroacetate, ClO_4, NO_3;

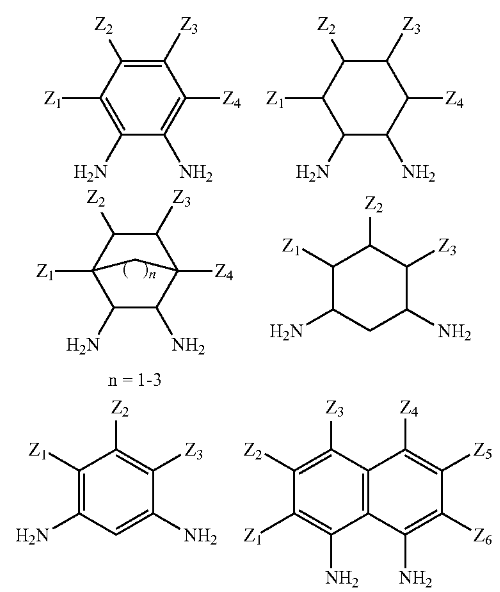
(g) Q=monovalent cation: PX_3 where X=alkyl, cyclic alkyl, aryl, O-alkyl, O-aryl, $N(R_6)_3$ where R_6=alkyl, cyclic alkyl, N-heterocyclic ring, imidazole;

(h)



where Y=—H, —COOH, —R_7OOH (R_7=alkyl ranging from 2-10 carbons);

—$[OCH_2CH_2]_n$—OR_9; —OH; —SO_3; —NO_2; amine, amide; or



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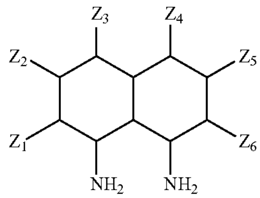
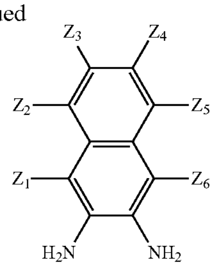
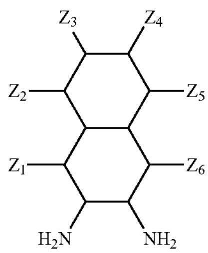




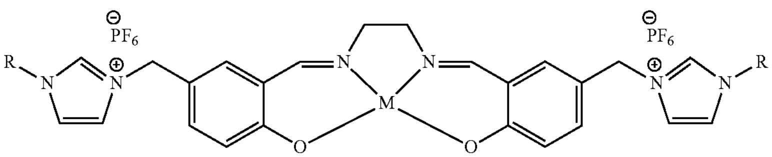


where Z_{1-6}=—H, any alkyl, —COOH,—R_8OOH (R_8=alkyl ranging from 2-10 carbons), —$[OCH_2CH_2]_n$—OR_9; OH; SO_3; NO_2, amine, amide;

(i) where n=1 to 10; and

(j) R_9=H or alkyl.

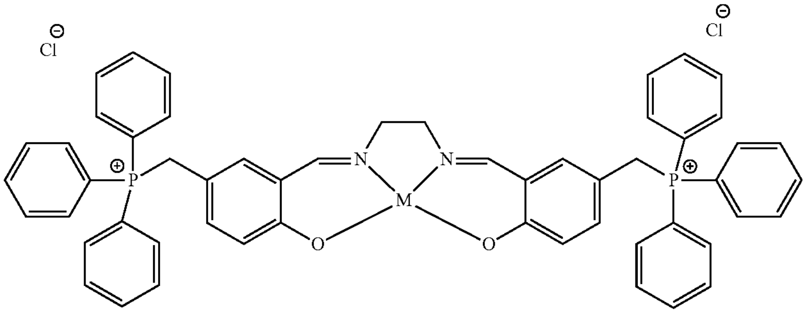
In one particular embodiment the catalyst compound has a chemical formula:



where R=any alkyl

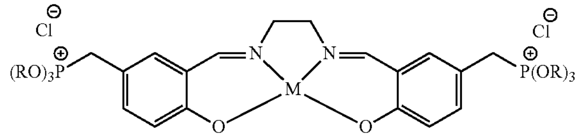
M=Co, Zn.

In another particular embodiment the catalyst compound has a chemical formula:



where M=Co, Zn.

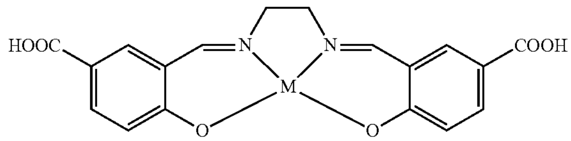
In another possible embodiment the catalyst compound has a chemical formula:



where M=Co, Zn

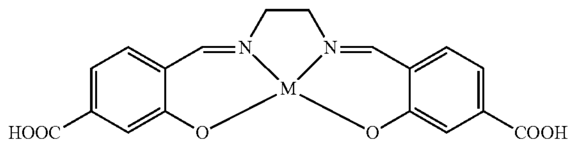
R=any alkyl.

In another possible embodiment the catalyst compound has a chemical formula:



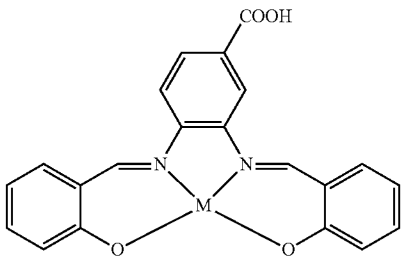
where M=Co, Zn.

In yet another possible embodiment the catalyst compound has a chemical formula:



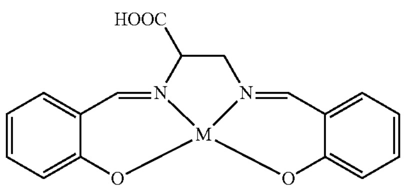
where M=Co, Zn.

In yet another possible embodiment the catalyst compound has a chemical formula:



where M=Co, Zn.

In still another possible embodiment the catalyst compound has a chemical formula:



where M=Co, Zn.

For any embodiment of catalyst compound, the terms “alkyl” or “any alkyl”, when not otherwise stipulated, include at least C_2-C_{10} alkyl compounds.

For any of the method embodiments the acid gas scrubbing solvent may include an amine. In one possible embodiment the acid gas scrubbing solvent includes a mixture of (a) a promoter amine, selected from a group of primary and secondary amines and (b) a tertiary amine.

Such a mixture is described in detail in copending U.S. patent application Ser. No. 13/853,186, filed on Mar. 29, 2013 and entitled “Solvent and Method for Removal of an Acid Gas from a Fluid Stream”, the full disclosure of which is incorporated herein by reference. Promoter amines useful in the present method include, but are not limited to, the primary and secondary amines such as 3-N-sulfonylamine (SA), 3-aminopropionitrile (APN), diethyl 2-aminoethanephosphonate (EtP2), N-methyltetrahydrothiophen-3-amine 1,1-dioxide, 2,2'-sulfonyldiethanamine, 3,3'-sulfonyldipropaneamine, 4,4'-sulfonyldibutanenamine, 2-aminoethyl methyl sulfone, 4-aminobutanenitrile, 6-aminohexanenitrile, 3-(methylamino)propanenitrile, diethyl [2-(methylamino)ethyl]phosphonate, diethyl (3-aminopropyl)phosphonate, diethyl (4-aminobutyl)phosphonate, diethyl (5-aminopentyl)phosphonate, diethyl (6-aminohexyl)phosphonate, 2-(tert-butoxy)ethan-1-amine, N-methyl-2-[(2-methyl-2-propanyl)oxy]ethanamine and mixtures thereof.

Tertiary amines and carbonate based salts useful in the present method include but are not limited to methyldiethanolamine (MDEA), triethanolamine (TEA), N,N,-dialkylethanolamine, N,N,N'N'-tetraalky-1,8-naphthalenediamine, N,N, -dialkylbenzylamine, 1,4-dialkylpiperazine, N,N,N',N'-tetraalkyl-1,6-hexanediamine, N,N,N'N'-tetraalkyl-1,5-pentanediamine, N,N,N'N'-tetraalkyl-1,4-butanediamine, N,N,N'N'-tetraalkyl-1,3-propanediamine, N,N,N',N'-tetraalkyl-1,2-ethanediamine, N,N,N'N'-tetrakis (2-hydroxyethyl)ethylenediamine, N,N,N;N;N"-pentaalkyldiethylenetriamine, N,N,N',N',N"-pentaalkyldipropylaminetriamine, N,N, -dialkylcyclohexylamine, N,N,N',N'-tetraalkylbis (aminoethyl)ether, N,N,-dimethyl-2(2-aminoethoxy)ethanol, alkali carbonates where alkyl represents any methyl, ethyl, propyl, butyl isomer, and mixtures thereof. In one possible embodiment, the catalyst compound is provided in the fluid stream with a concentration of between about 0.05 mM and about 50 mM. In another possible embodiment the catalyst compound is provided in the fluid stream with a concentration of between 50.1 mM and 75 mM. In yet another possible embodiment the catalyst compound is provided in the fluid stream with a concentration of between about 75.1 mM and 100 mM.

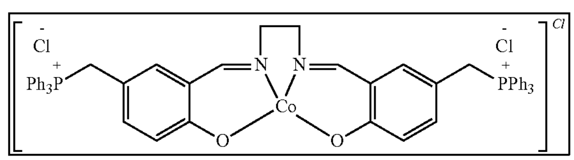
Primary and secondary amines useful in the present method include but are not limited to monoethanolamine (MEA), 1-amino-2-propanol (1A2P), 3-amino-1-propanol, 2-amino-1-propanol, 2-amino-1-butanol, 3-amino-2-butanol, 1-amino-2-butanol, 2-(alkylamino)ethanonol (MAE), diglycolamine, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxypiperadine, hydroxymethylpiperazine, 2-piperidineethanol, N-aminoethylpierazine (AEP), aminopropylmorpholine, 4-aminopiperidine, 3-aminopiperidine, 2-amino-piperidine, diethanolamine, 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), diisopropanolamine (DIPA), glycine, alanine, 13-alannine, sarcosine, isopropanolamine, benzylamine, ethylene diamine (EDA), 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, 1,6-hexanediamine.

In any of the embodiments, the catalyst compound must be stable under the relatively high temperature conditions (e.g. between perhaps 70 and 170° C.) found within the stripper 12. The present catalyst compounds meet this requirement.

The following examples further illustrate how to synthesize or manufacture certain representative catalysts used in the method of increasing the overall mass transfer rate of acid gas scrubbing solvents.

EXAMPLE 1

CAER-C1P

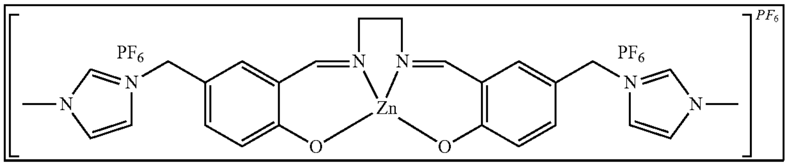


Preparation of H_2LP: To a solution of 1-(3-formyl-4-hydroxybenzyl)triphenylphosphoniumchloride (5.00 g, 11.55 mmol) in dry ethanol (40 mL) was added ethylenediamine (0.40 mL, 6 mmol) slowly at room temperature. The resulting solution was stirred at reflux temperature for 3 h. The solution was allowed to cool to room temperature and the solvent was removed under reduced pressure. The yellow residue was dissolved in dichloromethane (50 mL) and slowly added dropwise to 150 mL of stirring ethyl acetate to give a bright yellow powder which was collected via filtration (4.9958 g, 97%) in >95% purity based on ^{1}H NMR spectroscopy.

Preparation of CAER-ClP: A 100-mL round-bottom flask was charged with H_2LP (4.594 g, 5.17 mmol) and $CoCl_2.(H_2O)_6$ (1.3541 g, 5.7 mmol), and EtOH (40 mL) was added to make a slurry. 2 equiv. of Et_3N (1.5 mL, 11 mmol) was added and the mixture was heated at reflux for 3 hours. The mixture was cooled to room temperature and the solvent was removed under reduced pressure to give a brown powder. The brown powder was washed with ice cold water to remove ammonium salts and then triturated with ether to give the desired product as a brown solid (3.2295 g, 63%)

EXAMPLE 2

CAER-C3I

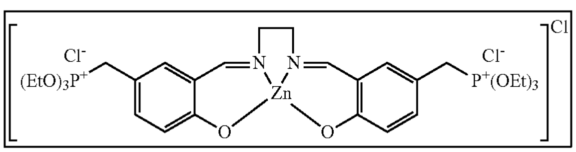


Preparation of H_2LI: To a solution of 1-(3-formyl-4-hydroxybenzyl)-3-methylimidazolium hexafluorophosphate (5.00 g, 13.80 mmol) in dry ethanol (40 mL) was added ethylenediamine (0.50 mL, 7.5 mmol) slowly at room temperature. The resulting solution was stirred at reflux temperature for 6 h. The solution was allowed to cool to room temperature after which a solid separated out. The solid was washed with ethanol (3×5 mL) then ether (3×10 mL) and dried in vacuo to give a yellow solid (5.4375 g, 97%) in >95% purity based on ^{1}H NMR spectroscopy.

Preparation of CAER-C3I: A 100-mL round-bottom flask was charged with H_2LI (5.011 g, 6.68 mmol) and $ZnCl_2$ (1.3630 g, 10 mmol), and EtOH (40 mL) was added to make a slurry. 2 equiv. of Et_3N (2.0 mL, 14 mmol) was added and the mixture was heated at reflux for 3 hours. The mixture was cooled to room temperature and a pale yellow solid was collected via filtration (4.6390 g, 85%) in >95% purity based on ^{1}H NMR spectroscopy.

EXAMPLE 3

CAER-C3P*

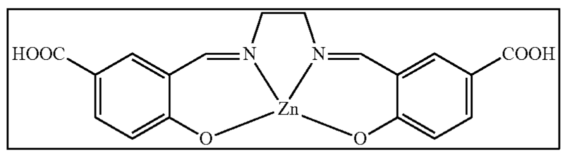


Preparation of H_2LP^*: A 100-mL round-bottom flask was charged with 5-chloromethyl-2-hydroxybenzaldehyde (10.3327 g, 60.4 mmol) and dissolved in ethyl acetate (40 mL) and triethylphosphite (11.5 mL, 67 mmol) was added. The mixture was heated at reflux (80° C.) for 3 hours. The mixture was cooled to room temperature and the solvent removed under reduced pressure to give triethoxy(3-formyl-4-hydroxybenzyl)phosphonium chloride as a viscous oil which was used without further purification. The viscous oil (10.003 g, 30 mmol) was dissolved in ethanol (40 mL) and ethylenediamine (1.2 mL, 18 mmol) was added slowly. The mixture was heated at reflux (80° C.) for 3 hours. The mixture was cooled to room temperature and the solvent was removed under reduced pressure to give a thick, yellow, oily substance. The oil was washed with ether (3×10 mL). The ether was evaporated slowly over 24 hours to produce a thick, yellow, viscous oil (10.2215 g, 98%) in ~85% purity based on ^{1}H NMR spectroscopy.

Preparation of CAER-C3P*: A 100-mL round-bottom flask was charged with H_2LP^* (5.028 g, 7.2 mmol) and $ZnCl_2$ (1.4652 g, 10.8 mmol), and dissolved in EtOH (40 mL). 2 equiv. of Et_3N (2.1 mL, 15 mmol) was added and the mixture was heated at reflux for 3 hours. The mixture was cooled to room temperature and the solvent was removed under reduced pressure to give a thick, oily substance. The oil was washed with ether (3×10 mL) to produce a white solid which was removed via filtration. The ether was evaporated slowly over 24 hours to produce a thick, colorless, viscous oil (4.8832 g, 89%) in >90% purity based on ^{1}H NMR spectroscopy.

EXAMPLE 4

CAER-C4

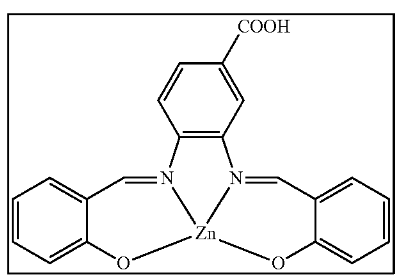


Preparation of H_2L4: A 50 mL round bottom flask was charged with 2 equiv. 4-formyl-3-hydroxybenzoic acid (0.2471 g, 1.49 mmol) and dissolved in EtOH followed by addition of 1 equiv. ethylenediamine (50 μL, 0.75 mmol). The mixture was heated at reflux for 2 hr. The reaction mixture was cooled to room temp. and a yellow powder was collected via filtration (247.3 mg, 93%) >95% purity based on ^{1}H NMR spectroscopy.

Preparation of CAER-C4: A 100-mL round-bottom flask was charged with H_2L4 (0.06980 g, 0.196 mmol) and $ZnCl_2$ (0.0433 g, 0.318 mmol), and EtOH was added to make a slurry. 2 equiv. of Et_3N (58 μL, 0.417 mmol) was added and the mixture was heated at reflux for 3 hours. The mixture was cooled to room temperature and a pale yellow solid was collected via filtration (66.7, 81%) in >95% purity based on ^{1}H NMR spectroscopy.

EXAMPLE 5

CAER-C5$_z$

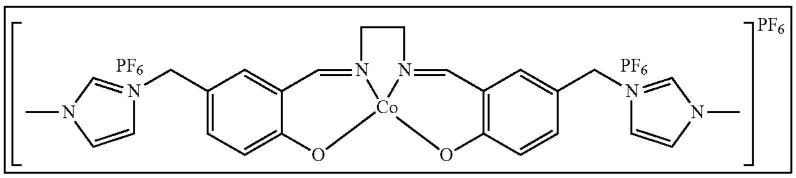


Preparation of H_2L5: A 100-mL round bottom flask was charged with 3,4-diaminobenzoic acid (2.0067 g, 13.2 mmol) and dissolved in EtOH. 2 equiv. salicylaldehyde (2.8 mL, 26.3 mmol) was added and the reaction mixture was heated at reflux for 2 hr, at which point an orange solid had formed. The mixture was cooled to room temp. and the orange solid was collected via filtration (1.8274, 38%). The orange filtrate was stored at 8° C. for 15 hours and a second crop of orange solids was collected via filtration (2.3211 g, 48%), for a combined 86% yield in >95% purity based on ^1H NMR spectroscopy.

Preparation of CAER-05$_z$: A 100-mL round-bottom flask was charged with H_2L5 (0.4921 g, 1.37 mmol) and $ZnCl_2$ (0.3224 g, 2.37 mmol), and EtOH was added to make a slurry. 2 equiv. of Et_3N (390 μL, 2.8 mmol) was added and the mixture was heated at reflux for 3 hours. The mixture was cooled to room temperature and a pale yellow/orange solid was collected via filtration (0.5613, 97%) in >95% purity based on ^1H NMR spectroscopy.

EXAMPLE 6

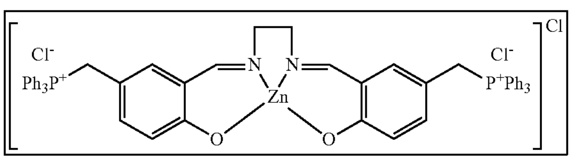
CAER-C1I



Preparation of CAER-C1: A 100-mL round-bottom flask was charged with H_2LI (3.023 g, 4.04 mmol) and $CoCl_2.(H_2O)_6$ (1.0641 g, 4.44 mmol), and EtOH (40 mL) was added to make a slurry. 2 equiv. of Et_3N (1.2 mL, 8.63 mmol) was added and the mixture was heated at reflux for 3 hours. The mixture was cooled to room temperature and a dark brown solid was collected via filtration (3.592 g, 93%).

EXAMPLE 7

CAER-C3P



Preparation of CAER-C3P: A 100-mL round-bottom flask was charged with H_2LP (5.002 g, 5.63 mmol) and $ZnCl_2$ (1.3630 g, 10 mmol), and EtOH (40 mL) was added to make a slurry. 2 equiv. of Et_3N (1.75 mL, 12 mmol) was added and the mixture was heated at reflux for 3 hours. The mixture was cooled to room temperature and a pale yellow solid was collected via filtration (4.9790 g, 93%) in >95% purity based on ^1H NMR spectroscopy.

Catalyst Testing in Concentrated Primary Amines: Breakthrough Method

A schematic of the apparatus used is shown in FIG. **2**. Briefly, 0.85 L/min feed gas containing ~13% CO_2 mixed with N_2 is firstly saturated with water in the first impinger and then bubbled through 15 ml of testing solvent in the second impinger. Both the saturator and bubbler are immersed in a water bath at 40° C. The gas effluent is dried through an ice condenser and a Drierite tube before it is analyzed for CO_2 concentration using a dual-beam NDIR online CO_2 analyzer (Model 510, HORIBA, Ltd). Data of CO_2 outlet concentration with respect to time is continuously recorded through a LABVIEW® package with 1 second interval. A line that bypasses the saturator and the bubbler is set up for inlet CO_2 concentration determination. Before each experiment, the alkalinity of the testing solvent is precisely determined through acid-base titration.

The difference of inlet and outlet CO_2 concentration represents the absorbed amount of CO_2 at a particular time. The integration of the concentration difference represents the CO_2 loading as expressed

$$CO_2\ \text{Loading}(t)(\text{mol } CO_2/\text{kg solution}) = \frac{\int_0^t (C_{in} - C_{out}(t))dt}{m_{sol}} \quad \text{Eq 1}$$

in which G_{in} is the CO_2 feed gas rate in mol/s, C_{out} is the CO_2 effluent rate in mol/s, t is the time in second, and mol is the mass of solution in kg. The CO_2 loading at G_{out}=G_{in} is the equilibrium CO_2 capacity at 13% CO_2 and 40° C. With the alkalinity (mol N/kg of solution) of the solution known, the CO_2 loading can also be written as

$$\alpha = \frac{\text{CO2 Loading(mol } CO_2/\text{kg solution)}}{\text{Alkalinity(mol N/kg solution)}} = \frac{\text{mole of } CO_2}{\text{mole of N}} \quad \text{Eq 2}$$

In addition, the absorption rate can be described by the derivate of CO_2 loading with respect to time:

$$\text{Absorption rate(mol } CO_2/\text{kg solution/s)} = \frac{dCO_2\ \text{Loading}}{dt} \quad \text{Eq 3}$$

As illustrated in FIGS. **3** and **4**, the current catalyst compounds improve the removal rate of a 30 wt % MEA acid gas scrubbing solvent.

Catalyst Testing in Concentrated Primary Amines: WWC Method

The wetted wall column (WWC) is used to determine mass transfer of CO_2 into a process absorption solvent. The

WWC apparatus is illustrated in FIG. **5**. The improved overall mass transfer resulting from the use of two catalysts is illustrated in FIG. **6**.

In each test, solvent is loaded to a $molCO_2/molN$ level of approximately 0.1 with CO_2 by sparging the solution reservoir with a concentrated CO_2/N_2 mixture. The initially loaded solution is then circulating through the wetted wall column and a pre-heater which heats the solution to the desired temperature. Once the solution is thermally stable, a simulated flue gas stream (CO_2 balanced with N_2) saturated with water flows into the wetted wall column. In the wetted wall column, liquid flows downwards on the outside surface on an annular tube while CO_2 gas stream flows upwards around the annular tube. CO_2 absorption from the gas phase into the liquid takes place along the tube's wall. Gas effluent from the WWC is dried and analyzed by an infrared CO_2 analyzer for CO_2 concentration determination. CO_2 inlet concentration is analyzed by directing the gas stream to bypass the WWC. A liquid sample downstream of the WWC is collected at each solution carbon loading and tested for total liquid CO_2 loading, viscosity, density, and pH measurements. Liquid film thickness is calculated by Eq. 1. The bulk solution is then loaded with more CO_2 and the data collection cycle is repeated

$$\delta = \sqrt[3]{\frac{3\mu Q_{sol}}{\rho g W}} \quad \text{Eq. 1}$$

in which μ is the viscosity, Q_{sol} is the liquid flow rate, ρ is the density of liquid, and W is the circumference of the column.

The overall mass transfer coefficient at the operating condition can be calculated from Eq. 2.

$$K_G = \frac{N_{CO_2}}{\Delta P_{CO_2}} \quad \text{Eq. 2}$$

in which N_{CO2} is the flux of CO_2, K_G is the overall mass transfer coefficient, ΔP_{CO2} is the log mean of driving force which is defined by

$$\Delta P_{CO_2} = \frac{P_{CO_2}^{in} - P_{CO_2}^{out}}{\ln\left(\frac{P_{CO_2}^{in} - P_{CO_2}^{*}}{P_{CO_2}^{out} - P_{CO_2}^{*}}\right)} \quad \text{Eq. 3}$$

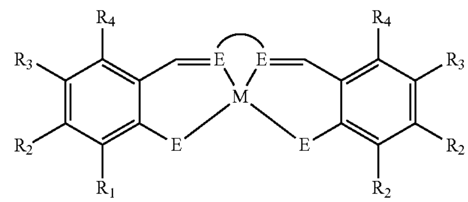
in which P_{CO2}^{in} and P_{CO2}^{cut} represent the CO_2 partial pressure at the inlet and outlet of the wetted wall column, and P^*_{CO2} is the equilibrium partial pressure of CO_2. The P^*_{CO2} is obtained by making the flux N_{CO2} to be zero at zero driving force and solving the 2 equations simultaneously using a trial-and-error routine in MATLAB®.

The foregoing has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the embodiments to the precise form disclosed. Obvious modifications and variations are possible in light of the above teachings. All such modifications and variations are within the scope of the appended claims when interpreted in accordance with the breadth to which they are fairly, legally and equitably entitled.

What is claimed:

1. A method of increasing overall mass transfer rate of acid gas scrubbing solvents, comprising:

adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent, said catalyst compound having a chemical formula:



where:

(a) M is any group VII B through XII B element;

(b) E is a combination of N with O and/or S having a net 2^- charge per individual ligand with N positioned as set forth in (i);

(c) $R_{1,\ 2,\ 4}$=—H, —COOH, —$[OCH_2CH_2]_{(n1)}OR_9$, amine, amide, phosphate, —OH, —R_5OH, —$[SO_3]^-$;

(d) R_3=—H, —COOH, —$[OCH_2CH_2]_{(n1)}OR_9$, amine, amide, phosphate, —OH, —R_5OH, —$[SO_3]^-$, —$[(CH_2)_nQ]^+[A]^-$;

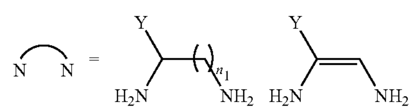
(e) R_5=C_1- C_5 alkyl;

(f) A =monovalent anion: CI, Br, I, F, PF_6, BF_4, acetate, trifluoroacetate, ClO_4, NO_3;

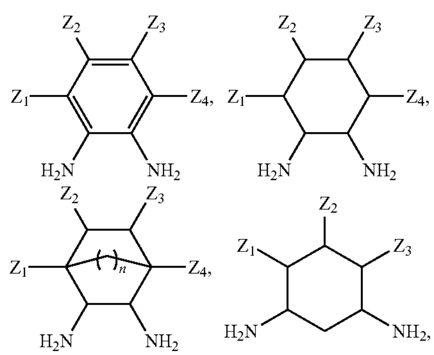
(g) Q=monovalent cation: PX_3 where X=alkyl, cyclic alkyl, aryl, O-alkyl, O-aryl, $N(R_6)_3$ where R_6=alkyl, cyclic alkyl, N-heterocyclic ring, imidazole;

(h) n_1=1 to 10;

(i)

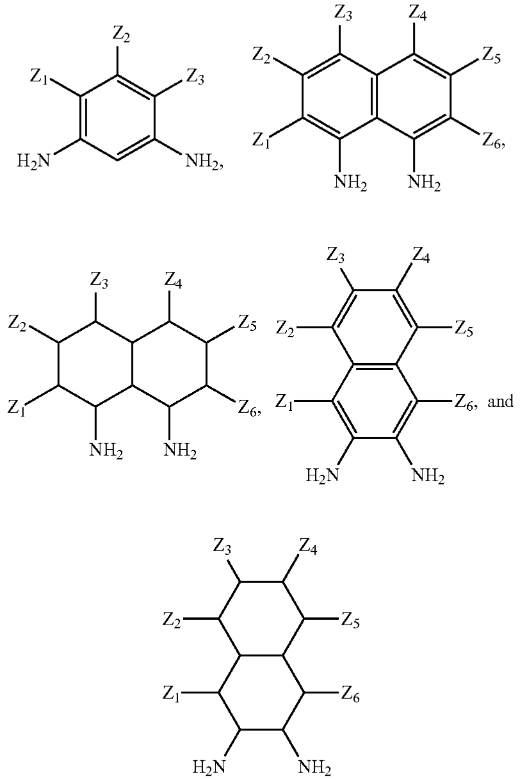


where Y=—H; —COOH; —R_7OOH where R_7 is an alkyl ranging from 2-10 carbons; —$[OCH_2CH_2]_n$—OR_9; —OH; —SO_3; —NO_2; amine, amide; or selecting from the group consisting of



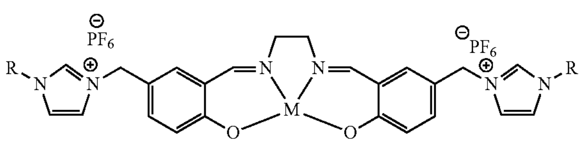
n = 1-3

-continued



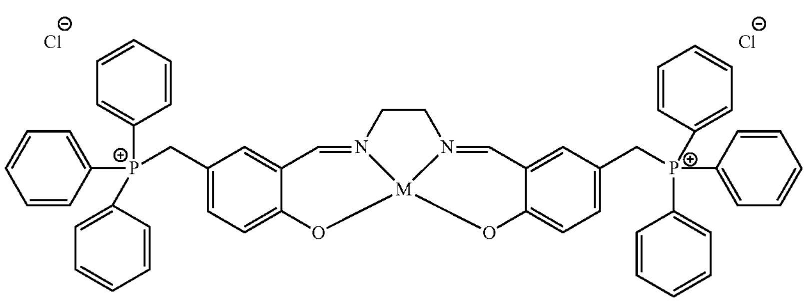
where Z_{1-6}=—H; any alkyl; —COOH; —R_8OOH where R_8 is an alkyl ranging from 2-10 carbons; —$[OCH_2CH_2]_n$—OR_9; OH; SO_3; NO_2; amine, amide; (i) R_9=H, or alkyl.

2. The method of claim **1** wherein said catalyst compound has a chemical formula:



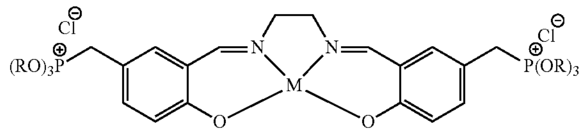
where R =any alkyl M=Co, Zn.

3. The method of claim **1** wherein said catalyst compound has a chemical formula:



where M =Co, Zn.

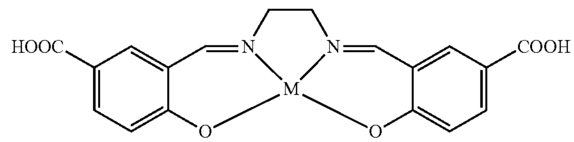
4. The method of claim **1** wherein said catalyst compound has a chemical formula:



where M =Co, Zn

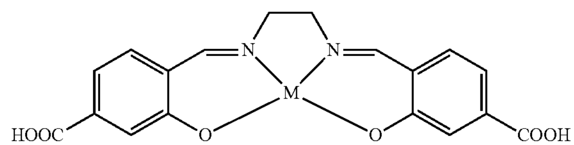
R =any alkyl.

5. The method of claim **1** wherein said catalyst compound has a chemical formula:



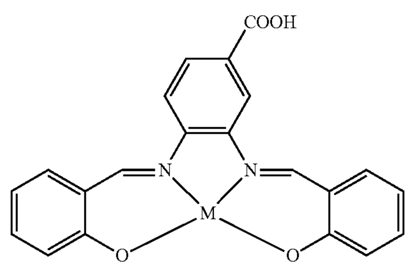
where M =Co, Zn.

6. The method of claim **1** wherein said catalyst compound has a chemical formula:



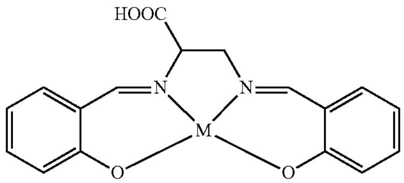
where M =Co, Zn.

7. The method of claim **1** wherein said catalyst compound has a chemical formula:



where M =Co, Zn.

8. The method of claim **1** wherein said catalyst compound has a chemical formula:



where M =Co, Zn.

9. The method of claim **1** wherein said acid gas scrubbing solvent includes an amine.

10. The method of claim **1**, wherein said acid gas scrubbing solvent includes a mixture of a primary or secondary amine and a tertiary amine.

11. The method of claim **1**, wherein said acid gas scrubbing solvent includes a material selected from a group consisting of monoethanolamine (MEA), 1-amino-2-propanol (1A2P), 3-amino-1-propanol, 2-amino-1-propanol, 2-amino-1-butanol, 1-amino-**2**-butanol, 3-amino-2-butanol, 2-(alkylamino)ethanonol (MAE), diglycolamine, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxypiperadine, hydroxyalkylpiperazine, 2-piperidineethanol, N-aminoethylpierazine (AEP), aminopropylmorpholine, **4**-aminopiperidine, 3-aminopiperidine, 2-amino-piperidine, diethanolamine, 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), diisopropanolamine (DTPA), glycine, alanine, ß-alannine, sarcosine, isopropanolamine, benzylamine, methyldiethanolamine (MDEA), triethanolamine (TEA), alkali carbonate, N,N,-dialkylethanolamine, N,N,N',N'-tetraalky-1,8-naphthalene-diamine, N,N, -dialkylbenzylamine, 1,4-dialkylpiperazine, N,N,N',N'-tetraalkyl-1,6-hexanediamine, N,N,N',N'-tetraalkyl-1,5-pentanediamine, N,N,N',N'-tetraalkyl-1,4-butanediamine, N,N,N',N'-tetraalkyl- 1,3-propanediamine, N,N,N',N'-tetraalkyl-1,2-ethanediamine, N,N,N',N'-tetrakis (2-hydroxyethyl)ethylenedia mine, N,N,N',N',N"-pentaalkyldiethylenetriamine, N,N,N',N',N"-pentaalkyldipropylaminetnamine, N,N,-dialkylcyclohexylamine, N,N,N',N'-tetraalkylbis(aminoethyl)ether, N,N,-dimethyl-2(2-aminoethoxy)ethanol, where alkyl represents any methyl, ethyl, propyl, butyl isomer, and mixtures thereof.

12. The method of claim **1**, wherein said catalyst compound is provided at a concentration of between about 0.05 mM and about 100 mM.

* * * * *