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Industrial Progress: New Energy-Efficient Absorbents for the CO_2 Separation from Natural Gas, Syngas and Flue Gas

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Abstract

The CO_2 separation from natural gas, syngas or flue gas represents an important industrial field of applications. An economic and energy-efficient CO_2 separation from these gas streams is a prerequisite for sustainable industry contributions to the megatrends resource efficiency and globalization of technologies. One way of reducing operational expenditure for these separation processes is the development of better performing CO_2 absorbents. Although a number of absorbents for the separation of CO_2 from process gas streams exist, the need for the development of CO_2 absorbents with an improved absorption performance, less corrosion and foaming, no nitrosamine formation, lower energy requirement and therefore less operational expenditure remains. Recent industrial activities have led to the development of novel high-performance CO_2 scrubbing agents that can be employed in numerous industrial processes such as natural gas treatment, purification of syngas and the scrubbing of flue gas. The objective of this paper is to introduce these new high-performance scrubbing agents and to compare their performance with other state-of-the-art absorbents. It turned out, that the evaluated absorbents offer high cyclic capacities in the range of 2.4 to 2.6 mol CO_2/kg absorbent and low absorption enthalpies (–30 kJ/mol) allowing for distinctive savings in the regeneration energy of the absorbent. Calculations with the modified Kremser model resulted in a reduction of the specific reboiler heat duty of 55%. Furthermore, the absorbents are less corrosive than standard amines as indicated by the measured corrosion rates of 0.21 mm/y versus 1.18 mm/y for a piperazine/methyldiethanolamine mixture. Based on new experimental results it is shown how substantial savings in operational and capital expenditure can be realized due to favorable absorbent properties. The novel high-performance CO_2 system solutions meet recent industrial absorbent requirements and allow for more efficient or new CO_2 separation processes.

Keywords: Absorbent, CO_2, Energy Efficiency, Sustainability, Operational Expenditure, Separation, Capture

1. Introduction

This paper focuses on the use of new amine systems for separating CO_2 from various gas streams such as those typical for natural gas and synthesis gas purification or the field of carbon capture and storage (CCS).

Generic amines like triethanolamine (TEA), diethanolamine (DEA), diisopropanolamine (DIPA) or monoethanolamine (MEA) as well as methyldiethanolamine (MDEA) have been used for acid gas removal for decades. The utilized systems were constantly improved over the years to show a better performance in terms of stability, kinetics or corrosion behavior as well as the energy input for regeneration [1]. While in the early years, more or less pure aqueous amine systems were used, formulated solvents with special additives (specialty amines) like corrosion inhibitors, defoaming agents or kinetic activators evolved and were tailored for special applications (e.g. selective removal of components, partial or bulk removal).

In recent years, the focus of absorption process optimization has been on energy efficient processes and solvents were tuned to realize drastic savings in regeneration energy. Especially the immense R & D programs for climate protection and CCS pointed out the need for optimized solvents and contributed to worldwide activities in the field of economical absorbents for post-combustion CO_2 removal from flue gases [2-7]. A broad range of different kind of amines were suggested for gas sweetening applications, such as primary amines with low loadings but fast kinetics and high enthalpies of absorption, sterically hindered or tertiary amines with slower kinetics, high cyclic capacities and moderate enthalpies of absorption each class offers pros and cons. In the end, an optimal solvent needs to be specified for each application and that is the treated gas stream with individual characteristics (e.g. CO_2 and/or H_2S partial pressure, side components) and requirements (specifications).

In the following, we will discuss the requirements and challenges for the use of new amine systems for sour gas removal. After presenting a brief state-of-the-art summary including a description of the most relevant industrial challenges, we will report the progress in developing new absorbents.

2. Acid Gas Removal

2.1. State-of-the-Art-Absorbents

Currently, CO_2 absorption is back on the agenda. Mainly the identification of CO_2 as greenhouse gas as well as demand for sustainability in the chemical industry have sparked enormous, often publicly funded research and development activities to identify energy efficient solvents for CCS applications in the field of post-combustion flue gas treating. Recently, several newly developed solvent formulations, mostly based on amine compounds were introduced to gas treating applications. But, so far in the CCS research no breakthrough has been achieved and even in the classical field of operation like gas sweetening of syngas and natural gas feeds, the demand for energy efficient technologies calls for improvements.

There are numerous different CO_2 removal processes available on the market and a proper choice of which is best suited always depends on various criteria like the kind of treated gas stream (natural gas, syngas, and flue gas), the partial pressure of carbon dioxide and the desired clean gas specifications. Basically, there are different process technologies that make use of physical solvents, chemical solvents or hybrid solvents (mixture of physical and chemical solvent). For each application the proper choice of the solvent determines whether the separation process is economically feasible. In **Table 1** different product specifications are listed and together with additional information about the feed composition and the CO_2-partial pressure it is possible to make a pre-selection of the process technology for the separation.

Processes with physical solvents are only applicable at higher CO_2 partial pressures. In comparison to chemical absorbents, lower solvent flow rates can be realized due to the higher solubility at high partial pressure of the sour gas. Therefore equipment size is reduced (pumps, absorber, flash, piping) leading to lower investment costs if additional equipment, e.g. for chilling of the absorbent, is not needed. Nevertheless, the solubility of hydrocarbons in these kinds of solvents can be quite high [1]. Selectivity, for example between CO_2 and H_2S results from different solubilities of the gases and is realized in processes like Rectisol or Selexol, as shown in **Table 2**.

Due to the low enthalpy of absorption of CO_2, the solvent regeneration requires less energy input. A thermal regeneration step is only implemented in the case of tight product specifications. Due to the lower binding forces of the CO_2, one or more flash stages with a simple pressure decrease are often sufficient (see **Table 2** for different processes with physical solvents). Tennyson and Schaaf specify a CO_2 partial pressure of >690 kPa in the feed gas as a typical set point for physical solvents. In the off-gas, purities of 14 kPa CO_2 partial pressure

Table 1. Typical CO_2 specifications for various applications [1,8].

Gas stream	CO_2 spec	CO_2 partial pressure/kPa	Additional impurities
Natural Gas	2% - 3% (v/v)	50 - 700	Hydrocarbons, H_2S
LNG	<50 ppmv		
Syngas (Oxo)	10 - 100 ppmv	200 - 2900	O_2, SO_2, HCN, H_2S, COS, C_mH_n
Syngas (Ammonia)	<500 ppmv		
Flue gas	85% - 95% removal	4 - 12	NO_x, SO_2, O_2

Table 2. Some state of the art processes with physical solvents and hybrid solvents [1]. C_1 = methane, C_2 = ethane, C_4 = butane.

Process	Solvent	Solubility of hydrocarbons		
Physical solvents		C_1/CO_2	C_2/CO_2	C_4/CO_2
Rectisol	Methanol	0.12	0.56	4.14
Purisol	N-methyl-2-pyrrolidone	0.07	0.38	3.47
Fluor solvent	Propylene Carbonate	0.04	0.17	1.75
Selexol	Dimethylether of polyethylene glycole	0.07	0.42	2.33
Hybrid solvents				
Sulfinol	Sulfolane + DIPA or MDEA	--	--	--
Amisol	Methanol + secondary alkylamine	--	--	--

Solubilities @ 1 bar, 25˚C.

can be obtained [9].Chemical solvents can meet much tighter product gas specifications and are always top on the list, when lower CO_2 partial pressures are present in the feed gas. In the off-gas, the CO_2 content can be reduced to very low partial pressures (<1 kPa) [9]. However, this comes along with reasonable energy costs for the solvent thermal regeneration. Three contributions account for the total amount of heat that is supplied in the reboiler:

1) Generation of water vapor as stripping steam

2) Desorption of the CO_2 from the solvent

3) Temperature increase of the entering liquid streams (rich solution, reflux) to boiling point conditions

The impact of these contributions on regeneration energy strongly depends on the kind of solvent [10,11]. The influence of the solvent (high or low absorption enthalpy) on the total regeneration energy according to Rochelle is depicted in **Table 3**. A straight forward approach for a low reboiler duty would ask for a low enthalpy of absorption to minimize the regeneration energy. But in terms of an overall process optimization approach (e.g. if additional CO_2 compression is required), a solvent with a high absorption enthalpy allowing for a high temperature and high pressure regeneration might be beneficial because the expensive gas compression at lower pressures is not needed. An interesting study was undertaken by the Rochelle group, but so far, there are no results available that take into account the performance of the power plant and the impact of the steam extraction on a higher exergetic level on the efficiency of the power plant [11,12].

It is not astonishing that this kind of optimization approach is discussed in the field of CO_2 removal from flue gases at power plants because in this special application, a further up-scale of the existing absorption process technology is necessary and several technical challenges come along the way and special attention has to be given to the interaction between absorption process and power plant.

The proper choice of the solvent is a powerful tool for process optimization. Absorbents like sterically hindered or tertiary amines have higher cyclic capacities than primary amines due to the different reaction mechanism. Cyclic capacity of the solvent means the difference in CO_2 loadings after the absorber and the stripper and determines the solvent flow rate in the separation process. Large cyclic capacities allow for lower solvent flow rates and thus reduce the regeneration energy in the stripper and keep the equipment sizes small.

Table 3. Qualitative Comparison of stripper steam requirement for different kinds of chemical solvents [13].

5 M amine	Primary Amine	Sterically hindered or tertiary Amine
Cyclic Capacity	100%	167%
Enthalpy of absorption	100%	60%
Stripping vapor (A)	100%	183%
Desorption of CO_2 (B)	100%	68%
Temperature increase (C)	100%	36%
Total regeneration energy	100%	78%

The simplified overall reaction mechanism is given below and it indicates that primary amines are limited to loadings of 0.5 mol CO_2/mol amine, while sterically hindered amines and tertiary amines absorb 1 mol CO_2/ mol amine if one amine group is present. This mechanism leads to lower solvent flow rates and hence smaller equipment sizes. More detailed descriptions of the reaction phenomena can be found elsewhere: [1,14]

Primary Amines:

$$2R_1\text{-}NH_2 + CO_2 \leftrightarrow R_1\text{-}NH_3 + R_1\text{-}NHCOO\text{-}$$

Sterically hindered and tertiary amines:

$$R_1R_2R_3\text{-}N + CO_2 + H_2O \leftrightarrow R_1R_2R_3\text{-}NH + HCO_3\text{-}$$

If the carbon dioxide is trapped as a carbamate as in primary amines this stronger fixation needs more heat in the reboiler to break up than the weaker bonding in the bicarbonate as can be seen in **Table 3**. The effect in terms of process optimization was impressively realized in syngas application by revamping older monoethanolamine systems with the activated methyldiethanolamine and reducing the heat requirements in the reboiler by the factor of 3.8 [15]. In a similar way sterically hindered amines might benefit for the absorption process as pointed out by Sartori and Savage [16]. In **Table 3**, the tertiary amine solution in the desorber consumes more stripping vapor in relation to the primary amine, but the overall energy requirement is by far less for sterically hindered or tertiary than for primary amines. In this estimation kinetics are not covered and it is not considered that tertiary amines have much slower absorption rates and need to be activated, but it is obvious that the specified chemical solvent plays a major role for process economics because the aforementioned contributions can be optimized.

From **Table 4**, it can be depicted that the amine formulations offer quite different features and it seems that it is nearly impossible to get an overall optimum solvent with fast kinetics, low regeneration energy and minimum solvent flow rate to please the customer’s demand of both low operational expenditure (OPEX) and capital expenditure (CAPEX). Subsequently, lots of different processes and technologies are available (see [1]) that are very often specially designed for certain applications, e.g. individual gas feeds (the content of sulphur compounds) or desired separation tasks (selective H_2S or non selective sour gas removal) [1] and often use special solvent formulations.

Table 4. State-of-the-art chemical absorbents [8]. AEE = Aminoethoxyethanol.

Solvent	Absorption Enthalpy	Regeneration energy	Absorption rates
MEA/prim. amine	85 kJ/mol	High	Fast
AEE/prim. amine	--	High	Fast
DIPA/second. amine	--	Moderate	Moderate
DEA/second. amine	70 kJ/mol	Moderate	Moderate
MDEA/tert. amine	60 kJ/mol	Low	Slow

In the end, the best performance conditions of the process technology are obtained as a trade-off between customer needs and featured solvent properties. Furthermore there are other requirements concerning the targeted favorable solvent properties like low corrosion, low viscosity, and no foaming, high thermal and chemical stability (degradation), low price, high selectivity for CO_2, low vapor pressure, no toxicity and low environmental impact. All these listed solvent properties have to match with the application and contribute to a proper solvent selection.

2.2. Requirements and Challenges

There are different routes for process optimization in terms of a more energy-efficient and more economical technology. An important role plays heat integration (using of latent heat from the reflux condenser, internal heat integration), but the right choice of the solvent is crucial for operational and expenditure costs because the key process parameters are determined by the utilized solvent.

2.2.1. Thermodynamics, Kinetics

On the one hand high loadings at absorber temperature are a prerequisite and many solvents offer a high solubility for CO_2, but at the same time low loadings at stripper temperature are asked for to have a high cyclic capacity. It is the solvent flow rate that contributes first to the investment costs when all sizes and geometries in the plant are fixed and second to the operational costs in terms of electricity demand for pumps and energy input for solvent regeneration. As discussed earlier, these needs favor tertiary or sterically hindered amines. At the same time the higher molar masses of these compounds might limit the higher cyclic capacity on a molar basis. This issue leaves room for molecular optimization/functionalizetion of the targeted molecules to reach the best achievable ratio between CO_2-active groups and the bulk structure of the molecule. Another trade-off has to be found for sufficient absorptions rates together with high cyclic capacities. Tertiary amines give a high cyclic capacity, but show very slow absorption rates. New solvent formulations will have to offer both, a high cyclic capacity and sufficient absorption rates.

2.2.2. Regeneration Energy

As discussed earlier the regeneration energy for absorption fluids is influenced by different contributions related more or less to the solvents properties. The enthalpy of absorption is one important contribution and has to be kept low. In case of amine systems this means that components are favoured that do not directly react with CO_2 to form carbamates, but solve CO_2 as bicarbonates because these reaction mechanism leads to lower regeneration energy demand [17,18].

2.2.3. Make Up and Corrosion Behavior

Absorption plants with standard amines like MEA or DEA suffer from a remarkable make-up demand because of solvent losses due to volatility and unwanted side reactions with CO_2 or oxygen (formation of heat stable salts) [19]. A strong tendency to react with side components also affords for reclaiming of the solvent with additional apparatuses and energy demand and hence should be minimized. Optimized systems with a high chemical stability which are often found with tertiary and hindered amines are advantageous [1].

3. Material and Methods

All experimental data were measured according to standard methods described earlier in the literature and will be only discussed briefly.

Solubility measurements were carried out in stirred gas-liquid equilibrium autoclaves (stainless steel, 0.5 dm3, 0 - 2000 kPa and a Büchi glass reactor, 0.5 dm^3, 0 - 450 kPa). The method was already described by Shen and Li and Dawodu and Meisen [20,21]. The solution (250 ml) was introduced to the evacuated cell and CO_2 was added with a flow meter until a specified pressure was reached. When the pressure was constant for one hour, equilibrium was assumed and liquid samples (1.5 ml) were taken and analyzed by the titration method described by [22]. The partial pressure of CO_2 was calculated by subtraction of the total pressure from the partial pressure of the aqueous amine solution. In case of sub-atmospheric pressure, the concentration of CO_2 in the liquid phase was calculated by means of the read-out of the flow meter and taking into account the gas phase correction (amount of CO_2 in the gas phase when the total volume of the cell and the liquid volume are known). Absorption rates were determined by purging unloaded solution with a defined volume of CO_2 while the liquid and the gas phase were stirred at low stirrer speed. By comparing the slope of the curve from the continuously recorded pressure loss versus time a qualitative absorption rate is obtained.

All experimental procedures were tested with standard systems like monoethanolamine and methyldiethanolamine solutions.

The enthalpy of absorption was measured in a calorimeter as described by [23].

Corrosion rates have been measured by using the standard test method for conducting potentiodynamic polarization resistance measurements as described in ASTM G59-97e1. Steel (1.0402) was used as material in the corrosion tests.

The foaming behavior was measured in terms of Bikerman index (Σ = foam volume/volumetric gas flow [s]). The test cell set-up was already described in [24]. The same amount of every unloaded solvent (700 ml) was used in the test cell and a water saturated nitrogen stream was bubbled through the liquid hold-up using a frit for equal distribution of the gas in the liquid. The resulting height of the foam in the test cell was measured for different gas flows. Before a higher gas flow was specified, the system was allowed to reach a steady state in terms of height of the foam which took 10 to 30 minutes.

The materials employed were CO_2 (Air Liquide, 0.9998 purity in mole fraction), deionised distilled water. The used amine compounds were introduced in [25] and [26] and were utilized in the experiments as aqueous solutions. The exact chemistry of the Evonik absorbents will be published in an amendment of Advances in Chemical Engineering and Science after the patents have been granted.

4. Results

The following presents selected experimental data for a novel and highly competitive solvent system that could overcome several limitations of the aforementioned state-of-the-art systems. **Table 5** show experimental solubility data for a new Evonik absorbent formulation and compared to state-of-the-art solvents like aqueous solutions of MEA and MDEA. The Evonik absorbent offers a cyclic capacity which is twice as high as for MEA. Therefore, the solvent flow rate in the Evonik system can be drastically reduced.

Table 5. Results for cyclic capacities of state-of-the-art and new Evonik absorbents. The cyclic capacity is given for isotherms between 40˚C and 120˚C at 1 bar. MEA = 30 wt% aqueous solution, Promoted MDEA = 3 wt% piperazine and 37 wt% MDEA, Evonik absorbents = 30 wt% aqueous solution.

Absorbent	Cyclic capacity [mol CO_2/kg absorbent]	Source
MEA	1.2	[22]
Promoted MDEA	2.3	Pitzer model
Evonik absorbent 1	2.4	This work
Evonik absorbent 2	2.6	

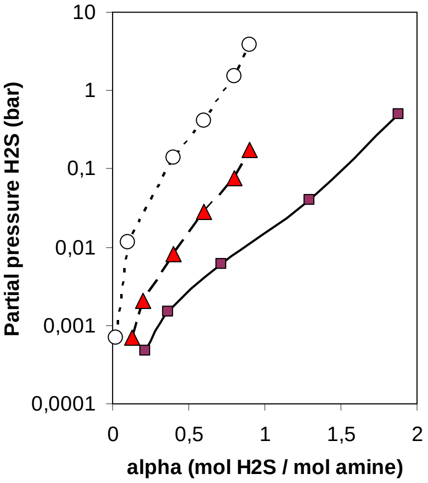

Figure 1. Absorption isotherms of H_2S in different absorbents at 40˚C. The data of the Evonik absorbent 2 (■) is given for 30 wt% solution in water. MDEA (o) and Flexsorb SE™ (▲) are taken from [28] (2.5 molar amine solution).

At the same time other sour gases like H_2S show significant high loadings in the Evonik absorbent, especially compared to state-of-the-art absorbents like MDEA or Flexsorb® SE, as depicted in **Figure 1**. Even at low partial pressures of H_2S, the Evonik absorbent will achieve remarkably high loadings up to 10 times higher than those of MDEA. As is known, the acid base reaction between H_2S and an amine is much faster than reactions of CO_2 with amines (either carbamate formation or the acid base reaction), it is expected that the absorbent for mulation will also be of great interest to selectively remove H_2S with a high CO_2 slip and supply enriched sour gases to sulfur recovery units. Further field test investigations on absorption rates and the obtainable CO_2 slip are ongoing.

As in absorption processes, the solvent in the absorber never reaches equilibrium conditions the processes are kinetically limited. Therefore, absorption rates play a significant role, too and have to be considered. As mentioned above, for example, MDEA can not compete with MEA without further activation. Because of the slower absorption rates, inactivated MDEA would not reach the high loadings in the absorber and could not utilize its high cyclic capacity [29,30].

Based on the experimental results for the kinetic performance, the following order can be derived for the CO_2-absorption rates: MEA (100%) > Evonik absorbent (85%) > MDEA (6%). As can be seen from the absorption results and the kinetic performance, the Evonik absorbent offers a unique opportunity to combine good kinetics with superior cyclic capacity.

The lower enthalpy of absorption is one major advantage of MDEA that helped to replace MEA in many gas sweetening applications. The heat of reaction, the physical enthalpy of solution and the excess enthalpy of mixing contribute to the enthalpy of absorption. As discussed above this represents a major part of the regeneration energy that has to be supplied in the stripper. From **Table 6** it can be seen that the Evonik absorbent has a considerable lower enthalpy of absorption compared to state-of-the-art solvents. This results in further energy savings in the regeneration of the solvent and makes the Evonik absorbent a highly energy-efficient and highly economically attractive alternative to state-of-the-art solvents like MEA and MDEA.

The solvent has to fulfill additional requirements as outlined above in order to lower the operational expenditure of a separation plant. For example one important point is corrosion, which is still a serious issue for absorption plants. The corrosion potential of the Evonik absorbents is much lower compared to uninhibited MEA—by the factor of 7—and compared to Piperazine and MDEA mixtures by a factor of 3.4 (see **Table 7**). The experiments utilized common carbon steel (1.0402) for plant construction to demonstrate the comparatively low corrosion rates.

As a result additional degrees of freedom from the choice of different materials for constructing the plant and the chosen corrosion inhibitor allowing for a reduction in both, capital and operational expenditure.

In order to determine the tendency of foaming of the new absorbent formulation, the Bikerman index was calculated according to the experimental procedure described above. The lower the number of the Bikerman index, the less is the foaming height of the system and hence the foaming tendency. **Figure 2** plots the Bikerman index for a promoted MDEA (10 wt% Evonik promoter and 20 wt% MDEA) and the Evonik absorbent 2 versus the gas flow rate. It can be concluded that even at higher gas flow rates the Evonik absorbent 2 did not show any tendency to foam which results in a Bikerman index of zero. MDEA is known to cause frequent foaming problems in gas sweetening plants and thus indicates a high number for the Bikerman index (approx. 14.5). From various reports in the literature it is well known, that the solution tends to foam, especially at high concentrations of MDEA [1,32,33]. Our field tests confirmed that the Evonik absorbent shows no foaming tendency, whereas promoted and pure MDEA solutions tended to foaming and needed an anti-foaming agent. Although foaming is a complex matter and basically influenced by various solution contaminants (water-soluble surfactants, liquid hydrocarbons, particles, heat stable salts and a host of others) these encouraging results indicate that a common problem of gas treating units might become less of an issue with this new high performance absorbents.

Table 6. Results of the enthalpy of absorption for CO_2 in different absorbents at 40˚C.

Solvent	Enthalpy of absorption [kJ/mol]	Source
MEA (30 wt%)	–85	[31]
MDEA (50 wt%)	–65	[27]
Evonik absorbent 1 (30 wt%)	–30	This work
Evonik absorbent 2 (30 wt%)	--	

Table 7. Corrosion test results from the Potentiodynamic Polarization Resistance Measurements with CO_2-saturated solutions at 25˚C for typical carbon steel (1.0402).

Solvent	Corrosion rate [mm/year]
MEA (30 wt%)	1.99
MDEA (27.9 wt%) + piperazine (2.1 wt%)	0.99
MDEA (37.2 wt%) + piperazine (2.8 wt%)	1.18
Evonik absorbent 1	0.21
Evonik absorbent 2	0.29

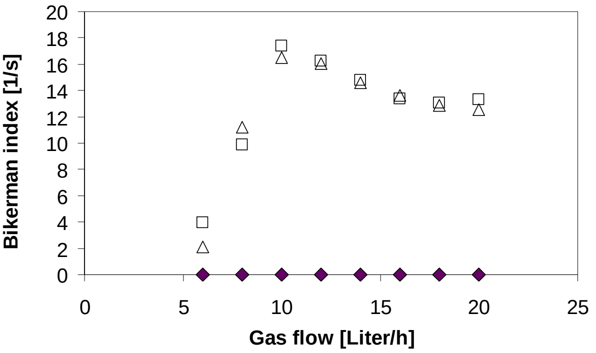

Figure 2. Foaming tendency of a promoted MDEA solution (10 wt% Evonik promoter and 20 wt% MDEA) (□, Δ) and of Evonik absorbent 2 (◆) without anti foaming agent. The Bikerman index is plotted versus the gas flow rate for different test runs at 40˚C.

In the following, results from an estimated process performance of the Evonik absorbent are derived based on the approach recently introduced by [34]. By means of a modified Kremser equation the absorber and the desorber are described and calculated on a simplified equilibrium stage model that uses isotherms at absorber and desorber temperature and caloric data (heat capacity, absorption enthalpy). The model predicts the minimum reboiler energy at an optimum solvent flow rate for given boundary conditions. The kinetics of absorption are not considered and a sufficient number of equilibrium stages is assumed. The calculation is based on a simplified absorber/desorber flow sheet without a flash, but with internal heat exchanger as illustrated by **Figure 3**.

The feed gas enters the absorber at the bottom, and the lean solvent is fed at the top of the absorber, where the treated gas leaves the column with its CO_2 content reduced.

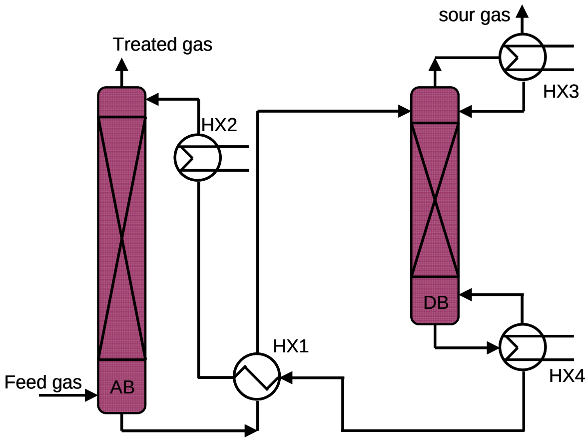

Figure 3. Simplified process scheme for sour gas absorption utilized for the Kremser method. (AB = Absorber; DB = Desorber; HX_1 = Internal heat exchanger; HX_2 = Absorbent cooler; HX_3 = Condenser; HX_4 = Reboiler).

The rich absorbent at absorber bottom is internally preheated and enters the desorber at the top. The reboiler at the bottom supplies the necessary heat for regeneration which consists of parts for desorption enthalpy, stripping steam, heating of the solvent and heating of the condensate reflux. The boundary conditions for the calculations are given in **Table 8**. **Table 9** depicts the necessary caloric data.

Calculations were performed for a natural gas and a syngas feed (see **Table 10**). As reference system, a mixture of piperazine (10 wt%) and MDEA (30 wt%) was chosen for a comparison with the Evonik absorbent (30 wt%).

In both cases, for natural and for syngas purification, a 90% CO_2 removal was specified to obtain an energetic comparison between the two absorbent systems in terms of specific reboiler duty.

In **Figures 4** and **5**, the specific reboiler duty (GJ/t CO_2 separated) is plotted against the corresponding absorbent flow rate to achieve 90% CO_2 separation. It can be concluded that in the case of the Evonik absorbent 2, the flow rate can be reduced to 74% (syngas) and 84% (natural gas) compared to the reference system. The specific reboiler duty even decreases to 80% (both cases) for the Evonik absorbent 2 achieving huge savings's in the reboiler's steam consumption which directly translates into lower operational expenditures. For the calculation of the natural gas purification, the Evonik absorbent 1 also offers a 16% reduction in absorbent flow rate and a drastic decrease of the specific reboiler duty which amounts to 55% compared to the reference absorbent. For all calculations the superior thermodynamic properties like large cyclic capacities and lower enthalpies of absorption allow for distinctive improvements in terms of an energy efficient process.

Table 8. Boundary conditions for the calculation.

Parameter	Value
CO_2 separation degree	90%
Absorber inlet temperature	40˚C
Desorber inlet temperature	110˚C
Desorber pressure	2 bar
Desorber bottom temperature	120˚C
Equilibrium stages absorber	10
Equilibrium stages desorber	15

Table 9. Caloric data for the calculations for the 10 wt% Piperazine and 30 wt% MDEA mixture and the 30 wt% Evonik absorbent. *Since no heat capacity data was available neither for the piperazine and MDEA mixture nor for the Evonik absorbent, the estimated data from [34] was applied. **The value was taken from [35] and estimated for 110˚C.

Caloric data	Value
Enthalpy of evaporation of water	2210.6 kJ/kg
Heat capacity of water	4.197 kJ/kgK*
Absorption Enthalpy of 10 wt% Piperazine and 30 wt% MDEA at 110 ˚C	2236 kJ/kg**
Absorption Enthalpy of 30 wt% Evonik absorbent 1 at 110 ˚C	811.2 kJ/kg
Absorption Enthalpy of 30 wt% Evonik absorbent 2 at 110 ˚C	1817.5 kJ/kg
Heat capacity of all absorbents	4.048 kJ/kgK*

Table 10. Natural gas and syngas feed utilized in the calculations.

Natural gas feed	Syngas feed
15 mol-% CO_2	17 mol-% CO_2
1 mol-% H_2O	0.3 mol-% CO
5 mol-% N_2	60 mol-% H_2
79 mol-% CH_4	22 mol-% N_2
	0.5 mol-% CH_4
	0.2 mol-% Ar
Total pressure = 10 bar	Total pressure = 36 bar

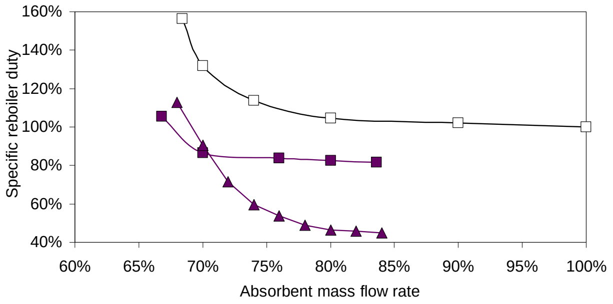

Figure 4. Results from calculation of modified Kremser equations for a 90% CO_2-separation from a natural gas feed. The specific reboiler duty is plotted against the solvent flow rate for a mixture of piperazine (10 wt%) and MDEA (30 wt%) (□) and Evonik absorbent 1 (30 wt%) (▲) and for the Evonik absorbent 2 (30 wt%) (■). 100% equals 2.68 GJ/t CO_2.

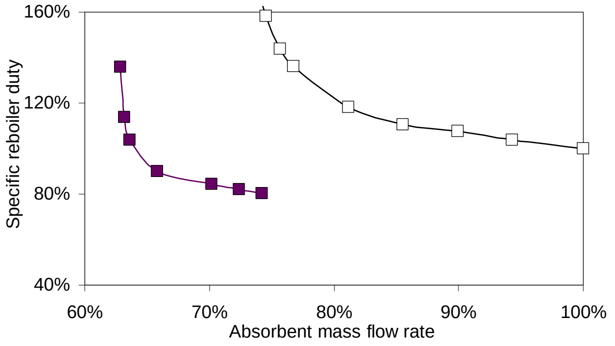

Figure 5. Results from calculation of modified Kremser equations for a 90% CO_2-separation from a syngas feed. The specific reboiler duty is plotted against the solvent flow rate for a mixture of piperazine (10 wt%) and MDEA (30 wt%) (☐) and for Evonik absorbent 2 (30 wt%) (■). 100% equals 2.60 GJ/t CO_2.

5. Conclusions

Recent industrial activities have led to the development of new high-performance CO_2 scrubbing agents that can be employed in industrial CO_2 separation processes such as natural gas treatment, purification of syngas and the scrubbing of flue gas. The Evonik absorbents fulfill several important prerequisites for a substantial improvement of state-of-the-art absorption processes such as those using solvents like MEA and MDEA. Larger cyclic capacities and a lower enthalpy of absorption as well as a drastically lower tendency of corrosion and foaming are crucial key features of the Evonik absorbents resulting in a lower regeneration energy demand of the separation process and lower maintenance costs. In addition, sour gases like H_2S show significantly higher loadings in the Evonik absorbents, especially compared to MDEA or other commercially available specialty amines. Even at low partial pressures of H_2S, the Evonik absorbents achieve remarkably high loadings of up to 10 times higher than those of MDEA.

Thus, Evonik's novel high-performance system solutions for CO_2 separation meet the latest industrial absorbent requirements and allow for substantial savings in operational and capital expenditure [36].

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7. References

[1] A. L. Kohl and R. B. Nielsen, “Gas Purification,” 4th Edition, Gulf Publishing, Houston, 1997.

[2] C. M. White, B. R. Strazisar, E. J. Granite, J. S. Hoffman and H. W. Pennline, “Separation and Capture of CO_2 from large Stationary Sources and Sequestration in Geological Formations,” *Journal of the Air & Waste Management Association*, Vol. 53, No. 6, 2003, pp. 645-715.

[3] M. Ramezan, N. Nsakala, G. N. Liljedahl, L. E. Gearhart, R. Hestermann and B. Rederstorff, “Carbon Dioxide Capture from Existing Coal Fired Power Plants,” DOE/NETL-401/120106, National Energy Technology Laboratory, 2006.

[4] D. Aaron and C. Tsouris, “Separation of CO_2 from Flue Gas: A Review,” *Separation Science and Technology*, Vol. 40, No. 1, 2005, pp. 321-348. doi:10.1081/SS-200042244

[5] O. Davidson, H. C. de Coninck, M. Loos and L. A. Meyer, Eds., “IPCC Special Report on Carbon Dioxide Capture and Storage,” Cambridge University Working Group III of the Intergovernmental Panel on Climate Change Press, Cambridge, New York, 2005.

[6] J. Van Straelen, F. Geuzebroek, N. Goodchild, G. Protopapas and L. Mahony, “CO_2 Capture for Refineries, a Practical Approach,” *International Journal of Greenhouse Gas Control*, Vol. 4, No. 1, 2010, pp. 316-320. doi:10.1016/j.ijggc.2009.09.022

[7] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, “Advances in CO_2 Capture Technology—The U.S. Department of Energy's Carbon Sequestration Program,” *International Journal of Greenhouse Gas Control*, Vol. 2, No. 1, 2008, pp. 9-20. doi:10.1016/S1750-5836(07)00094-1

[8] J. Seagraves, M. Quinlan and J. Corley, “Fundamentals of Gas Treating,” Laurance Reid Gas Conditioning Conference (LRGCC), 2010.

[9] R. N. Tennyson and R. P. Schaaf, “Guidelines Can Help Choose Proper Processes for Gas Treating Plants,” *Oil & Gas Journal*, Vol. 10, No. 1, 1977, pp. 78-86.

[10] B. T. Oyenekan and G. T. Rochelle, “Energy Performance of Stripper Configurations for CO_2 Capture by Aqueous Amines,” *Industrial & Engineering Chemistry Resarch*, Vol. 45, No. 1, 2006, pp. 2457-2464. doi:10.1021/ie050548k

[11] J. Oexmann and A. Kather, “Minimising the Regeneration Heat Duty of Post-Combustion CO_2 Capture by Wet Chemical Absorption: The Misguided Focus on Low Heat of Absorptions Solvents.” *International Journal of Greenhouse Gas Control*, Vol. 4, No. 1, 2010, pp. 36-43. doi:10.1016/j.ijggc.2009.09.010

[12] B. A. Oyenekan and G. T. Rochelle, “Alternative Stripper Configurations for CO_2 Capture by Aqueous Amines,” *AIChE Journal*, Vol. 53, No. 1, 2007, pp. 3144-3154. doi:10.1002/aic.11316

[13] G. T. Rochelle, “CO_2 Capture by Aqueous Absorption/ Stripping Opportunities for Better Technology,” Workshop on Carbon Sequestration Science, Washington, D.C., 2001.

[14] P. V. Danckwerts, “Gas-Liquid Reactions,” McGraw-Hill, New York, 1970.

[15] Wiley-VCH and LASTWiley-VCH, “Ullmann's Agro-

chemicals," Vol. 1, Wiley-VCH, Weinheim, 2007.

[16] G. Sartori and D. W. Savage, "Sterically Hindered Amines for CO_2 Removal from Gases," *Industrial & Engineering Chemistry Fundamentals*, Vol. 22, No. 1, 1983, pp. 239-249. doi:10.1021/i100010a016

[17] J.-Y. Park, S. J. Yoon and H. Lee, "Effect of Steric Hindrance on Carbon Dioxide Absorption into New Amine Solutions: Thermodynamic and Spectroscopic Verification through Solubility and NMR Analysis," *Environmental Science & Technology*, Vol. 37, No. 1, 2003, pp. 1670-1675. doi:10.1021/es0260519

[18] F. Bougie and M. C. Iliuta, "Analysis of Regeneration of Sterically Hindered Alkanolamines Aqueous Solutions with and without Activator," *Chemical Engineering Science*, Vol. 65, No. 1, 2010, pp. 4746-4750. doi:10.1016/j.ces.2010.05.021

[19] R. G. F. Albry and M. S. DuPart, "Amine Plant Trouble-Shooting and Optimization," Gulf Publishing Co., Houston, April 1995, pp. 3-11.

[20] K. P. Shen and M.-H. Li, "Solubility of CO_2 in Aqueous Mixtures of Monoethanolamine with Methyldiethanolamine," *Journal of Chemical Engineering Data*, Vol. 37, No. 1, 1992, pp. 96-100. doi:10.1021/je00005a025

[21] O. F. Dawodu and A. Meisen, "Solubility of Carbon Dioxide in Aqueous Mixtures of Alkanoamines," *Journal of Chemical Engineering Data*, Vol. 39, No. 1, 1994, pp. 548-552. doi:10.1021/je00015a034

[22] F.-Y. Jou, A. E. Mather and F. E. Otto, "The Solubility of CO_2 in a 30 Mass Percent Monoethanolamine Solution," *Canadian Journal of Chemical Engineering*, Vol. 73, No. 1, 1995, pp.140-145. doi:10.1002/cjce.5450730116

[23] J. Gmehling, "Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters," *Journal of Chemical Engineering Data*, Vol. 38, No. 1, 1993, pp. 143-146. doi:10.1021/je00009a036

[24] G. Senger and G. Wozny, "Experimentelle Untersuchung von Schaum in Packungskolonnen," *Chemie Ingenieur Technik*, Vol. 83, No. 4, 2011, pp. 503-510. doi:10.1002/cite.201000210

[25] M. Seiler and J. Rolker, "Verfahren, Absorptionsmedien und Vorrichtung zur Absorption von CO_2 aus Gasmischungen," Evonik Degussa, PCT/EP 2010/051083, 2010.

[26] M. Seiler and J. Rolker, "Verfahren zur Absorption von sauren Gasen aus Gasgemischen," Evonik Degussa, 2010, DE 102010043838.3.

[27] F.-Y. Jou, A. E. Mather and F. E. Otto, "Solubility of H_2S and CO_2 in Aqueous Methyldiethanolamine Solutions," *Industrial Engineering Chemistry Process Design and Development*, Vol. 21, No. 1, 1982, pp. 539-544. doi:10.1021/i200019a001

[28] T. R. Aikins, L. E. Parks, J. N. Iyengar, R. B. Fedich and D. Perry, "Sterically Hindered Amines-Thirty Years of Gas Treating Practice," *Annual Laurance Reid Gas Conditioning Conference*, Norman, 20-23 February 2011.

[29] G. W. Xu, C.-F. Zhang, S.-J. Qin and Y.-W. Wang, "Kinetics Study on Absorption of Carbon Dioxide into Solutions of Activated Methyldiethanolamine," *Industrial & Engineering Chemistry Resesrch*, Vol. 31, No. 1, 1992, pp. 921-927. doi:10.1021/ie00003a038

[30] P. W. J. Derks, "Carbon Dioxide Absorption in Piperazine Activated n-Methyldiethanolamine," Ph.D. Thesis, University of Twente, Nederland, 2006.

[31] F.-Y. Jou, F.-E. Otto and A. E. Mather, "Vapor-Liquid Equlibrium of Carbon Dioxide in Aqueous Mixtures of Monoethanolamine and Methyldiethanolamine," *Industrial & Engineering Chemistry Resesrch*, Vol. 33, No. 1, 1994, pp. 2002-2005. doi:10.1021/ie00032a016

[32] J. Seagraves and R. H. Weiland, "Treating High CO_2 Gases with MDEA," *Petroleum Technology Quarterly GAS*, 2009, pp. 103-109.

[33] J. A. Bullin, J. C. Polasek and S. T. Donnelly, "The Use of MDEA and Mixtures of Amines for Bulk CO_2 Removal," Bryan Research & Engineering, Inc., 2006. http://www.bre.com

[34] R. Notz, I. Tönnies, H. P. Mangalapally, S. Hoch and H. Hasse, "A Short-Cutmethod for Assessing Absorbents for Post-Combustion Carbon Dioxide Capture," *International Journal of Greenhouse Gas Control*, Vol. 5, No. 3, 2010, pp. 413-421. doi:10.1016/j.ijggc.2010.03.008

[35] B. Schäfer, A. E. Mather and K. N. Marsh, "Enthalpies of Solution of Carbon Dioxide in Mixed Solvents," *Fluid Phase Equilibria*, Vol. 194-197, 2002, pp. 929-935. doi:10.1016/S0378-3812(01)00722-1

[36] J. Rolker and M. Seiler, "Elements 37," *Quaterly Science Newsletter*, Vol. 4, 2011.