IBP0963_17

AN ALTERNATIVE PROCESS FOR CO_2 SEPARATION BY IL BASED CHEMICAL ABSORPTION

F. Ortloff[12], M. Roschitz[1], F. Graf[1], T. Kolb[12]

Abstract

The major disadvantage of state-of-the-art processes for CO_2 separation by chemical absorption (Kohl, 1997; Stolten, 2011) from e.g. biogas or flue gas streams is the high thermal energy demand for CO_2 desorption. Industrial and scientific R&D therefore focus on developing new solvent systems. Examples of some recent improvements in industrial scale are aMDEA (MDEA+PZ), aqueous amino acids and the chilled ammonia process (Darde, 2011).

Applying ionic liquids (IL) for the removal of CO_2 from gas streams is discussed in science ever since the class of substances gained public attention in early 21st century (Wasserscheid, 2008; Welton, 2002). But due to several weaknesses, such as high viscosity, slow mass transfer, high prices etc. they have not yet reached a breakthrough.

The CO_2 separation process proposed by DVGW-EBI focusses on a different approach: Not only on improving the solvents but adapting the separation process itself for exploiting the mayor advantages of ionic liquids (the negligible vapor pressure) and compensating for their disadvantages (the high viscosity). This is done by adjusting the operating temperatures of the absorption and the regeneration units to the same temperature level of approximately 80 °C. Thus, the change of operating concept is associated with the benefit that the thermal energy for regeneration of the solvent does not have to be supplied from an external source. Nevertheless, a driving force for the regeneration of the solvent is mandatory. Desorption of CO_2 is therefore carried out by a reduction of CO_2 partial pressure by applying a moderate vacuum to the regeneration unit, which can only be done when ionic liquids are applied as solvents.

With the proposed operating concept, the major disadvantages of IL can be largely overcome. Therefore several mixtures of non-functionalized IL (Room Temperature Ionic Liquids; RTIL) and functionalized IL (Task Specific Ionic Liquids; TSIL) were tested for being applied in the new separation process. Important characteristics of the solvent system, such as thermal stability, chemical absorption capacity, rate of absorption, heat of reaction and mixture ratio of the RTIL and TSIL were evaluated. For the proof-of-concept of the general operating and design concept and to validate the experimental data from the lab tests, a mini plant was built and some of the most promising mixtures of RTIL and TSIL are currently under examination.

CO_2 separation with Monoethanolamine (MEA) causes an energy demand of approximately 3 - 3.5 GJ/t CO_2 (small/medium scale) and costs in range of 40 - 60 EUR/t CO_2 (Stolten, 2011). Costs for CO_2 separation for industrial applications can be even higher. Pre-assessment of the performance of the proposed CO_2 separation process with IL resulted in a reduction of the energy demand to a level of about 1.3 - 1.6 GJ/t CO_2. Do to the large savings in OPEX, the higher solvent costs for IL are compensated and the proposed process is economic feasible within short to medium payback periods.

1. Introduction

Even if the political situation today is more uncertain than it was before the elections in the U.S., COP21 has proven that willingness for change does exist in the world. In short to mid-term, substitution of coal & oil based power & fuel production by natural gas can help to reduce the global CO_2 emissions. Nevertheless, the gas industry will have to go one step further and face the truth that natural gas is also a fossil fuel that contributes to GHG emissions. If we do not want to risk the 2 °C global warming goal, we may not emit more than additional 1,000 Gt of CO_2 (based on 2011) – of which we have again already spent a large share up to the present day (IPCC, 2014).

Chemical Engineers[1,2]
DVGW Research center at Engler-Bunte-Institute (DVGW-EBI), Karlsruhe, Germany[1]
Engler-Bunte-Institute (EBI), Fuel Technology Division, KIT, Karlsruhe, Germany[2]

Today, widespread "decarbonization" and "electrification" strategies across the world do not draw a gas friendly future perspective. Consequently, the gas industry has to widen its scope and think about how their contribution to climate and environment protection beyond short term GHG emissions reduction can look like.

Will carbon based energy carriers lose their right to exist in future? – No, in large parts of the world, there will always be a certain demand for carbon based mobility fuels, e.g. for air traffic or heavy duty road transport or for wind/PV backup. Besides, natural gas today plays an important role in the heating sector – and many existing urban buildings cannot be equipped with heat pumps etc. So the race for these applications is now open and the gas industry should put strong efforts in increasing the share of renewable gases in order to be able to cope with the future demands of an environmentally friendly (gas based) energy supply.

This can either be done by using biomass as a feedstock, e.g. as in biogas production or SNG production via biomass gasification, or via the PtG (power to gas) route for the production of hydrogen or methane from renewable electricity (Götz, 2015). The use of biomass suffers limited feedstock availability but the PtG route has the potential to overcome these limitations by coupling in CO_2 from various sources. These could be either from biogas or from others with a rather high CO_2 concentration, preferably from sources which will be present mandatorily in future, e.g. from chemical industry, cement industry etc. and at the end even directly from air.

For any of these CO_2 sources, appropriate processes for CO_2 removal are necessary. The CO_2 separation process proposed by DVGW-EBI (see Figure 1) focusses on a special approach for small and medium scale applications. A conventional chemical scrubbing system forms the basis of the DVGW-EBI process but it is adapted and optimized to meet the future requirements (low energy demand but driven by electricity).

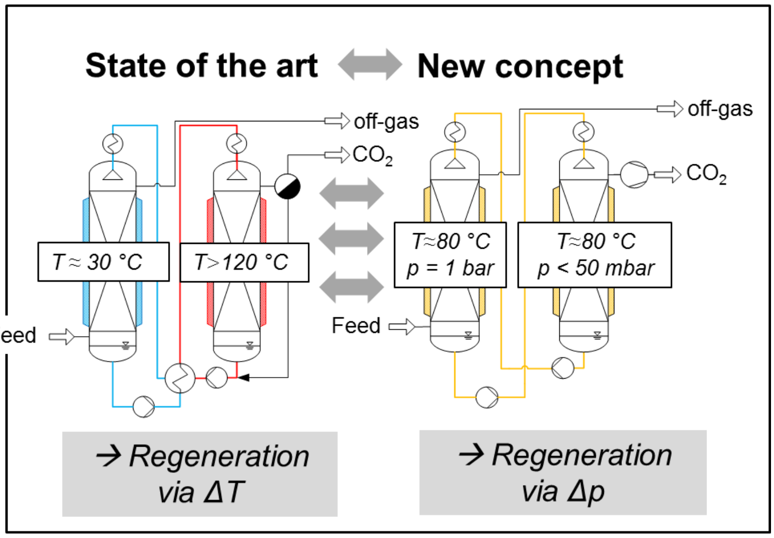


Figure 1. DVGW-EBI CO_2 separation concept: "isothermal chemical absorption"

The proposed process is characterized by an adjustment of the operating temperatures of the absorption and the regeneration units to the same temperature level of approximately 80 °C. By doing so the thermal energy for regeneration of the solvent does not have to be supplied from an external source. Instead, the energy is taken directly from the liquid enthalpy (the exothermal absorption heats up the liquid and compensates the energy demand of the endothermal desorption). Nevertheless, a driving force for the regeneration of the solvent is mandatory. Desorption of CO_2 is therefore carried out by a reduction of CO_2 partial pressure by applying a moderate vacuum to the regeneration unit, which can only be done, when ionic liquids are applied as solvents, as they feature a negligible vapor pressure at the desired operating temperature range.

Due to several weaknesses, such as high viscosity, slow mass transfer, high prices etc. ionic liquids have not yet reached a breakthrough in chemical industry. Even though there are some applications present, e.g. mercury removal (by Petronas), liquid piston in hydraulic hydrogen compression (Linde), acid scavenging (BASF), as electrolytes in advanced battery concepts (FluidicEnergy) or as solvents and catalysts (e.g. PetroChina, Honeywell, etc.). ILs have not yet been successfully applied in conventional gas scrubbing. Even though ionic liquids have often been proposed for CCS etc. in fairly all examined cases, conventional operating concept was applied. Even if the physico-chemical properties of IL are tuneable in a certain range, it is hardly possible to reduce the heat of absorption of CO_2 with IL to a level which offers an economic feasible process with the state of the art setup.

Even though the new concept might not be applied to large scale applications due to the use of vacuum equipment, the present approach is promising in terms of energetic savings, closely linked to significant reductions in OPEX.

2. Process development at Engler-Bunte-Institut

The proposed IL based absorption process has been examined within nationally funded research projects up to now for approximately three years. Together with partners from academia and industry, the starting point of the process development work was the search for an appropriate solvent system. Due to the high viscosity of chemically functionalized ionic liquids – their viscosity even sharply increases during CO_2 absorption – it was decided from the very beginning that the IL solvent would be a mixture of TSIL and RTIL. In the desired solvent system the TSIL captures the CO_2 from the gas stream chemically, the RTILs´ primary objective within the mixture is to reduce the solvent systems viscosity.

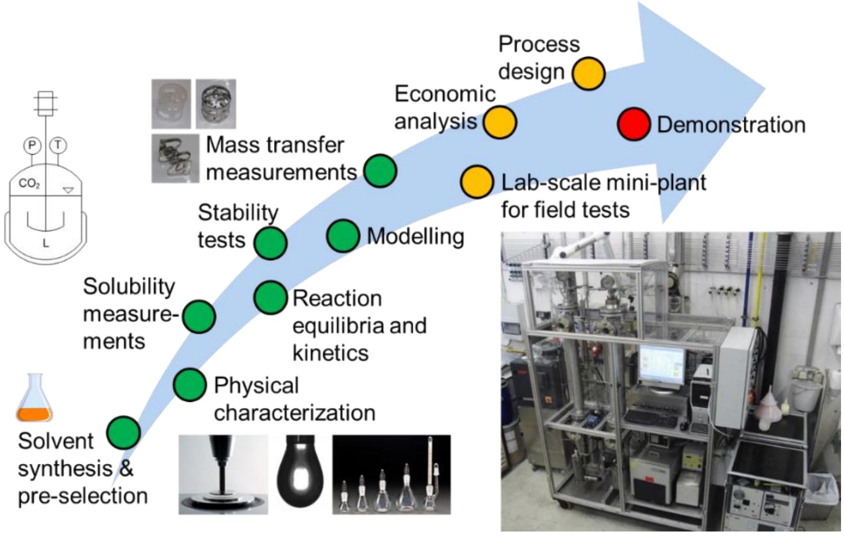
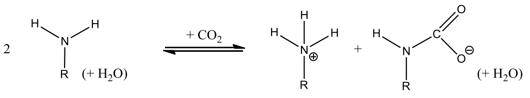
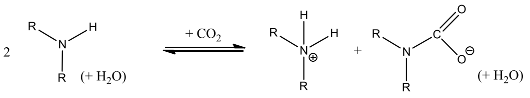
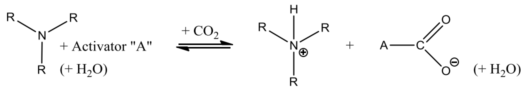


Figure 2. Progress in the development of the CO_2 separation process based on isothermal chemical absorption with IL

The corresponding TSIL were restricted to anion functionalization with amine groups, selected according to conventional primary, secondary and tertiary amine systems (see Table 1), and synthesized in our lab. As the tertiary amine can only act as proton acceptor, piperazine was added to the conventional solvent system as well as to the TSIL system. In general, the absorption kinetics and heat of reaction decrease from primary to tertiary amine, while CO_2 capacity and thermal stability increase. Any of the undertaken measurements were conducted with the TSIL/RTIL systems, but for direct comparison also with the conventional amines.

Table 1. Common amines for CO_2 absorption and corresponding task specific ionic liquids (TSIL) with amine functionalization of the ILs´ anions

Common amines	e.g.	Characteristics				Reaction equation	IL
Primary	MEA	reaction kinetics ↑	heat of reaction ↑	CO_2 capacity ↓	thermal stability ↓		$[K^+]$[Ala]
Secondary	DEA						$[K^+]$[Pro]
Tertiary	MDEA (+PZ)						$[K^+]$[Gly][1] + PZ

Besides synthesis and basic physico-chemical characterization of the solvent systems solubility measurements (physical and chemical CO_2 uptake), reaction kinetics, chemical and thermal stability tests of the TSIL, mass transfer measurements in common absorption equipment were carried out. Any data as well as the developed and validated models of sub-processes have then been implemented into a general model of the absorption process. A validation of this model, based on the acquired data from our lab scale absorption mini-plant is currently in progress. A first economic analysis of the process has been conducted. The results are presented in section 3 of this article.

---

[1] [Gly] = N,N-Dimethylgylcinate

2.1. CO_2 uptake

When chemical absorption takes place the chemical loading capacity of CO_2 (B_{ij}, see eq. 1) in the solvent is typically dominated by the stoichiometry of the chemical reaction. Methane is chemically inert, only CO_2 is able to participate in the chemical reaction.

$$B_{ij}(T) = \frac{N_i}{N_{amine\ groups\ in\ the\ solvent\ j}} \qquad \text{eq. 1}$$

Figure 3 shows a comparison of experimental solubility results of common aqueous amine solutions (all 30 wt% in water) at 30 °C vs. 10 wt% TSIL in [BDiMIM][BTA] at 80 °C. As expected, conventional solvents show an increase of solubility from primary to tertiary amines (see Table 1). Any of the applied conventional amines show a higher CO_2 capacity B_{CO2} than 0.5 as the general eq. 2 of the reaction of CO_2 with primary and secondary amines allows:

$$2\,R - NH_2 + CO_2 \rightleftharpoons R - NH_3^+ + R - NH - COO^- \qquad \text{eq. 2}$$

This is induced by water participating in the reaction when high CO_2 partial pressures are applied: When R-NH-COO$^-$ concentration reaches the value of 0.5 certain amounts of HCO_3^- are reversely formed from the carbamate, with R-NH_2 again acting as base for CO_2 uptake (via H_3O^+ neutralization).

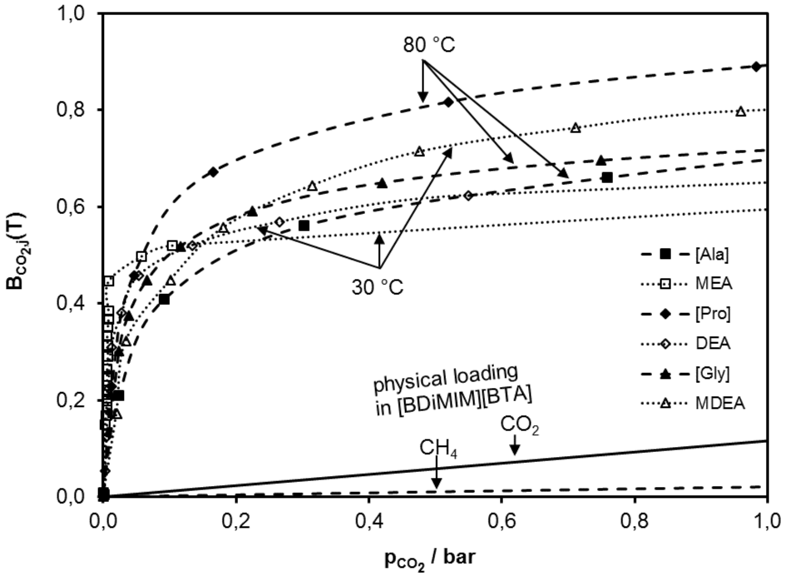


Figure 3. CO_2 solubility in common aqueous amines at T = 30°C (30 wt%: MEA, DEA, MDEA), in the corresponding primary ([Ala]), secondary ([Pro]) and tertiary TSIL ([Gly]+PZ in a ratio of 2:1) with 10 wt% of TSIL in [BDiMIM][BTA] and the physical solubility of CO_2 and CH_4 in [BDiMIM][BTA] at T = 80 °C

In contrast to conventional amine solutions the TSIL are applied as dry mixtures with RTIL. A maximum capacity of 0.5 is expected (similar to eq. 2) in absence of water for the primary and secondary amino-acid based anions alaninate [Ala] and prolinate [Pro]. Nevertheless, it is already known from literature and also observed in the experiments in this work, that higher CO_2 loadings, close to or even higher than 1 mole CO_2 per mole of amine-functionalized anion are possible with the applied TSIL. Chemical complexation of protons in the solvent is the reason for this evidence.

Figure 3 further shows that the CO_2 capacity increases from primary [Ala] to secondary [Pro] amino acid based anions. The primary and secondary amino acid based anions are able to capture CO_2 directly via carbamate formation. The dimethylglycinate (= [Gly]) anion can only act as proton acceptor (see Table 1). CO_2 fixation must take place elsewhere. Therefore, (in absence of any water) piperazine (a cyclical bi functionalized secondary amine) was added to the solvent system, which is able to form the carbamate when reacting with CO_2. The residual CO_2 capacity of the dimethylglycinate based TSIL is in the same range (or even lower) as for the alalinate IL. Applying tertiary amines in dry IL systems therefore provides no additional benefit. As the piperazine dissolution in the examined dimethylgylcinate based IL mixture is inadequate, the prolinate based IL was chosen as best option for the specified task out of the tested IL and therefore further characterized.

For comparison reasons, the physical solubility of the applied RTIL [BDiMIM][BTA] was added to Figure 3. As can be seen, the chemical solubility of CO_2 at p_{CO2} = 0.5 bar is 14 times larger than the physical solubility. Furthermore the selectivity of dissolved CO_2 (chemically and physically) to dissolved CH_4 is in the range of 100, which is comparably low for chemical solvents but can be further optimized by increasing the concentration of TSIL in the mixture or by substituting [BDiMIM][BTA] by an RTIL with a lower methane solubility, e.g. by a [TCM] anion based RTIL.

2.2. Absorption kinetics

As it is known from the literature, low temperatures are crucial for the performance of ionic liquids due to their elevated viscosity. Therefore, measurements on absorption kinetics have been carried out in a lab scale autoclave. The RTIL [BDiMIM][BTA] features a viscosity of 25 x 10^{-3} Pas at 60 °C, which is 23 times higher than the aqueous MEA system. But still, the [Ala] based mixture shows equal effective absorption performance than the aqueous DEA solvent, the [Pro] based IL is only slightly slower (see Figure 4). This indicates that the examined IL based solvents feature a relatively good mass transfer performance, which is fast enough to apply the tested IL to CO_2 separation in technical scale. The experiment further indicates that the size of the necessary mass transfer columns will probably be in the same order of magnitude for the IL based solvents in the optimized separation process operated at approximately 60 - 80 °C as for the conventional aqueous secondary amine based CO_2 separation processes.

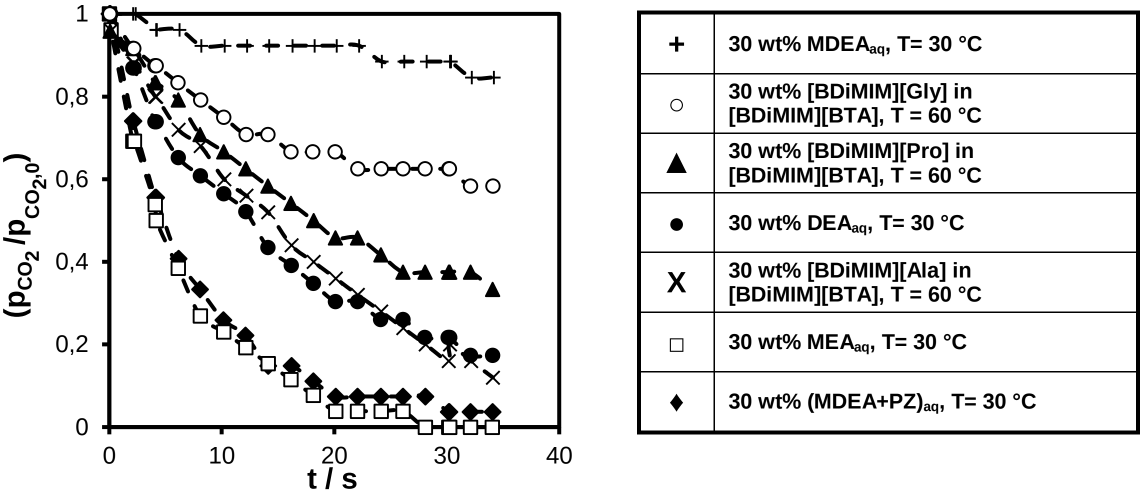


Figure 4. Normalized pressure decrease by CO_2 absorption for different conventional amines and functionalized ionic liquid mixtures.

3. Process efficiency estimation

Based on the characterization of the IL solvent, a first efficiency estimation of the proposed process was carried out by calculating the thermal and the electrical energy demand and comparing it to state-of-the-art technologies. The flow sheet of the upgrading process is given in Figure 5. The calculations are based on the following boundaries and simplifications:

- The feed gas volume flow is 1,000 m^3/h (25 °C) with $y_{CO2,in} = 0.5$ in methane (which corresponds to biogas upgrading)
- The feed gas temperature at the inlet of the scrubbing unit is 35 °C
- For heat capacity and density of the TSIL, the values of the RTIL are applied
- The temperature of the absorption equals the temperature of the desorption (80 °C)
- The minimum temperature difference in any heat exchangers is $\Delta T_{min} = 10$ K
- Heat losses to the ambient are neglected
- Vacuum (200 mbar in Col-02 and 50 mbar in Col-03) is applied via roots pump (isochoric operation)
- Loss of TSIL: 10 %/a; Loss of RTIL: 0 %/a

The liquid circulation rate can be calculated from the loading capacity isotherms (80 °C in Figure 6) and the CO_2 partial pressure in the regeneration units (200 mbar in Col-02 and 50 mbar in Col-03), respectively. In total a ΔB of 0.36 can be achieved under these conditions. The mass balance is given in Table 2 for a mixture of 10 wt% [BDiMIM][Pro] in [BDiMIM][BTA].

Table 2. Mass balance of the proposed process for 1,000 m³/h (25 °C) gas input with $y_{CO2,in} = 0.5$

Mass flows / $t{\cdot}h^{-1}$							
$F_{m,Feed}$	**$F_{m,L1}$**	**$F_{m,L2}$**	**$F_{m,L3}$**	**$F_{m,G1}$**	**$F_{m,G2}$**	**$F_{m,G3}$**	**$F_{m,Gas}$**
1.17	270	160	110	0.86	0.41	0.45	0.31

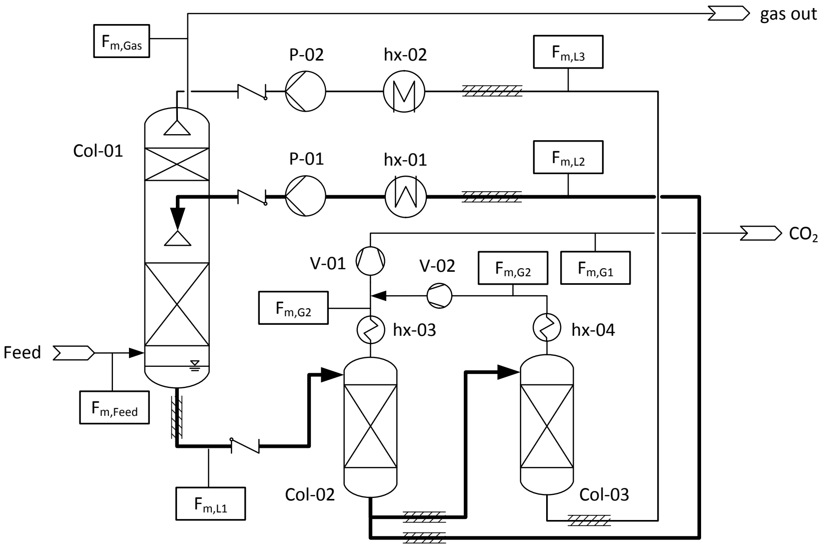


Figure 5. Proposed process concept with G and L mass flows indicated

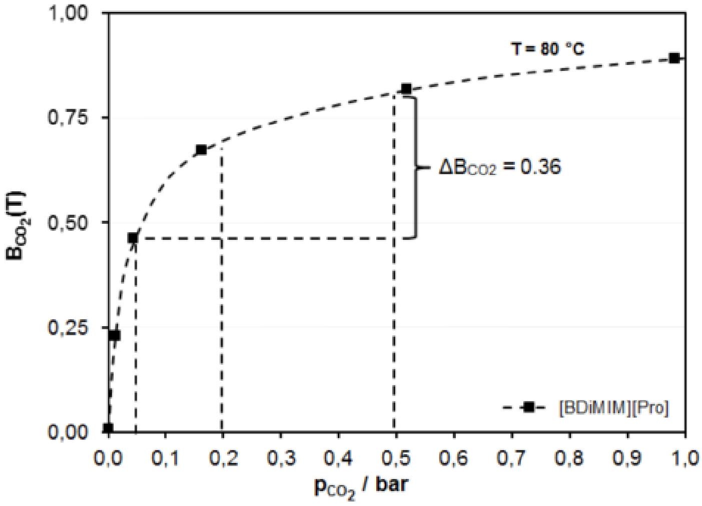


Figure 6. 10 wt% [BDiMIM][Pro] in [BDiMIM][BTA] isotherm and loading capacity per liquid cycle ΔB_{CO2}

Comparing the total energy demand of the process, the proposed IL based scrubbing process requires a larger share of electrical energy than thermal energy. The major share of the required electrical energy is applied for the vacuum pumps connected to the desorption units. The remaining electric energy demand is caused by the liquid pumps.

Table 3 shows the results of the calculations. The proposed process enables primary energy savings of 50 - 75 % in comparison to SoA. As it is clear that ionic liquids are cost-intensive solvents (and will certainly always remain more expensive than conventional solvents), the proposed process can only be profitable when OPEX savings compensate for the additional solvent costs.

Table 3. Comparison of thermal, electrical and primary energy demand of state-of-the-art technologies for biogas upgrading with the proposed isothermal IL process (Graf et al., 2014)

	e_{thermal} / $\mathrm{kWh \cdot m^{-3}_{Feed,\,STP}}$	e_{electric} / $\mathrm{kWh \cdot m^{-3}_{Feed,\,STP}}$	e_{primary} / $\mathrm{kWh \cdot m^{-3}_{Feed,\,STP}}$
Water scrubber	-	0.23 - 0.33	0.58 - 0.8
PSA	-	0.26	0.65
Chemical scrubber	0.6	0.05	0.8
Membrane separation	-	0.2 - 0.25	0.5 - 0.6
IL upgrading	0.02	0.09	0.24

Taking 8,000 h of operation per year and an average price for electricity (in Germany) of 0.15 € ct/kWh (heat 5 ct/kWh) as a basis (the biogas upgrading case), about 120 k€ can potentially be saved per year in comparison to conventional physical upgrading concepts. Compared to chemical scrubbing, these savings can be nearly doubled by additional biomethane production, as heating of the regeneration unit has to be fired by biogas in Germany. Therefore, savings strongly depend on the actual prices received for injection of biomethane into the gas grid.

With an average solvent inventory of around 5 l of solvent per m³ of raw biogas to be treated in conventional chemical scrubbing plants, 30 - 60 € per kg of solvent can be saved annually and therefore reinvested for the IL solvent. Wasserscheid and others proposed that prices of approximately 30 - 50 €/kg were possible when imidazolium based IL were produced in a commercial scale and halides were avoided (e.g. when using [BDiMIM][TCM]). If solvent costs of 65 € per kg were assumed and the solvent inventory was doubled (due to the higher viscosity of the IL), a payback period of far less than 5 years results. The calculations include 10 % loss of TSIL per year.

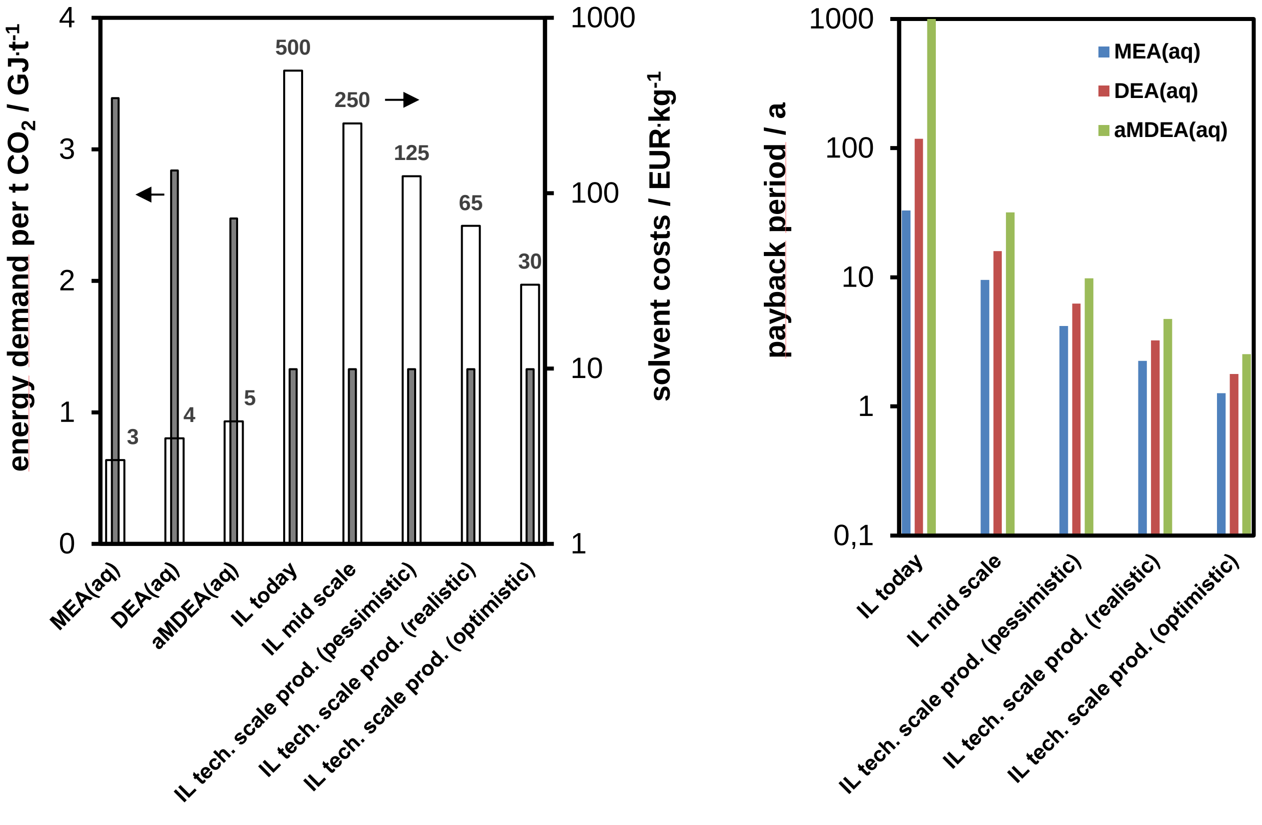


Figure 7. Results of the economic analysis of the proposed IL based process

3. Proof-of-concept

For validation of the proposed CO_2 separation process and the corresponding process model, a fully automated lab scale mini plant was designed and built and is currently used for testing various IL systems. A picture of the setup is included in Figure 2, the flow scheme is shown in Figure 8.

The mini plant consists of an absorption and a desorption column and it is equipped with all necessary equipment for heating, cooling, measuring and balancing the gas and the liquid phase entering and leaving any of the two columns. The plant is designed for stand-alone operation and can be fed with synthetic gas mixtures (e.g. from gas cylinders) or with feed gas from an external source (e.g. with biogas etc.).

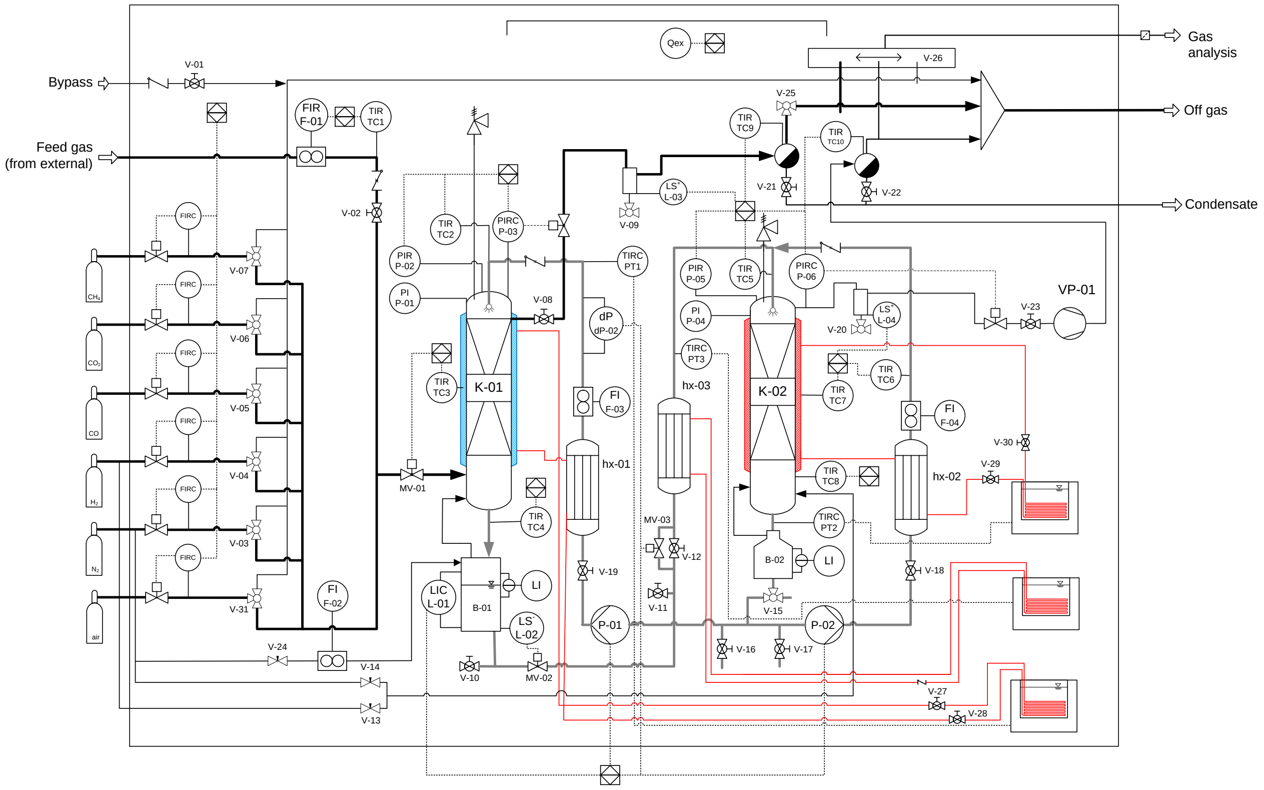


Figure 8. Mini plant for testing of solvents for CO_2 removal from gas streams

First measurements (TOS ≈ 300 h) have shown that the concept of operating the process in isothermal mode at approximately 80 °C is possible and the CO_2 can be extracted from the inlet gas stream to a remaining level of approximately 5 vol% (see Figure 9), which corresponds to the operating pressure of the regeneration unit (50 mbar). This equals 90 % of CO_2 recovery (when the CO_2 concentration in the inlet is 50 vol%) – and the outlet CO_2 concentration is low enough to apply the process to e.g. upgrading of biogas. Due to the chemical reaction taking place, the process can also easily deal with lower CO_2 concentrations - Figure 9 shows a variation of inlet CO_2 content down to 20 vol%. Measuring lower concentrations at the low gas inlet flow rate was not possible due to insufficient wetting of the packing material at the low liquid loads. This will be catched-up in the next campaign at higher inlet gas flow rates.

The most interesting result (besides the proof-of-concept) is the ratio of liquid to gas load of the absorption column, which is in the range of 9 $m^3/(m^2h)$ / 26 $m^3/(m^2h)$ = 0.34 for the biogas upgrading case. Conventional physical scrubbing systems are operated at a L/G ratio of around 0.1 - 0.2, conventional chemical scrubbing systems at 0.05 or even below (but also have a 3 - 5 times higher amine content in the solvent mixture).

Nevertheless, the high liquid circulation rate is not critical as the temperature of the liquid stream is not altered. Co absorption of gases is marginal because the process is operated at elevated temperature and atmospheric pressure in the absorption column. Furthermore, the ratio of TSIL in the mixture can be increased to reduce the slip of any gases to the CO_2 stream. In the biogas case, the slip of methane can be reduced to values below 0.5 % by increasing the content of TSIL in the mixture to 20 wt%.

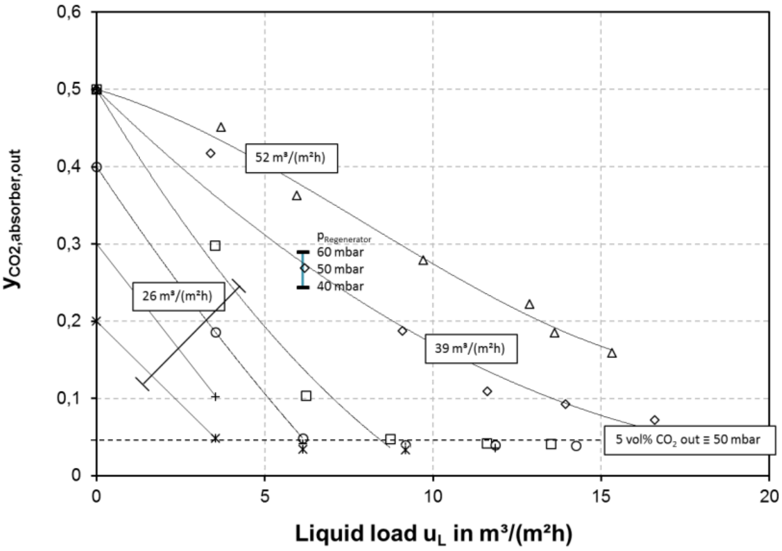


Figure 9. Results of first mini plant campaign with 15 wt% [BDiMIM][Pro] in [BDiMIM][BTA]

4. Summary and Conclusion

An alternative process for CO_2 separation based on the application of ionic liquids has been developed and evaluated for applying it to the upgrading of biogas. The proposed chemical scrubbing process is operated in a virtually “isothermal” mode, saving the thermal energy for regeneration of the solvent from an external source. Instead, the solvent is regenerated by reducing the CO_2 partial pressure in the gas phase of the regenerator by applying moderate vacuum in a pressure range of 50 mbar.

The proposed CO_2 separation concept favors ionic liquids as solvents, as this class of substances features a negligible vapor pressure at temperatures of up to 150 °C. Additionally, the increase of operating temperature helps to compensate for the common disadvantages of IL (high solvent viscosity, low energetic benefits).

Taking the example of biogas upgrading, ionic liquids were screened and an appropriate solvent was developed as a mixture of RTIL and TSIL with separate focus on minimizing the viscosity of the mixture and providing an appropriate chemical CO_2 absorption capacity. As RTIL [BDiMIM][BTA] was used. Future optimization options are to switch to [BDiMIM][TCM] to significantly increase the selectivity and to reduce the viscosity of the solvent mixture by a factor of 2. [BDiMIM][TCM] is non-fluorinated IL, which is an advantage over [BDiMIM][BTA]. Concerning chemisorption, prolinate [Pro] based TSIL are promising, as they feature sufficient thermal stability and proper CO_2 loading capacity and kinetics.

During screening and characterization phase, thermal stability, physical CO_2 and CH_4 solubility, effective and intrinsic absorption kinetics, heat of reaction, and some additional solvent properties of various examined ionic liquid solvents were evaluated in a temperature range, exceeding the common range of literature values considerably. The measurements on absorption kinetics showed, that the absorption of CO_2 at the desired operating conditions is about as fast as with conventional DEA, which has already been applied for biogas upgrading. Due to this, the conclusion can be drawn that the necessary absorber volume for applying the desired ionic liquid mixture is in the same dimension as for conventional DEA based solvent.

Based on the experimental findings a first process efficiency estimation was performed. As expected from the flow sheet, the major part of the required electrical energy for the process is applied for the vacuum pumps connected to the desorption units. Nevertheless, the calculations predict energetic benefits in terms of primary energy savings compared to the state-of-the-art of biogas upgrading processes in the range of 50 - 75%.

The corresponding savings in OPEX can be applied for the additional investment of the ionic liquid solvents which indeed are more expensive than conventional solvents. Assuming the IL price at 65 EUR/kg which might be realistic when non-fluorinated substances were applied and the IL were produced in large quantities, decent paypack periods in the range of less than 5 years would result, making an investment in this technology an attractive option.

Acknowledgements

The authors are thankful for the funding from MWK (Ministry of Science, Research and Arts) Baden-Wuerttemberg: 7533-10-5-105, the BMWi (Federal Ministry of Economic Affairs and Energy) and the DVGW (German Technical and Scientific Association for Gas and Water): 03KB104A-C.

References

DARDE, V. et al.: Chilled ammonia process for CO_2 capture. Int. J. Greenhouse Gas Control 4 (2010) 2, 131–136
GOETZ, M. et al.: Renewable Power-to-Gas: A technological and economic review. Renewable Energy (2016) 85, 1371–1390
GRAF, F. et al.: Biogas: Erzeugung - Aufbereitung – Einspeisung (2. Auflage). DIV (2014)
IPCC: Fifth assessment reports. (2014) www.ipcc.ch
KOHL, A., NIELSEN, R.: Gas Purification, 5th ed., Gulf (1997)
STOLTEN, D.; SCHERER, V.: Efficient Carbon Capture for Coal Power Plants. Wiley-VCH (2011)
WASSERSCHEID, P.; WELTON, T.: Ionic Liquids in Synthesis (2nd ed.). Wiley-VCH (2008).
WILKES, J.S.: Ionic Liquids in Perspective: The Past with an Eye toward the Industrial Future, in: ROGERS, R.D., SEDDON K.R. (Eds.), Ionic Liquids, American Chemical Society, Washington, DC, 2002, 214–229.