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(72) **Inventor; and**
(71) **Applicant** : **BUMB, Prateek** [IN/IN]; 9, Joshi Ji Ka Bagh, Near Sayyed Ka Gatta, Tonk Road, Jaipur, Rajasthan 302018 (IN).

(74) **Agents**: **VIJAYAKRISHNAN, Sindhu** et al.; K&S Partners, Intellectual Property Attorneys, 4121/B, 6th Cross, 19A Main, HAL II Stage (Extension), Bangalore, Karnataka 560038 (IN).

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(54) **Title**: SOLVENT COMPOSITION FOR CARBON DIOXIDE RECOVERY

(57) **Abstract**: The present disclosure provides for a solvent composition for recovery of carbon dioxide from gaseous mixture, comprising diethanolamine, piperazine or its derivative, alkali salt, optionally along with cupric carbonate.. The disclosure relates to improved solvent formulations that utilizes less energy and increased carbon capture efficiency. The disclosure also addresses the high CO_2 loading capacity and energy requirement over the existing carbon dioxide capture solvent.

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"SOLVENT COMPOSITION FOR CARBON DIOXIDE RECOVERY"

TECHNICAL FIELD

The present disclosure relates to a solvent composition for recovering carbon dioxide from gaseous mixture. More particularly, the disclosure relates to improved solvent formulations that utilizes less energy and increased carbon capture efficiency. The disclosure also addresses the high CO_2 loading capacity and energy requirement over the existing carbon dioxide capture solvent.

BACKGROUND

Carbon dioxide (CO_2) is a major Greenhouse gas responsible for global warming, and hence, much effort is being put on the development of technologies for its capture from process gas streams (e.g., flue gas, natural gas, coke oven gas and refinery off-gas).

Carbon dioxide is emitted in large quantities from large stationary sources. The largest single sources of carbon dioxide are conventional coal-fired power plants. Technology developed for such sources should also be applicable to CO_2. capture from gas and oil fired boilers, combined cycle power plants, coal gasification, and hydrogen plants. Absorption/stripping are primarily a tail-end technology and are therefore suitable for both existing and new boilers. The use of absorption and stripping processes for recovery of the carbon dioxide from the gaseous mixture is known in the art. The conventional carbon capture process consists of an absorber column, a stripper column and compression unit. Gaseous mixture enters the absorber where it comes in contact with the solvent. The rich stream leaving the absorber has carbon dioxide trapped in solvent composition. The captured carbon dioxide is stripped in the stripper column with the help of steam energy provided by the reboiler. The overhead stream from the stripper is condensed and the condensate is passed back to the stripper while the gaseous stream, rich in carbon dioxide is compressed and sent for the suitable applications.

The major drawback of conventional carbon capture system is that the high energy is needed to strip the carbon dioxide from the rich solvent. Steam of higher pressure is required to strip the carbon dioxide and thus stripper reboiler and compressor account for major derating of the industrial unit.

Further, a number of different CO_2 separation technologies are available, absorption performed with chemical solvents representing the most feasible option. In such operations, alkanolamine-based absorbents and their blends are extensively applied. Industrially important alkanolamines for CO_2 removal are the primary amine, the secondary amine and the tertiary amine. The invention addresses the high CO_2 loading capacity and energy requirement over the existing carbon dioxide capture solvent. The disadvantage with the conventional solvent is that the system requires more energy. Conventional solvent has several disadvantages with the treating gaseous mixture such as chemical degradation, thermal degradation and corrosivity.

In light of foregoing discussion, it is necessary to develop a system which consumes less energy for recovering the carbon dioxide from the gaseous mixture. And also to provide an improved solvent formulations that seek to overcome the obstacles associated with the conventional solvent system and reduce the energy requirement in the whole capture process.

SUMMARY OF THE DISCLOSURE

An embodiment of the present disclosure relates to a solvent composition for recovery of carbon dioxide from gaseous mixture, comprising diethanolamine, piperazine or its derivative, alkali salt, optionally along with cupric carbonate.

In an embodiment of the disclosure, the amine is selected from group comprising Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA), Dimethylethanolamine (DMEA), N-methyldiethanolamine (MDEA), Monomethylethanolamine (MMEA), 2-(2-aminoethoxy)ethanol, Aminoethylethanolamine (AEEA), Ethylenediamine (EDA), Diethylenetriamine (DETA), Triethylenetetramine (TETA), Tetraethylenepentamine (TEPA), 2-amino-2methyl-1-proponal (AMP), 2-(ethyamino)-ethanol (EAE), 2-(methylamino)-ethanol (MAE), 2-(diethylamino)-ethanol (DEAE), diethanolamine (DEA), diisopropanolamine

(DIPA), methylaminopropylamine (MAPA), 3-aminopropanol (AP), 2,2-dimethyl-1,3-propanediamine (DMPDA), 3-amino-1-cyclohexylaminopropane (ACHP), diglycolamine (DGA), 1-amino-2-propanol (MIPA), 2-methyl-methanolamine (MMEA) or any combinations thereof, preferably N-methyl diethanolamine, at concentration ranging from about 10 wt% to about 50 wt%.

In an embodiment of the disclosure, the piperazine derivative is selected from group comprising N-aminoethylpiperazine (AEP), N-methylpiperazine, 2-methylpiperazine, 1-ethylpiperazine, 1-(2-hydroxyethyl)piperazine, 1,4-dimethylpiperazine or any combinations thereof, preferably piperazine, at concentration ranging from about 0.5 wt% to about 50 wt% or N - methyl piperazine at concentration ranging from about 0.5 wt% to about 50 wt%.

In an embodiment of the disclosure, the alkali salt is selected from a group comprising potassium carbonate, sodium carbonate salt, lithium carbonate, a bicarbonate salt, a bisulfide salt, hydroxide salt or any combination thereof, preferably potassium carbonate and a bicarbonate salt, at concentration ranging from about 2 wt% to about 25 wt%.

In an embodiment of the disclosure, the cupric carbonate is at concentration ranging from about 50ppm to 300ppm.

BRIEF DESCRIPTION OF ACCOMPANYING FIGURES

In order that the disclosure may be readily understood and put into practical effect, reference will now be made to exemplary embodiments as illustrated with reference to the accompanying figures. The figure together with a detailed description below, are incorporated in and form part of the specification, and serve to further illustrate the embodiments and explain various principles and advantages, in accordance with the present disclosure where:

Figure 1 shows experimental set-up for stirred cell reactor.

Figure 2 shows experimental set up for Vapor liquid Equilibrium

Figure 3 shows experimental results and Model predicted equilibrium partial pressure of CO_2 above aqueous 20 wt% K_2CO_3 solution at different temperatures.

Figure 4 shows experimental results and Model predicted equilibrium partial pressure of CO_2 above aqueous 30 wt% K_2CO_3 solution at different temperatures.

Figure 5 shows Equilibrium partial pressure of CO_2 over aqueous mixtures of (MDEA+PZ).

Figure 6 shows ENRTL model predicted equilibrium CO2 partial pressure over (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) in the temperature range of (313 – 333) K.

Figure 7 shows ENRTL model predicted activity coefficients of species in liquid phase of a (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent loaded with CO_2 at 313 K.

Figure 8 shows ENRTL model predicted equilibrium liquid phase concentration of different species of a (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent loaded with CO_2 at 323 K.

Figure 9 shows ENRTL model predicted pH of a (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent loaded with CO_2 at different temperatures.

Figure 10 shows ENRTL model predicted equilibrium amine partial pressure (amine volatility) of a (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent loaded with CO_2 at different temperatures.

Figure 11 shows ENRTL model predicted specific heat of the mixture of a (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent loaded with CO_2 at different temperatures.

Figure 12 shows ENRTL model predicted equilibrium liquid phase concentration (mol/kg water) of different species of a (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent loaded with CO_2 at 323 K.

Figure 13 shows differential Heat of Absorption ($-\Delta H_{abs}$) vs loading of APBS1 Solvent.

Figure 14 shows differential Heat of Absorption ($-\Delta H_{abs}$) vs loading (between 0.2 to 0.6) of APBS1 Solvent.

Figure 15 shows equilibrium CO_2 partial pressure over MDEA-MPZ-K_2CO_3-$KHCO_3$-H_2O blend at temperature 25 ^{0}C.

Figure 16 shows literature Comparision with (CO_2 + MDEA) and (CO_2 + MDEA-MPZ-K_2CO_3-$KHCO_3$).

Figure 17 shows a process flow diagram of conventional carbon capture system.

DETAILED DESCRIPTION OF THE DISCLOSURE

The proposed solvent mixture provides faster CO_2 absorption rates and greater capacity for CO_2 and exhibit lower heat of CO_2 desorption. The lower heat of CO_2 desorption decreases the reboiler steam requirements. The faster absorption kinetics creates richer solutions given the same absorber capital costs. The proposed solvent mixture composition has 10 wt% to 50 wt% N-methyldiethanolamine, 0.5% to 50 wt% piperazine or its derivatives, 2 wt% to 25 wt% alkali salts and optionally with cupric carbonate.

In the present disclosure, kinetics of the CO_2 reaction with MDEA + piperazine (PZ) + K_2CO_3 + $KHCO_3$ + H_2O mixture is investigated. Besides, PZ is replaced by another promoter, viz. N-methyl piperazine (MPZ) and the reaction kinetics is investigated using the formulated aqueous solution, viz. MDEA + MPZ + K_2CO_3 + $KHCO_3$ + H_2O. Due to its tertiary amine characteristics, MDEA has high CO_2 removal capacity. Although potassium carbonate has low reactivity with CO_2, it has low regeneration cost. PZ and MPZ, which is a cyclic diamine, are used as a promoter.

In an embodiment of the present disclosure, the technology of the instant Application is further elaborated with the help of following examples. However, the examples should not be construed to limit the scope of the disclosure.

ABBREVIATIONS USED:

MDEA	N-methyldiethanolamine
MPZ	n-Methyl Piperazine
PZ	Piperazine
APBS	Amine promoted buffer solvent
K_2CO_3	Potassium carbonate
$KHCO_3$	Potassium bicarbonate
VLE	Vapor liquid equilibrium
ρ	Density
M	Viscosity
D_{CO2}	Diffusivity
$\mathbf{H_{CO_2}}$	Solubility
k_{obs}	Observed rate constant
α_{co2}	Loading
P_{CO2}	Partial pressure of carbon dioxide
ΔH_{abs}	Heat of absorption

EXAMPLE 1: CHARACTERIZATION OF THE SOLVENT SYSTEM

The conventional CO_2 capture solvents has several disadvantages with the treating flue gas such as chemical degradation, thermal degradation, corrosivity, high capital and operating expenditure. This invention relates the improved solvent formulations that seek to overcome the obstacles associated with the conventional solvent system. The solvent formulation refers to a mixture of solvent with specific concentration for each component. The proposed solvent mixture provides faster CO_2 absorption rates, greater capacity for CO_2 and exhibit lower heat of CO_2 desorption. The lower heat of CO_2

desorption can decrease the reboiler steam requirements. The faster absorption kinetics can create richer solutions given the same absorber capital costs.

Experimental Setup for stirred cell reactor

A glass stirred cell reactor with a plane, horizontal gas-liquid interface was used for the absorption studies (see Figure 1). The main advantage of the stirred cell is that the rates of absorption can be measured using a liquid with a single, known composition. This easy-to-use experimental device (inner diameter 97 mm, height 187 mm) is operated batch wise. The total volume of the reactor is 1.45 dm^3 and the interfacial surface area is 7.5×10^{-3} m^2. The reactor is equipped with a flange made of stainless steel. A pressure transducer (Trans Instruments, UK, 0-1 bar), mounted on this flange and coupled with a data acquisition system, enabled measurement of the total pressure inside the reactor, the uncertainty in this measurement being ±1 mbar. The reactor is also equipped with inlet and outlet ports for the gas and liquid phases. The entire assembly is proven to have no leak. The setup is supplied by a variable speed magnetic drive. The gas and liquid are stirred by two impellers, mounted on the same shaft. The speed of stirring could be adjusted to the desired value with an accuracy of ±1 rpm. The impeller speed during kinetic measurements is limited to 60 rpm, in order to ensure that the gas-liquid interface is undisturbed. The reactor is immersed in a water bath to guarantee isothermal conditions. The temperature is adjusted to the desired value with an accuracy of ±0.1 K. The solute gas passed through a coil, also kept in the water bath, before being charged inside the reactor.

Experimental Procedure on stirred cell reactor

In each experiment, the reactor is charged with 0.4 dm^3 of the absorbent. The gas inside the reactor is then purged with N_2 to ensure an inert atmosphere. Thereafter, N_2 is released through the gas outlet port. All the lines are closed and the reactor content attained the desired temperature. CO_2 from the gas cylinder is then charged inside the reactor, this being considered as the starting point for the reaction. The reactor content is stirred at the desired speed of agitation. The decrease in system pressure due to reaction is monitored by the pressure transducer and the " P_{CO_2} vs. t" data are recorded during 30 seconds using the data acquisition system. These data are plotted for the time interval between t = 5 s and t = 25 s and fitted to a third degree polynomial using the least-square regression. The absorption rates are calculated from the values of the slope $-dP_{CO_2}/dt$. This measurement method based on the fall-in-pressure technique enabled a simple and straightforward estimation of the absorption rates. Further, no analysis of the liquid phase is required and the pressure decrease is the only factor necessary for the evaluation of the kinetic parameters. In the range of agitation speeds studied, the mass transfer rate is independent of the gas-side mass transfer coefficient, k_G. Therefore, the CO_2 absorption process is liquid-phase-controlled. The stirred-cell reactor is also used for measuring N_2O solubility in the aqueous mixtures. To measure solubility, the reactor content is stirred at high agitation speed (~1000 rpm) for 6 h to ensure that equilibrium is attained. Using the recorded values of the initial and final pressure, the solubility is determined. The reproducibility of results is checked and the error in all experimental measurements is found to be less than 3 %.

The density and viscosity of the aqueous blend comprising MDEA, K_2CO_3,$KHCO_3$, promoter (viz. piperazine and N-methyl piperazine) are measured at 298, 303 and 308 K using a commercial densitometer and Ostwald viscometer, respectively. From viscosity measurements, the values of the N_2O diffusivity in the activated solutions by using the modified Stokes-Einstein correlation:

$$(D_{N_2O}\,\mu^{0.80})_{Amine} = \text{const} = (D_{N_2O}\,\mu^{0.80})_{Water}$$

The values of D_{CO_2} in solutions are found using the N_2O analogy. It states that, at any given temperature, the ratio of the diffusivities of N_2O and CO_2 in amine solution is equal to that ratio in water.

$$\left(\frac{D_{N_2O}}{D_{CO_2}}\right)_{Amine} = \left(\frac{D_{N_2O}}{D_{CO_2}}\right)_{Water}$$

N_2O solubility in amine blends is estimated. The CO_2 solubility in solution is estimated using the N_2O analogy as follows:

$$\left(\frac{H_{N_2O}}{H_{CO_2}}\right)_{Amine} = \left(\frac{H_{N_2O}}{H_{CO_2}}\right)_{Water}$$

Formulae Used for Diffusivity (m^2/s) Measurement:

$$D_{N_2O} = 5.07 x 10^{-6} \exp\left(-\frac{2371}{T}\right)$$

$$D_{CO_2} = 2.35 \times 10^{-6} \exp\left(-\frac{2119}{T}\right)$$

Experimental set-up and experimental procedure for Vapor Liquid equilibrium

The experimental set-up (Figure 2, consisted of a gas saturator or gas bubbler, equilibrium cell and gas reservoir). The equilibrium cell, in which the gas-liquid equilibrium is allowed to attain, is fitted with magnetic stirrer to enhance the equilibrium process. Conductivity probe is inserted in equilibrium cell to ensure attained gas-liquid equilibrium. The exit of the cell is connected to a glass reservoir. The gas circulating blower is used to circulate gas in the system. It took gas from reservoir and bubbled in gas saturator. The pressure maintained in the system is practically near atmosphere. The entire assembly is placed in constant temperature bath except gas circulating blower. Since the temperatures are not widely different from ambient 303 K, the heat loss from blower to surrounding can safely be neglected. Figure 4 shows the complete experimental set-up.

A known quantity of solvent solution is taken in an equilibrium cell. CO_2 gas is injected into reservoir to get the desired partial pressure. The gas circulating blower is then started. Some CO_2 would get absorbed into solvent solution. To compensate this, an additional quantity of CO_2 gas is injected so that system is near atmospheric pressure. The approach to equilibrium is monitored with the help of conductivity probe. Since the reaction of CO_2 with aqueous solvent solution is ionic in nature, the concentration of ionic species remains constant after reaching equilibrium. The constant reading of conductivity probe over two - three days suggests that equilibrium is achieved. At this stage, the gas composition is identical in cell as well as in gas reservoir.

The reservoir is then isolated from the system with the help of valves. A known quantity of caustic, which is in far excess, than required, is added to the reservoir with the help of a gas syringe. It is the well mixed by shaking and kept for 48 h, so that entire amount of CO_2 gas is absorbed into aqueous NaOH solution. A sample is taken from the reservoir with the help of gas tight syringe and introduced into caustic solution to convert it into Na_2CO_3. With the help of CO_2 ion-selective electrode, both samples are analyzed for carbonate, hence CO_2 content is back calculated both is gas phase and in liquid phase.

EXAMPLE 2: CO_2-MDEA-PZ-K_2CO_3-$KHCO_3$-H_2O SYSTEM

Promoted amines/carbonate blends are potentially attractive solvents for CO_2 capture, and may be recommended for flue gas cleaning. In the present disclosure, the CO_2 reaction with MDEA + PZ + K_2CO_3 + $KHCO_3$ + H_2O mixture is investigated. Due to its tertiary amine characteristics, MDEA has high CO_2 removal capacity. Although potassium bicarbonate has low reactivity with CO_2, it has low regeneration cost. Piperazine (PZ), which is a cyclic diamine, is used as a promoter.

The CO_2 reaction with promoted amines/carbonate blend is investigated over the ranges in temperature, 298 to 308 K and PZ concentrations, 0.15 to 0.45 M. The concentrations of MDEA, K_2CO_3 and $KHCO_3$ in solution are 2.5, 0.4 and 0.09 M, respectively. In the fast reaction regime, the rate of absorption is independent of the liquid-side mass transfer coefficient and hence it should not depend on the agitation speed. Experimentally there is no change in the absorption rate, while varying the stirring speed in the range 50-90 rpm at 308 K. Hence, it can be concluded that the investigated system belongs to the fast reaction regime systems.

a) Estimation of physical properties for MDEA-PZ-K_2CO_3-$KHCO_3$-H_2O blends

Knowledge on physical properties is essential for the estimation of reaction kinetics. The density and viscosity of the blend comprising MDEA, K_2CO_3, $KHCO_3$, promoter (piperazine) and H_2O are measured at 298 K, 303 K and 308 K.

MIX* = MDEA (2.5 M), $KHCO_3$ (0.09M), K_2CO_3 (0.4 M) and Piperizine

Density (ρ), Viscosity (μ) and Diffusivity Data (D_{CO2}) for MIX*:

Table 1: Density (ρ), Viscosity (μ) and Diffusivity Data (D_{CO2}) for MIX* at different Piperazine concentration, at 298, 303 and 308 K.

T	**PZ Conc.**	**ρ**	**μ**	**$D_{CO_2} \times 10^9$**
(K)	(M)	(kg/m^3)	(mPa.s)	(m^2/s)
298	Mix + 0.15	1059.12	1.53	1.312
	Mix + 0.25	1071.08	1.62	1.249
	Mix + 0.35	1082.26	1.70	1.202
	Mix + 0.45	1092.79	1.80	1.149
303	Mix + 0.15	1058.37	1.25	1.581
	Mix + 0.25	1070.23	1.36	1.484
	Mix + 0.35	1081.07	1.46	1.398
	Mix + 0.45	1091.00	1.58	1.316
308	Mix + 0.15	1057.04	1.10	1.831
	Mix + 0.25	1069.38	1.18	1.721
	Mix + 0.35	1079.84	1.25	1.651
	Mix + 0.45	1088.21	1.35	1.549

b) Reaction kinetic data for MDEA-PZ-K_2CO_3-$KHCO_3$-H_2O blends

With increase in temperature & promoter concentration cause the expected increase in the values of the observed reaction rate constants.

Mix* = MDEA (2.5 M), $KHCO_3$ (0.09M), K_2CO_3 (0.4 M) and Piperizine.

$k_{obs} = r/(CO_2)$ = observed reaction rate constant (1/s).

Table 2: Observed reaction rate constant for Mix* at different piperazine concentration at 298, 303 and 308 K.

T	**PZ Conc.**	**k_{obs}**
(K)	(M)	(1/sec)
298	Mix + 0.15	4787
	Mix + 0.25	11371
	Mix + 0.35	15159
	Mix + 0.45	16675
303	Mix + 0.15	6253
	Mix + 0.25	15569
	Mix + 0.35	24703
	Mix + 0.45	29292
308	Mix + 0.15	9829
	Mix + 0.25	19915
	Mix + 0.35	23370
	Mix + 0.45	36394

Table 3. The effect of CO_2 partial pressure on the absorption rates into aqueous mixtures of MDEA (2.5 M), PZ, K_2CO_3 (0.4 M) and $KHCO_3$ (0.09 M) at 298, 303 and 308 K

Temp. (K)	CO_2 pressure (kPa)	PZ (M)	R x 10^6 (kmol/(m^2 s))
298	8.57	0.15	7.32
	8.16	0.25	10.8
	7.05	0.35	11.2
	3.37	0.45	5.71
303	6.92	0.15	5.81
	8.64	0.25	11.8
	6.77	0.35	12.3

	12.64	0.45	25.8
308	8.1	0.15	8.84
	6.03	0.25	9.84
	9.08	0.35	17.0
	13.04	0.45	31.6

Table 4 Kinetic and thermodynamic characteristics of mixture (MDEA = 2.5 M, PZ = 0.25 M, K_2CO_3 = 0.4 M and $KHCO_3$ = 0.09 M)

Temp K	CO_2 Pressure kPa	R x 10^6 kmol/ (m^2s)	k_{obs} 1/s
298	8.16	10.8	11371
303	8.64	11.8	15569
308	6.03	9.84	19915

c) Solubility data for MDEA-PZ-K_2CO_3-$KHCO_3$-H_2O blends

Knowledge on CO_2 solubility in solution is essential for estimation of reaction kinetics.

Table 5 Solubility of CO_2 in the mixture [MDEA (2.5M) + K_2CO_3 (0.4M) + $KHCO_3$ (0.0925M) + PZ] at 298, 303 and 308 K

T	**PZ Conc.**	$H_{CO_2} \times 10^4$
(K)	(M)	[kmol/(m^3.kPa)]

298	Mix + 0.15	3.49
	Mix + 0.25	3.51
	Mix + 0.35	3.65
	Mix + 0.45	3.71
303	Mix + 0.15	2.76
	Mix + 0.25	2.84
	Mix + 0.35	2.99
	Mix + 0.45	3.10
308	Mix + 0.15	2.65
	Mix + 0.25	2.79
	Mix + 0.35	2.96
	Mix + 0.45	3.06

d) Vapour – Liquid Equilibrium Data for MDEA-PZ-K_2CO_3,-$KHCO_3$-H_2O blend.

Knowledge of the equilibrium partial pressure of CO_2 over alkanolamine solution is essential, particularly in the design of top portion of absorber. The CO_2 slip in treated gas is mainly depends on equilibrium partial pressure. Under design of absorber will effect on production cost. Therefore, gas-liquid equilibrium data is of importance.

Electrolyte-NRTL model is developed to describe the (Vapour+Liquid) equilibria (VLE) of CO_2 in aqueous (MDEA+K_2CO_3-$KHCO_3$+PZ) solution. The electrolyte-NRTL model predicted different thermodynamic properties for the system (CO_2+MDEA+K_2CO_3-$KHCO_3$+PZ+H_2O) and are presented in table 6 and 7 and from Figures 3 - 12.

Table 6. ENRTL model predicted solubility of CO_2 in aqueous (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) in the temperature range of (313- 333) K. α_{CO_2} is defined as mole CO_2/mole amine (MDEA+K_2CO_3+$KHCO_3$+PZ)

T = 313 K		T =323 K		T = 333 K	
α_{CO_2}	p_{CO_2}/kPa	α_{CO_2}	p_{CO_2}/kPa	α_{CO_2}	p_{CO_2}/kPa
0.134	0.084	0.134	0.138	120.519	0.229
0.153	0.248	0.153	0.417	0.153	0.698
0.172	0.426	0.172	0.738	0.172	1.263
0.191	0.616	0.191	1.095	0.191	1.913
0.210	0.817	0.210	1.487	0.210	2.650
0.229	1.034	0.229	1.920	0.229	3.480
0.248	1.271	0.248	2.402	0.248	4.418
0.267	1.535	0.267	2.944	0.267	5.484
0.286	1.833	0.286	3.561	0.285	6.700
0.304	2.173	0.304	4.265	0.304	8.091
0.323	2.563	0.323	5.074	0.323	9.685
0.342	3.014	0.342	6.005	0.342	11.512
0.361	3.536	0.361	7.077	0.361	13.605
0.380	4.141	0.380	8.312	0.380	15.998
0.399	4.841	0.399	9.732	0.399	18.729
0.418	5.653	0.418	11.363	0.418	21.835
0.438	6.444	0.438	13.149	0.437	25.360
0.458	7.630	0.456	15.155	0.456	29.347
0.477	8.724	0.478	17.576	0.475	33.846
0.496	9.968	0.495	19.576	0.493	38.908
0.514	11.289	0.517	22.249	0.512	40.591
0.532	12.785	0.532	24.627	0.531	44.958
0.552	14.691	0.552	27.615	0.550	45.219
0.570	16.457	0.570	30.966	0.569	51.407
0.589	18.204	0.589	34.303	0.588	58.312
0.606	20.393	0.608	38.427	0.607	66.015
0.625	22.558	0.626	42.507	0.626	74.611

0.645	25.631	0.645	47.547	0.645	84.212
0.664	29.524	0.664	54.145	0.664	94.951
0.683	34.015	0.683	61.637	0.683	106.988
0.701	39.216	0.701	70.171	0.701	120.519
0.720	45.265	0.720	79.928	0.720	135.786
0.739	52.336	0.739	91.139	0.739	153.088
0.758	60.657	0.758	104.096	0.758	172.797
0.777	70.526	0.777	119.177	0.777	195.384
0.796	82.344	0.796	136.879	0.796	221.442
0.815	96.653	0.815	157.856	0.815	251.720
0.834	114.210	0.834	182.984	0.834	287.167

Table 7 Comparison of VLE (P_{CO2} Vs Loading) for different solvents at 40 °C and at 5 kPa of CO_2 partial pressure at absorber condition.

	Composition	Loading	P-CO_2= 5 kPa, T = 40 C
H_2O+MDEA	30 wt% MDEA	0.38	Mol CO_2/mol Amine
H_2O+MDEA+PZ	7.9 m MDEA+1.19 m PZ (4M MDEA+ 0.6M PZ)	0.36	Mol CO_2/mol Amine
PZ+H_2O	3.2 M PZ	0.793	Mol CO_2/ mol Amine
H_2O+K_2CO_3	30 wt% K_2CO_3 (= 6.2 m K^+)	0.45	Mol CO_2/mol K_2CO_3
		0.225	Mol CO_2/mol K^+
APBS1 (total 38.7 wt%) or (5.48 m, Mol/kg water)	MDEA = 30 wt %	0.401	Mol CO_2/mol (Amine + K^+)
	PZ =2.5 wt%		
	K_2CO_3 =5.5 wt%		
	$KHCO_3$=0.9 wt%		

e) <u>Heat of Absorption for MDEA-PZ-K_2CO_3-$KHCO_3$-H_2O blend</u>

The heat of absorption of CO_2 into a solvent is an important parameter, since it gives magnitude of heat released during the absorption process. Besides, it represents the energy required in the regenerator to reverse the reaction and release CO_2 from the solvent. The differential heat of absorption of CO_2 into (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent is estimated from the ENRTL model based on the Clausius - Clapeyron equation:

$$\frac{-\Delta H_{abs}}{R} = \frac{d \ln P_{CO_2}}{d(1/T)}$$

Figure 13 and Figure 14 shows the calculated heat of absorption for (4.081 m MDEA+0.653 m K_2CO_3+ 0.147 m $KHCO_3$+ 0.408 m PZ) solvent at 323 K as a function of CO_2 loading. The ΔH_{abs} is estimated to be around 56 kJ/mol CO_2 by taking an average value between loading 0.2 to 0.6.

EXAMPLE 3: CO_2-MDEA-MPZ-K_2CO_3-$KHCO_3$-H_2O SYSTEM

The CO_2 reaction with promoted amines/carbonate blend is investigated over the ranges in temperature, 298 to 308 K, and MPZ concentrations, 0.15 to 0.45 M. The concentrations of MDEA, K_2CO_3 and $KHCO_3$ in solution are 2.5, 0.4 and 0.09 M, respectively. This reaction system belongs to the fast reaction regime systems.

a) Estimation of physical properties for MDEA-MPZ-K_2CO_3-$KHCO_3$-H_2O blends

Knowledge on physical properties is essential for the estimation of reaction kinetics. The density and viscosity of the blend comprising MDEA, K_2CO_3/$KHCO_3$, promoter (methyl piperazine) and H_2O were measured at 298, 303 and 308.

MIX* = MDEA (2.5 M), $KHCO_3$ (0.09M), K_2CO_3 (0.4 M) and n-Methyl Piperizine

Table 8: Density (ρ), Viscosity (μ) and Diffusivity Data (D_{CO2}) for MIX* at different methyl Piperazine concentration at 298, 303 and 308 K

T	MPZ Conc.	ρ	μ	$D_{CO_2} \times 10^9$

(K)	(M)	(kg/m^3)	(kg/(m.s))	(m^2/s)
298	Mix + 0.15	1066.35	1.70	1.20
	Mix + 0.25	1074.04	1.74	1.18
	Mix + 0.35	1081.61	1.80	1.15
	Mix + 0.45	1088.85	1.84	1.13
303	Mix + 0.15	1065.87	1.37	1.48
	Mix + 0.25	1073.19	1.43	1.42
	Mix + 0.35	1080.44	1.48	1.38
	Mix + 0.45	1087.04	1.54	1.34
308	Mix + 0.15	1064.96	1.23	1.67
	Mix + 0.25	1072.35	1.27	1.62
	Mix + 0.35	1079.07	1.30	1.60
	Mix + 0.45	1086.22	1.35	1.55

b) Reaction kinetic data for MDEA-MPZ-K_2CO_3-$KHCO_3$-H_2O blends

With increase in temperature & promoter concentration cause the expected increase in the values of the observed reaction rate constants.

Table 9. CO_2 absorption rates and values of the observed reaction rate constant into aqueous mixtures of MDEA (2.5 M), MPZ, K_2CO_3 (0.4 M) and $KHCO_3$ (0.09 M) at 298, 303 and 308 K

Temp. (K)	CO_2 pressure (kPa)	MPZ (M)	Rx 10^6 (kmol/(m^2 s))	k_{obs} (1/s)
298	9.5	0.15	8.70	8062
	5.7	0.25	5.94	8508
	4.7	0.35	5.72	9253

	5.7	0.45	7.78	10355
303	7.9	0.15	7.72	8465
	5.5	0.25	6.44	9053
	5.76	0.35	7.60	9384
	5.75	0.45	8.38	10556
308	5.92	0.15	4.5	9940
	7.02	0.25	8.33	12385
	4.3	0.35	6.22	14248
	7.56	0.45	13.9	20246

Table 10. Effect of MDEA concentration into aqueous mixtures of MDEA, MPZ (0.25 M), K_2CO_3 (0.4 M) and $KHCO_3$ (0.09 M) at 303 K

MDEA (M)	CO_2 Pressure (kPa)	Rx 10^6 (kmol/(m^2 s))
1.5	4.9	5.22
2.5	5.5	6.44
3.5	5.8	6.89

c) Solubility data for MDEA-MPZ-K_2CO_3-$KHCO_3$-H_2O blends

Solubility of CO_2 in the mixture [MDEA (2.5M) + K_2CO_3 (0.4M) + $KHCO_3$ (0.0925M) + MPZ]

Knowledge on CO_2 solubility in solution is essential for estimation of reaction kinetics.

Table 11. Solubility of CO_2 in the mixture [MDEA (2.5M) + K_2CO_3 (0.4M) + $KHCO_3$ (0.0925M) + M-PZ] 298, 303 and 308 K

T	**MPZ Conc.**	**$H_{CO_2} \times 10^4$**
(K)	(M)	[kmol/(m^3.kPa)]

298	Mix + 0.15	2.95
	Mix + 0.15	3.30
	Mix + 0.15	3.73
	Mix + 0.15	3.98
303	Mix + 0.15	2.76
	Mix + 0.15	3.26
	Mix + 0.15	3.66
	Mix + 0.15	3.87
308	Mix + 0.15	1.91
	Mix + 0.15	2.67
	Mix + 0.15	3.03
	Mix + 0.15	3.23

d) Vapour – Liquid Equilibrium Data for MDEA-MPZ-K_2CO_3-$KHCO_3$-H_2Oblend

Knowledge of the equilibrium partial pressure of CO_2 over alkanolamine solution is essential, particularly in the design of top portion of absorber. The CO_2 slip in treated gas is mainly depends on equilibrium partial pressure. Under design of absorber will effect on production cost. Therefore, gas-liquid equilibrium data is of importance. See Table 12 and 13 and Figure 15.

Table 12: Equilibrium CO_2 partial pressure over MDEA-MPZ-K_2CO_3-$KHCO_3$-H_2O blend.α_{CO_2} is defined as mole CO_2/mole amine (MDEA + MPZ + $KHCO_3$ + K_2CO_3)

Temperature: 303 K

α_{Mix}	$p^*_{CO_2}$
(mole CO_2/mole	(kPa)

amine)	
0.142	2.03
0.174	2.21
0.215	2.53
0.235	3.38
0.293	4.59
0.302	5.86
0.355	8.78

Literature Comparision with (CO_2 + MDEA) and (CO_2 + MDEA-MPZ-K_2CO_3-$KHCO_3$). See table 13 and figure16.

Table 13:

Derks et al 2010		Jou et al 1982		Kundu et al 2006	
α_{Mix}	$p^*_{CO_2}$	α_{Mix}	$p^*_{CO_2}$	α_{Mix}	$p^*_{CO_2}$
(mole CO_2/mole amine)	(kPa)	(mole CO_2/mole amine)	(kPa)	(mole CO_2/mole amine)	(kPa)
0.122	1.25	0.012	0.0132	0.22	3.7
0.213	3.24	0.0676	0.184	0.401	11
0.294	5.97	0.224	2.38	0.505	21
0.361	8.5	0.441	11.2	-	-
0.382	9.2	-	-	-	-

The obtained experimental vapour – liquid data is in good agreement with previously published research articles.

EXAMPLE 4: EFFICIENCY OF THE SOLVENT SYSTEMS IN COMPARISON WITH THE CONVENTIONAL SOLVENT SYSTEM

The present example illustrates the results of solvents tested on Promax, a simulation software licensed by Bryan Research and Engineering with conventional carbon capture process configuration.

The coventional process has an absorber operating at 1 atm. The flue gas enters at 46 ^{0}C and 1 atm and comes in contact with lean solvent from the stripper. The bottom stream leaving the absorber known as rich solvent enters the cross exchanger which has a temperature approach of 5 ^{0}C and enters the stripper. The stripper operates at 100-120 ^{0}C and 2 atm for different solvents. The stream leaving from top of the stripper is cooled and condensed to remove the water present in the strip gas. Thus condenser's top stream is compressed to 2.97 atm to achieve 90% carbon dioxide recovery with 99% (% wt) purity. Figure 17 shows a process flow diagram of conventional carbon capture system

Table 14: APBS Solvent Composition

Solvents	Composition			
	MDEA	PZ	K^+	Water
APBS1	29.1	2.1	4.89	36.09
APBS2	38.25	6.75	5	50
APBS3	30	6.75	13.25	50
APBS4	50	6	15	29

The above chart shows that ABPS2, ABPS3 and APBS4 have less steam demand with respect to other solvents. The above chart shows that ABPS2, ABPS3 and ABPS4 have comparable recirculation rate to existing solvents

Results:

Following are results which are derived from simulation on above process configuration

Table 15:

Parameters	**Units**	**30 (%wt) MEA**	**41.6 (wt %) MDEA & 8.58 (wt %) PZ**	**50 (%wt) MDEA & 5% wt PZ**	**7.95 (wt %) K+ & 3.96 (wt %) PZ**

Steam Demand	kg of steam/ kg of CO_2	1.76	1.88	1.49	4.42
Lean solvent flowrate	kg/h	168.26	160.02	346.84	1013.2
Lean solvent loading	mol/mol	0.22	0.018	0.077	0.56
Rich solvent flowrate	kg/h	173.19	166.1	357.01	1023.78
Rich solvent loading	mol/mol	0.53	0.38	0.23	0.7
CO_2 capture Auxiliary loads	W	19.47	21.35	41.62	117.76
CO_2 compressor auxiliary loads	W	201.75	277.69	181.15	200.7
Total auxiliary loads	W	221.22	299.04	222.77	318.46
Cooling water duty	kW	7.15	9.02	9.3	28.66
Total steam duty	kW	11.88	12.95	10	29.8

Table 16:

Parameters	**Units**	**APBS1**	**APBS2**	**APBS3**	**APBS4**
Steam Demand	kg of steam/kg of CO_2	3.76	1.41	1.3	1.16
Lean solvent flowrate	kg/h	1888	301.19	297.02	277.29
Lean solvent loading	mol/mol	0.22	0.21	0.38	0.32
Rich solvent flowrate	kg/h	1899	311.53	308.08	290.43
Rich solvent loading	mol/mol	0.26	0.387	0.543	0.45
CO_2 capture Auxiliary loads	W	217.07	34.09	30.46	27.06
CO_2 compressor auxiliary loads	W	190.63	184.86	182.64	178.72
Total auxiliary loads	W	407.7	218.95	213.1	205.78
Cooling water duty	kW	25.25	8.91	8.56	8.86
Total Reboiler duty	kW	25.4	9.7	8.8	7.8

The above result is a detailed comparison of various solvents simulated on conventional system using Promax. The proposed APBS solvent shows lower steam demand in comparison to other existing solvent or combination of solvents. The steam used in reboiler in all the above cases is at 4.4 atm and 151 ^{0}C. The recirculation rate i.e. lean solvent flow rate is illustrated in the above table. Due to decreased lean solvent flowrate the power requirement of pump i.e. auxiliary load is also lower for ABPS2, APBS3 and ABPS4. Thus overall power requirement for entire carbon capture and compressing of CO_2 goes down. The steam demand is also less in case of APBS solvent hence the total steam duty is also less for ABPS2, APBS3 and ABPS4. The cooling water duty is higher only in APBS1 while in ABPS2, APBS3 and APBS4 is lower in comparison to other solvents.

Equivalents

With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (e.g., bodies of the appended claims) are generally intended as "open" terms (e.g., the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to inventions containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (e.g., "a" and/or "an" should typically be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation *is* explicitly recited, those skilled in the art will recognize that such recitation should typically be interpreted to mean *at least* the recited number (e.g., the bare recitation of "two recitations," without other modifiers, typically means *at least* two recitations, or *two or more* recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

While various aspects and embodiments have been disclosed herein, other aspects and embodiments will be apparent to those skilled in the art. The various aspects andembodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.

I claim:

1. A solvent composition for recovery of carbon dioxide from gaseous mixture, comprising diethanolamine, piperazine or its derivative, alkali salt, optionally along with cupric carbonate.

2. The solvent composition as claimed in claim 1, wherein the amine is selected from group comprising Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA), Dimethylethanolamine (DMEA), N-methyldiethanolamine (MDEA), Monomethylethanolamine (MMEA), 2-(2-aminoethoxy)ethanol, Aminoethylethanolamine (AEEA), Ethylenediamine (EDA), Diethylenetriamine (DETA), Triethylenetetramine (TETA), Tetraethylenepentamine (TEPA), 2-amino-2methyl-1-proponal (AMP), 2-(ethyamino)-ethanol (EAE), 2-(methylamino)-ethanol (MAE), 2-(diethylamino)-ethanol (DEAE), diethanolamine (DEA), diisopropanolamine (DIPA), methylaminopropylamine (MAPA), 3-aminopropanol (AP), 2,2-dimethyl-1,3-propanediamine (DMPDA), 3-amino-1-cyclohexylaminopropane (ACHP), diglycolamine (DGA), 1-amino-2-propanol (MIPA), 2-methyl-methanolamine (MMEA) or any combinations thereof, preferably N-methyl diethanolamine, at concentration ranging from about 10 wt% to about 50 wt%.

3. The solvent composition as claimed in claim 1, wherein the piperazine derivative is selected from group comprising N-aminoethylpiperazine (AEP), N-methylpiperazine, 2-methylpiperazine, 1-ethylpiperazine, 1-(2-hydroxyethyl) piperazine, 1,4-dimethylpiperazine or any combinations thereof, preferably piperazine, at concentration ranging from about 0.5 wt% to about 50 wt% or N -methyl piperazine at concentration ranging from about 0.5 wt% to about 50 wt%.

4. The solvent composition as claimed in claim 1, wherein the alkali salt is selected from a group comprising potassium carbonate, sodium carbonate salt, lithium carbonate, a bicarbonate salt, a bisulfide salt, hydroxide salt or any combination

thereof, preferably potassium carbonate and a bicarbonate salt, at concentration ranging from about 2 wt% to about 25 wt%.

5. The solvent composition as claimed in claim 1, wherein the cupric carbonate is at concentration ranging from about 50ppm to 300ppm.

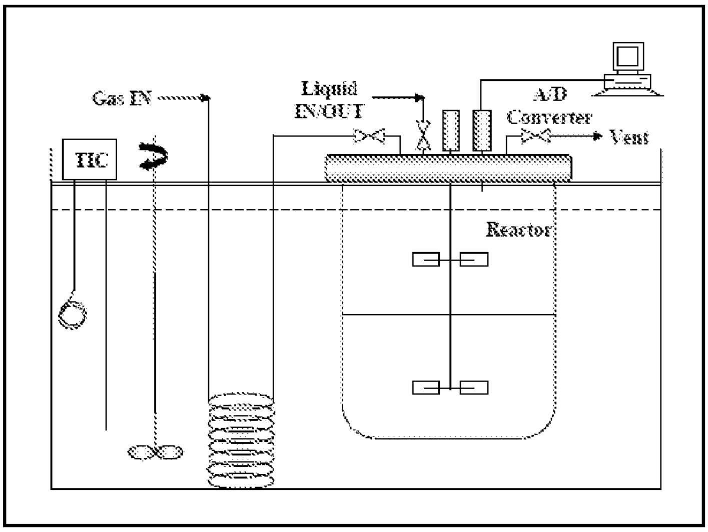

FIGURE 1

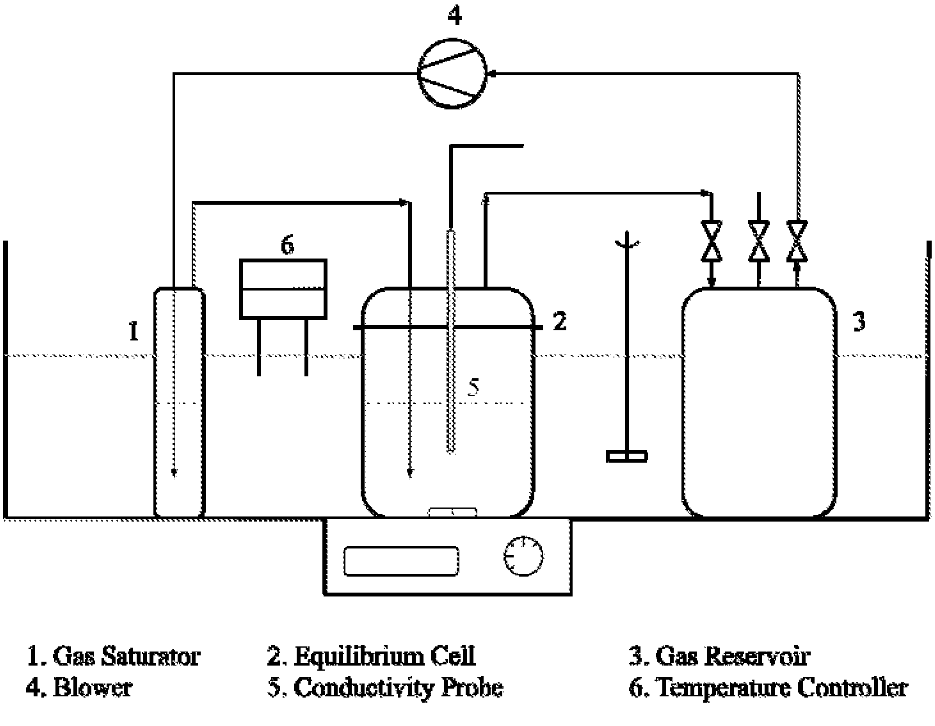

FIGURE 2

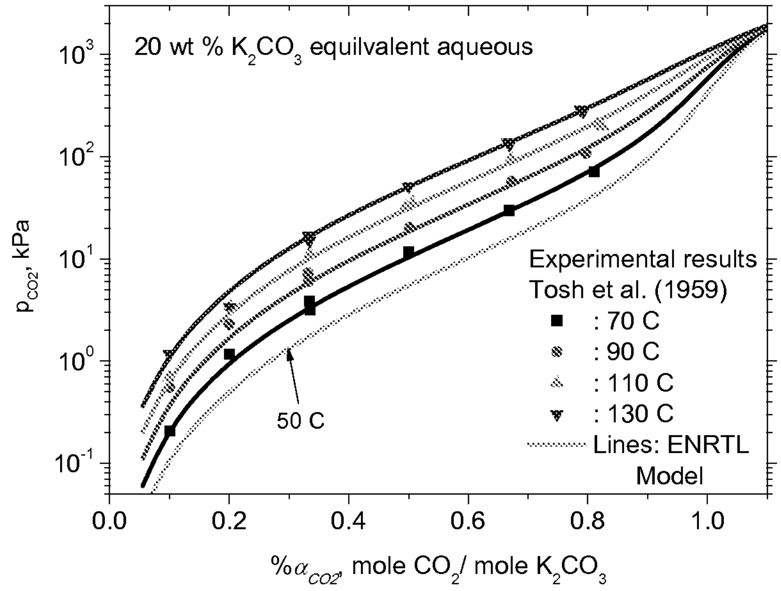

FIGURE 3

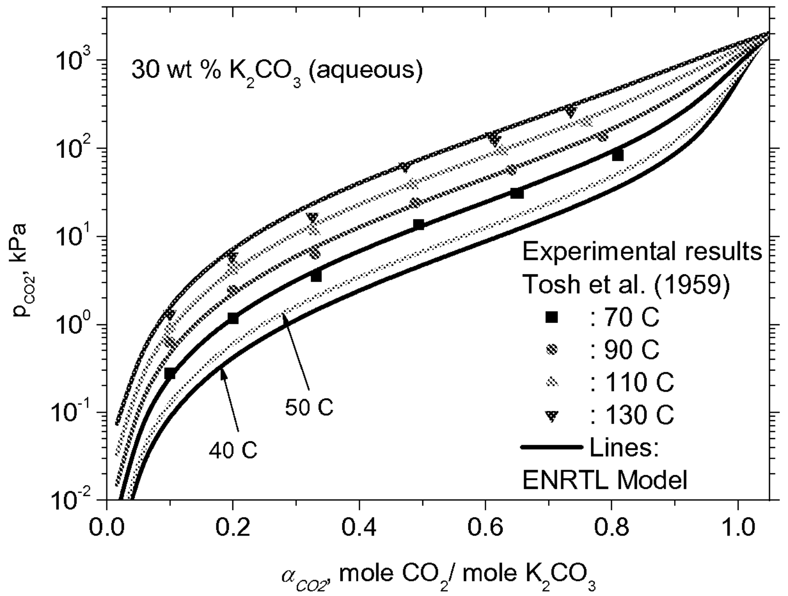

FIGURE 4

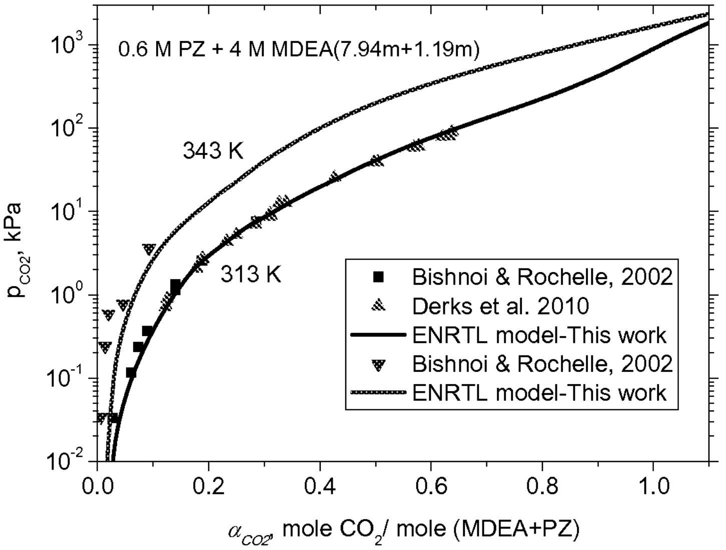

FIGURE 5

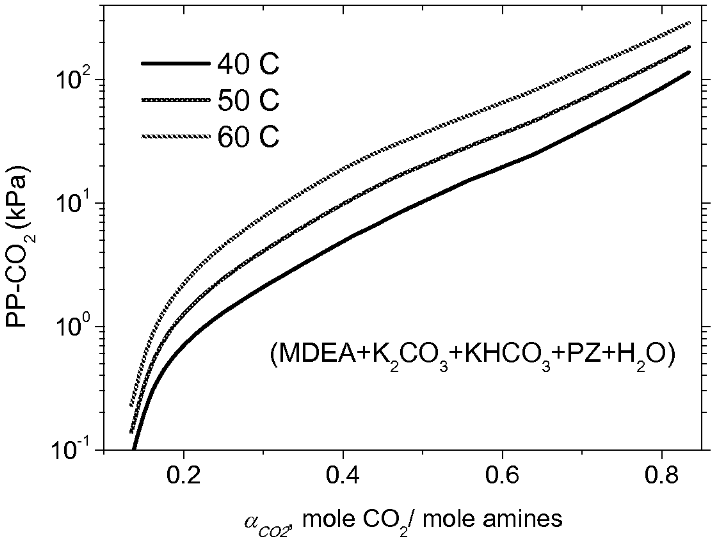

FIGURE 6

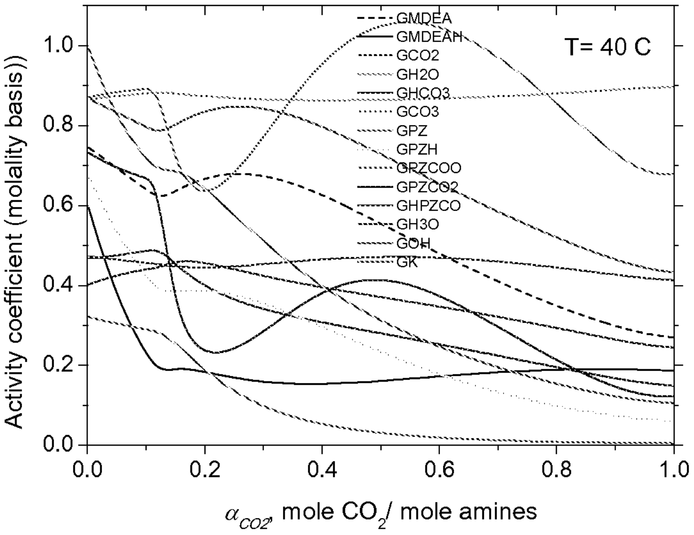

FIGURE 7

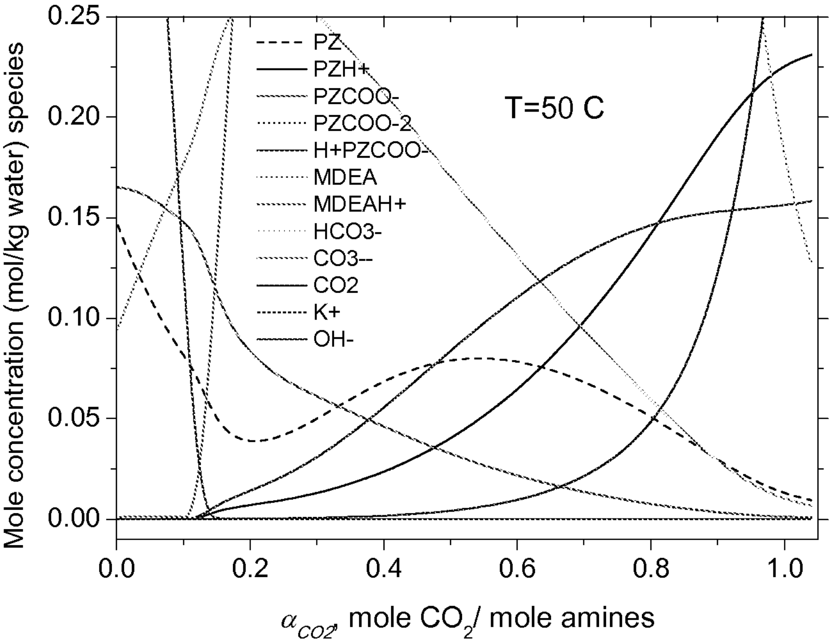

FIGURE 8

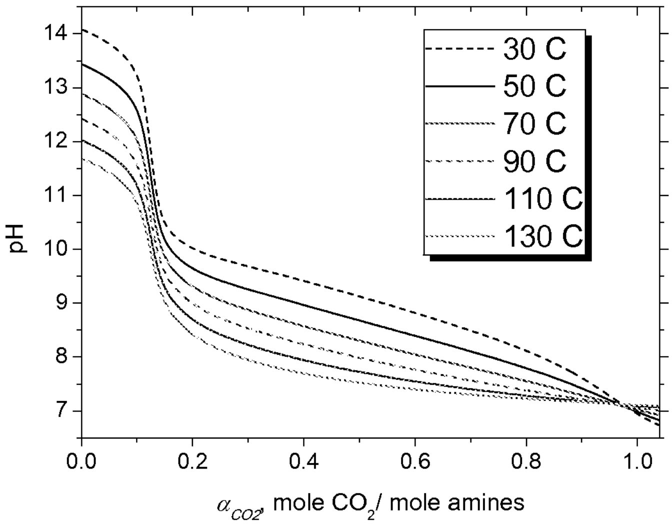

FIGURE 9

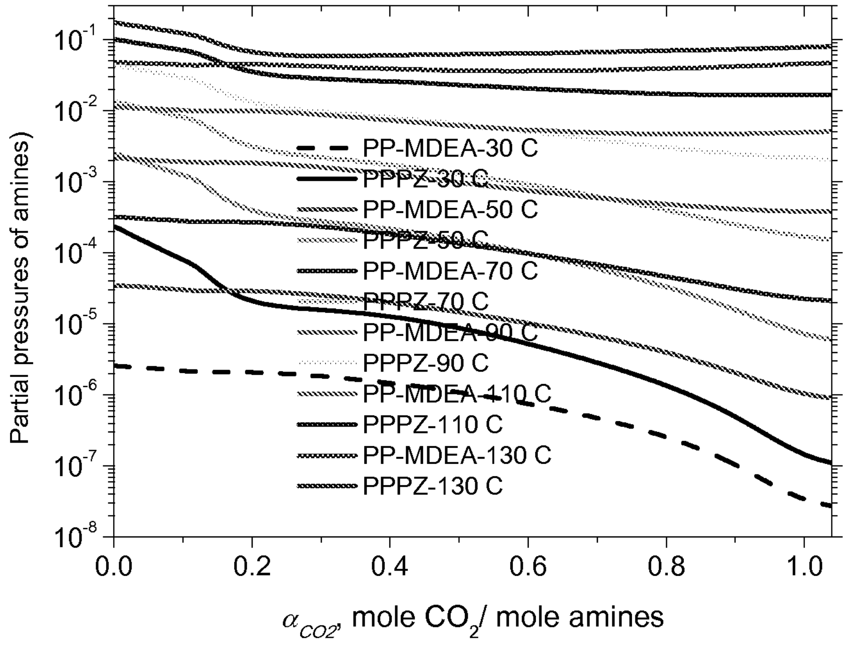

FIGURE 10

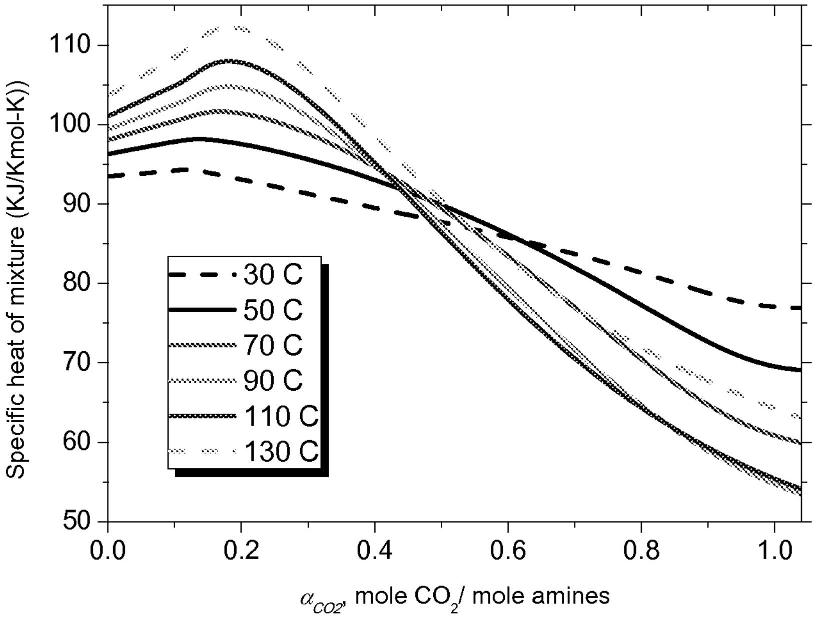

FIGURE 11

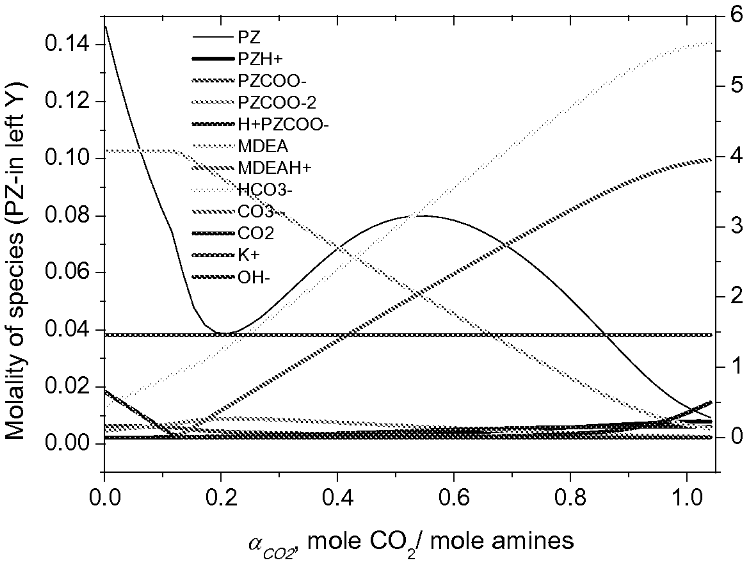

FIGURE 12

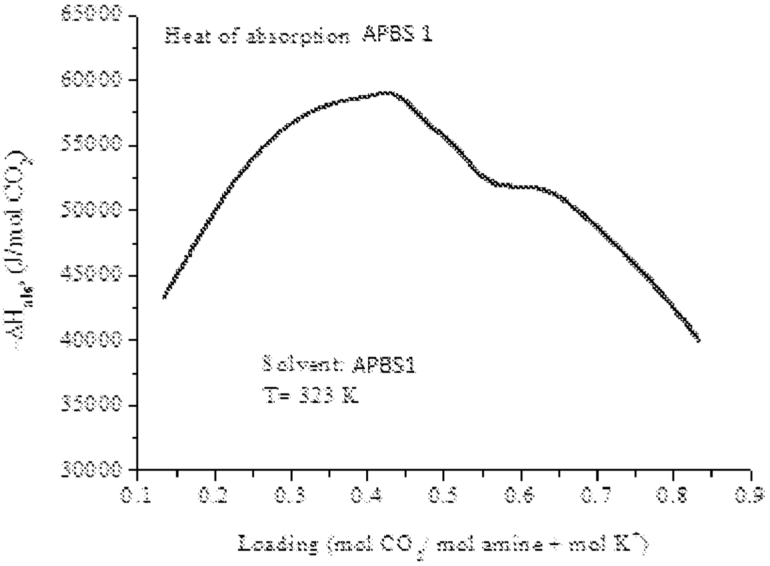

FIGURE 13

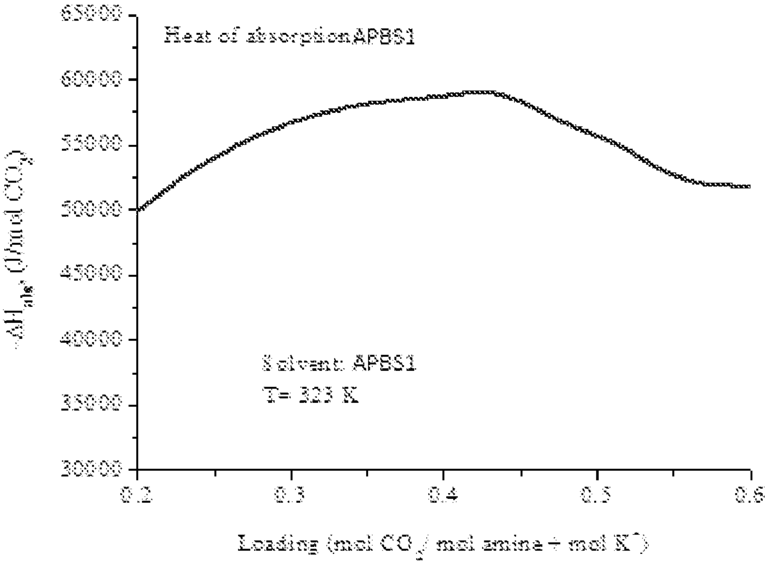

FIGURE 14

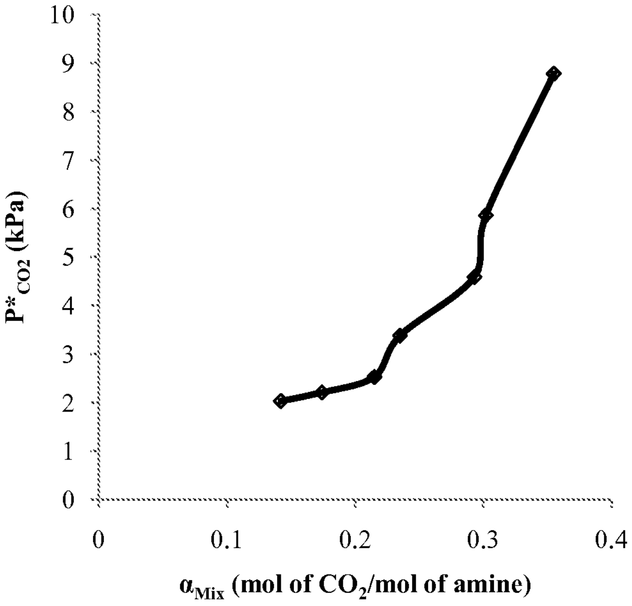

FIGURE 15

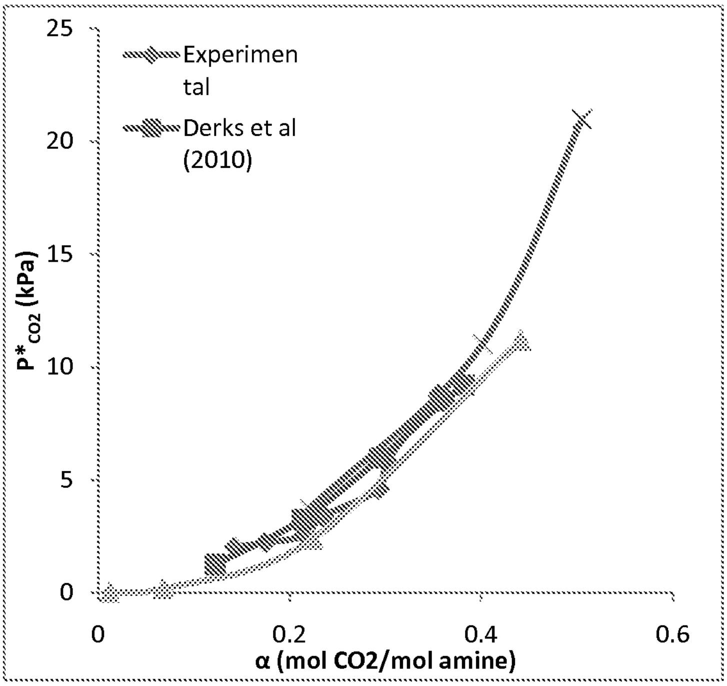

FIGURE 16

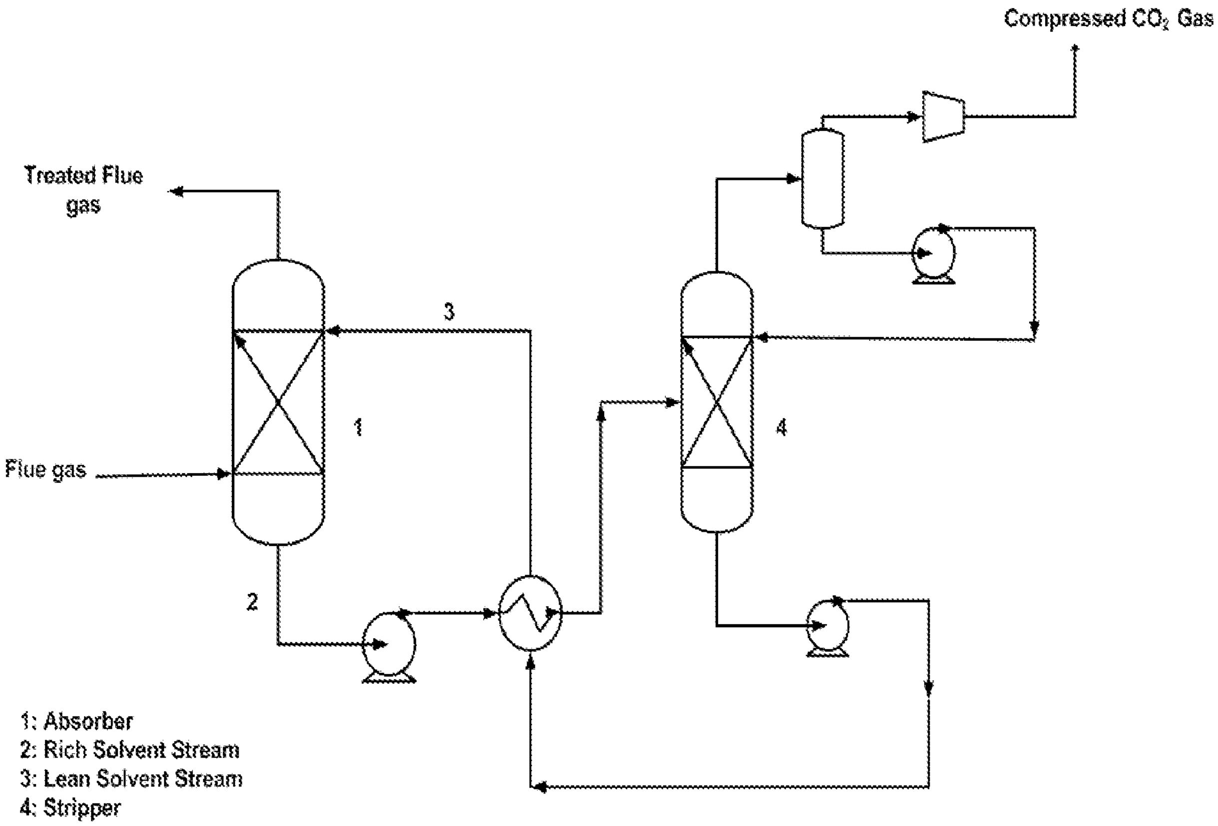
Compressed CO_2 Gas
Treated Flue gas
3
1
4
Flue gas
2
1: Absorber
2: Rich Solvent Stream
3: Lean Solvent Stream
4: Stripper

FIGURE 17

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/054062

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 224 348 A2 (ICI PLC [GB]) 3 June 1987 (1987-06-03)	1-4
Y	page 2, line 1 - line 33 claims; example -----	5
A	DE 198 28 977 A1 (BASF AG [DE]) 30 December 1999 (1999-12-30) column 2, line 5 - column 3, line 53; claims -----	1-5
A	WO 2004/089512 A1 (UNIV TEXAS [US]; ROCHELLE GARY [US]; CULLINANE JOHN [US]) 21 October 2004 (2004-10-21) page 3, line 3 - line 21; claims -----	1-5
Y	US 4 440 731 A (PEARCE ROSCOE L [US]) 3 April 1984 (1984-04-03)	5
A	column 2, line 19 - line 50; claims; examples -----	1-4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 5 December 2011	Date of mailing of the international search report 13/12/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fourgeaud, Damien

International application No.
PCT/IB2011/054062

INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-5(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-5(partially)

Present claims 1-5, in particular when considering claim 2 which is broader than claim 1 (claim 1 comprises a reference to diethanolamine, whereas claim 2 refers to several different amines which are different from diethanolamine), relate to an extremely large number of possible compounds and thus to a huge number of compositions. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compositions (see p.5 l.28-34, and all examples of the present application). The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-5 (PCT Guidelines 9.19 and 9.23). The search of claims 1-5 was restricted to those claimed compositions which appear to be supported, namely a composition comprising MDEA, PZ or MPZ, potassium carbonate, water and optionally cupric carbonate.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2011/054062

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