

Minimum Gas/Liquid Flow Rate for Absorption Columns

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Global warming has motivated a widespread concern about carbon dioxide emissions. Although various capture technologies are available, absorption is currently believed in the industry to be one of the most suitable. It is well known that high gas volumes with low partial pressure of CO₂ make the chemical absorption more suitable than physical absorption that is more advantageous for high pressures and low temperatures. The suitability of absorption solvent alternatives is quantified according to its minimum flow rate. The potential of the absorbent used and influence of its alkaline chemical compound concentration on its minimum flow rate is evaluated in the present paper for different partial pressures of carbon dioxide. To simplify the problem, infinite analysis is applied for first time to the absorption process. In the early process design stages, simple models based only on thermodynamic data without the need of detailed unit specifications allow to take important decisions.

1. Introduction

The infinite analysis widely used in distillation processes is applied for the first time to absorption processes in the present manuscript. Carbon dioxide capture is used as study case due to its nowadays-widespread concern. Atmospheric carbon dioxide concentration has reached values significantly higher than in preindustrial human history. Its future effect on weather is uncertain and an increasing conscience to mitigate its emissions is increasing in industrialized nations. Nowadays, 40 % of biomass upgrading is performed using water scrubber (Niesner et al, 2013). However, the improvement of the carbon dioxide capture and storage technologies is object of intense study. Although various capture technologies are available, absorption is currently believed in the industry to be one of the most suitable. The separation is usually performed in absorption columns filled with structured packing and counter-currently operated. Physical absorption is used at high partial pressure of carbon dioxide and low temperatures; on the other hand, chemical absorption is used at low partial pressure.

Many new absorption media are proposed in literature. Usually, these are compared for specific packing and operating conditions with some other well-known absorption media, such as mono-ethanol-amine (MEA). There is a need to investigate new solvents to minimize the carbon dioxide emissions since the traditional amines have low CO₂ loading capacity and require high energy for regeneration and their properties are investigated. Modelling of gas/vapour-liquid separation processes usually requires experimentally determined parameters, e.g. mass transfer coefficients. A novel modelling approach based on hydrodynamic analogies (HA) has recently been developed without using mass transfer coefficient correlations (Yazgi and Kenig, 2013). Such a modelling approach can be used for the identification of most suitable packing type as well as its adjustment to the specific process conditions. However, there is still a lack of shortcut methods for the early design for absorption processes. The concept of infinite analysis applied to the absorption processes provides important insights to this unit. Usually, at the early design stages, the packing type used and other column design details are unknown. The feed stream characteristics and the thermodynamic model, that in many cases is just estimated, are the only available data e.g. SAFT model (Chremos et al, 2013). The first questions that arise are not related to the detailed

design of the column but to which absorber could work better and at which concentration, which minimum flowrate of absorber is required (CO_2 absorbent load) or which are the minimum energy requirements. Instead of choosing some arbitrary conditions for the unknown parameters, it is advisable to fix them to infinite. In this way, the mathematical model and its resolution become simplified and the limit conditions and its minimum values are easily analysed. This approach is used in distillation to determine its feasibility, the minimum number of transfer units or the minimum energy requirements for a certain separation (Plesu et al, 2013). In this paper, a simplified resolution is used for absorption columns to determine the carbon dioxide load of the absorbent.

First, the CO_2 load in physical absorption is analysed versus pressure, the readily available water is compared with other physical absorbent compounds such as dimethyl-ether-polyethylene-glycol, n-methyl-2-pyrrolidone, propylene-carbonate, diethylene-glycol-dimethyl-ether and methanol. Methanol is used successfully for CO_2 absorption with low energy requirements when the streams and columns are properly pressurized (Gatti et al, 2013). Secondly, the use of chemical absorbent aqueous solutions is evaluated from CO_2 load point of view. CO_2 removal is usually carried out using ammonia (NH_3) or alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), diisopropanolamine (DIPA), 2-amine-2-methyl-1 propanol (AMP), diglycolamine (DGA). A major problem is amine degradation, after long exposure to oxygen (O_2) and other reactive contaminants, to unwanted compounds in the absorption unit with no ability to absorb CO_2 . These compounds introduce corrosion, fouling, and foaming, therefore they must be removed from the amine solution (Suppaibulsuka et al, 2013). Ionic liquids are claimed as more stable alternative to alkanolamines (Nonthanasin et al, 2013), but their viscosity is higher and they are not industrially used nowadays. Ionic liquids have a number of advantages, as determined by their unique physicochemical properties, such as negligibly low vapour pressure, high thermal stability, and structural advantages.

2. Method

Assuming an infinite number of transfer units in an absorption column (NTU infinite), a minimum absorbent flow rate (ABSIN) is calculated to reach a certain recovery of a compound from input gaseous stream (GASIN). For a certain feed composition and assuming a fixed temperature in the isothermal absorption column, the minimum absorbent flow rate (ABSIN) depends on the partial pressure of carbon dioxide and on concentration of chemical absorbent. To simplify the system and provide general insights for any carbon dioxide capture process, it is assumed that the input gas stream is composed of pure carbon dioxide at a certain pressure and a total recovery of CO_2 is reached. A total recovery of a pure CO_2 stream implies that there is no gas output (GASOUT) stream. Therefore all the CO_2 entering the column is captured by the liquid stream (ABSOUT). Moreover, as NTU is infinite, the output liquid stream (ABSOUT) is in equilibrium with the gas input (GASIN).

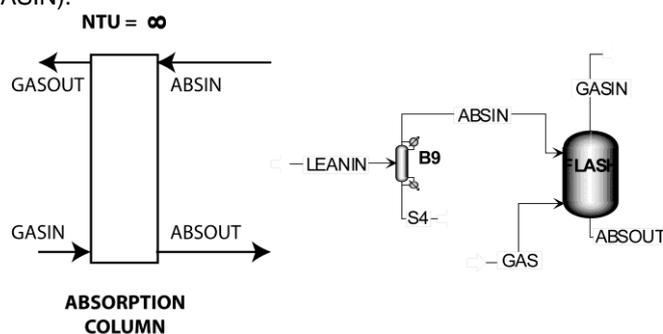


Figure 1: Process scheme and simplified simulation with one flash

According to the above-mentioned simplifications and assumptions, the process is assimilated to the simulation flowsheet shown in Figure 1 using AspenPlus v8.2[®]. The thermodynamic method used for simulation of physical absorption is PC-SAFT, while for the chemical absorption ELECNRTL was selected. The simulated flowsheet is not intended to reproduce the process itself but to characterise the streams involved. The calculation basis is 1 kg/s of CO_2 feed to the absorption column (GASIN). As the entire CO_2 is absorbed, then the CO_2 flow rate in the output liquid stream (ABSOUT) of the absorption column must be of the same value of 1 kg/s. As mentioned before, the liquid output stream is in equilibrium with the gas input stream at the absorption column. Therefore, for equilibrium calculations in the simulation, both streams are considered as output streams of a flash unit. In this way, for stream

calculation purposes, GASIN stream is inverted, becoming an output stream. At this point, to fulfil the mass balances in the simulation, a new virtual input stream (GAS) is added, having a flow rate of 2 kg/s of CO₂. A Design Specification is used to obtain the absorbent flow rate required to fulfil the above-mentioned CO₂ flow rate at the flash output streams. To perform a Sensitivity Analysis of the chemical compound absorbent mole fraction, a SEP2 unit is placed in the simulation flowsheet.. This simplified simulation method allows to approach the behaviour of a NTU infinite absorption column, using a simple vapour-liquid equilibrium unit (FLASH).

3. Results

The CO₂ loading capacity of the absorbent and the energy for its regeneration are two main parameters to choose between alternative absorbents. In the present paper, we focus on the CO₂ loading capacity quantified as the minimum lean flow rate to capture a kilogram of CO₂ in an absorption column where gas input and rich lean out stream are in equilibrium. The results are calculated at 20 °C.

First, the physical absorption is evaluated (Figure 2). As the pressure of CO₂ becomes smaller, the minimum absorbent flow rate requirements increase abruptly requiring great amounts of absorbent. Water requires larger amounts than the other compounds evaluated, but it is more readily available and safe. The lowest minimum absorbent flow rate corresponds to methanol, but it is quite close to other compounds such as diethylene-glycol-dimethyl-ether. For the other chemical compounds analysed as physical adsorbents of CO₂, Figure 2 illustrates that the minimum flowrate requirements are slightly higher than the ones of methanol but much lower than the ones of water. For dimethyl-ether-polyethylene-glycol, this can be justified, as there are a greater number of ethylene groups in its chemical structure.

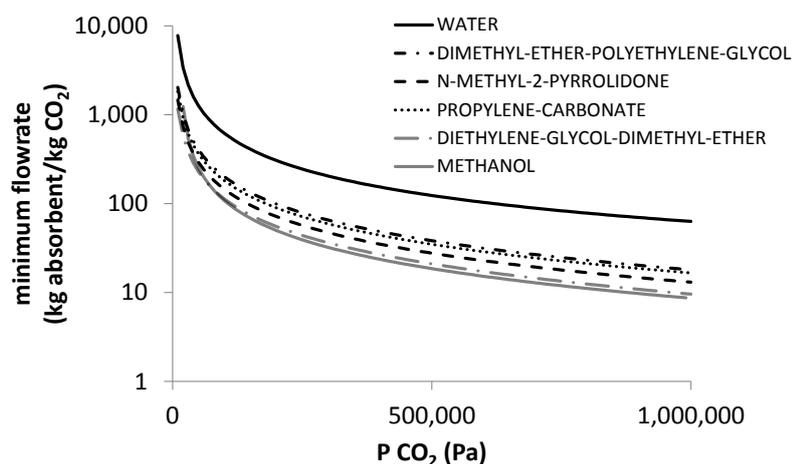


Figure 2: Minimum flowrate for physical absorption of carbon dioxide

CO₂ is an acid gas and a slight basification of the aqueous media decreases sharply the minimum absorbent flow rate (Figure 3). Among the evaluated compounds, NH₃ has the highest CO₂ loading capacity; furthermore, it is thermally and chemically stable to oxidation. In the presence of SO₂, valuable ammonium sulphate is produced. However, salts condensation can be experimentally observed in the recovery distillation column condenser. For aqueous solutions with more than 30 % ammonia and low content of carbon dioxide, ammonia vapours are formed. To solve this drawback, alkanolamines are used in many applications instead of ammonia.

On the other hand, the amines are degraded by other compounds present in gases such as O₂, SO₂, NO_x, HCl. According to Figure 4, MEA has a high CO₂ loading capacity compared to other alkanolamines. Although its capacity is lower than ammonia, its reactivity is higher requiring a smaller contact area. MEA is the chemical absorbent more extensively studied in literature and is used as comparison basis for the other alternatives studied. Some other sterically hindered alkanolamines, such as AMP, present a CO₂ load very close to MEA. This is due to the attachment of the bulky amino group to tertiary carbon and the carbamate formation is very unstable. DGA, DEA and MDEA present a very similar behaviour according to the minimum flowrate requirements, with a value higher than the previously mentioned compounds due to a lower basicity. Finally, DIPA has the highest minimum absorbent flow rate among the evaluated

compounds. However, it presents some advantages, such as: it is less corrosive in comparison to other primary or secondary alkanolamines and it has a greater selectivity to H₂S than to CO₂. Furthermore, at low partial pressures of CO₂, DIPA is much more advantageous than any other chemical absorbent.

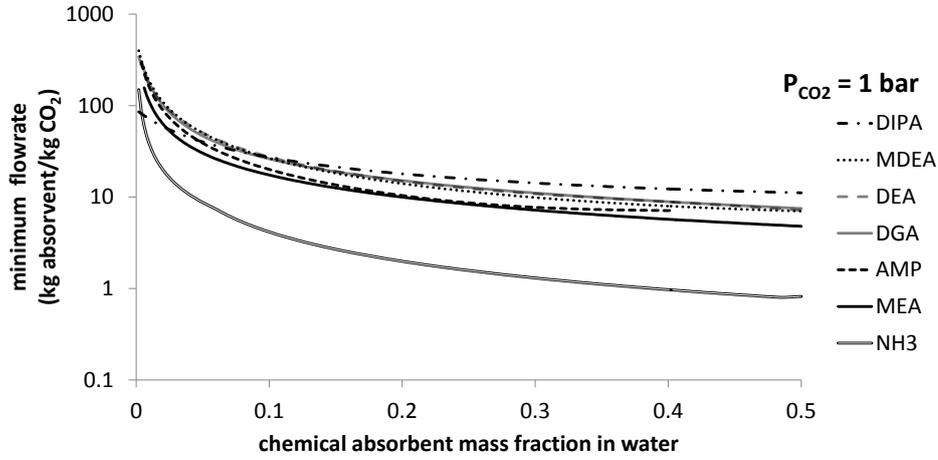


Figure 3: Chemical absorption of carbon dioxide at 1 bar

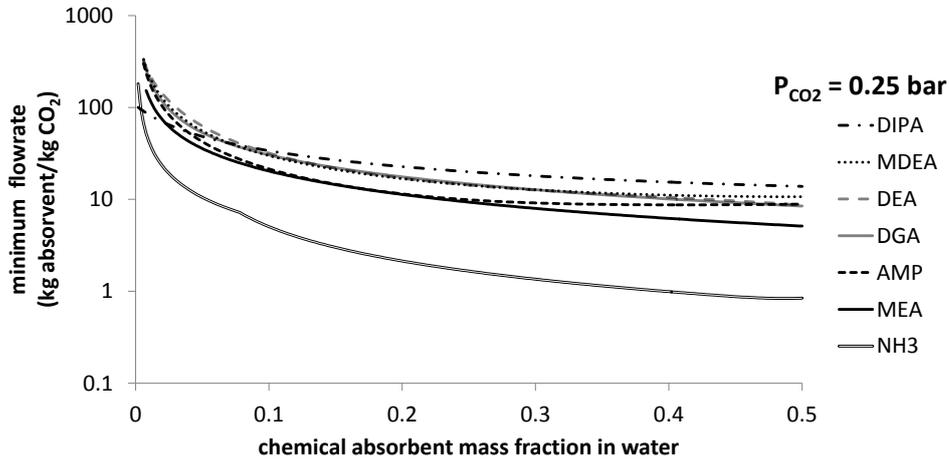


Figure 4: Chemical absorption of carbon dioxide at 0.25 bar

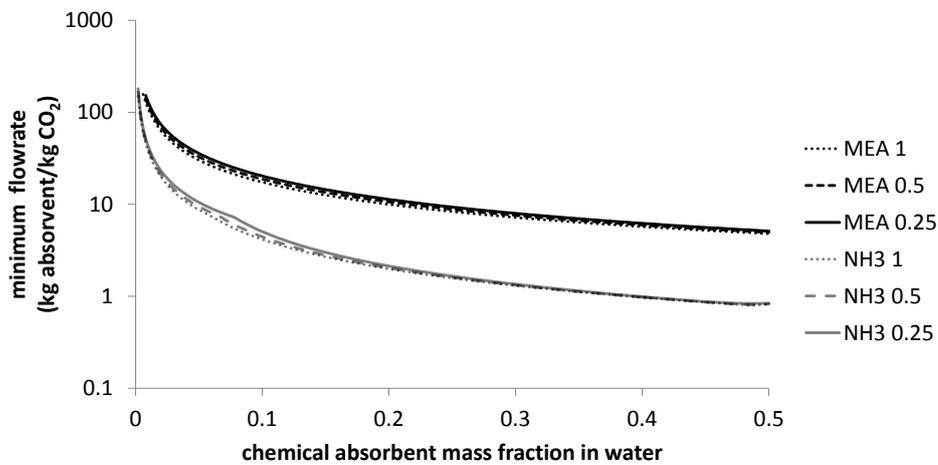


Figure 5: Pressure influence on chemical absorption for components with low minimum flowrate

At the contrary of the situation illustrated in Figure 2, where the pressure had a great influence, the differences between Figure 3, where the pressure of carbon dioxide is 1 bar and the Figure 4, where the pressure of CO₂ is 0.25 bar, are minor. The same commentaries for Figure 3 apply to Figure 4. The pressure has a great influence on the physical equilibrium between liquid and gas but it has no effect on the chemical adsorption. However, a change of temperature affects both physical and reaction aspects.

The quantity of chemical absorbents with a lower minimum absorbent flow rate depends mainly on the reaction kinetics that leads to their formation. Therefore, a pressure change does not affect their minimum flowrate requirements (Figure 5).

However, for the chemical absorbents with a higher minimum absorbent flow rate the physical equilibrium becomes more important, then the effect of pressure change is reflected in the minimum flow rate curves (Figure 6).

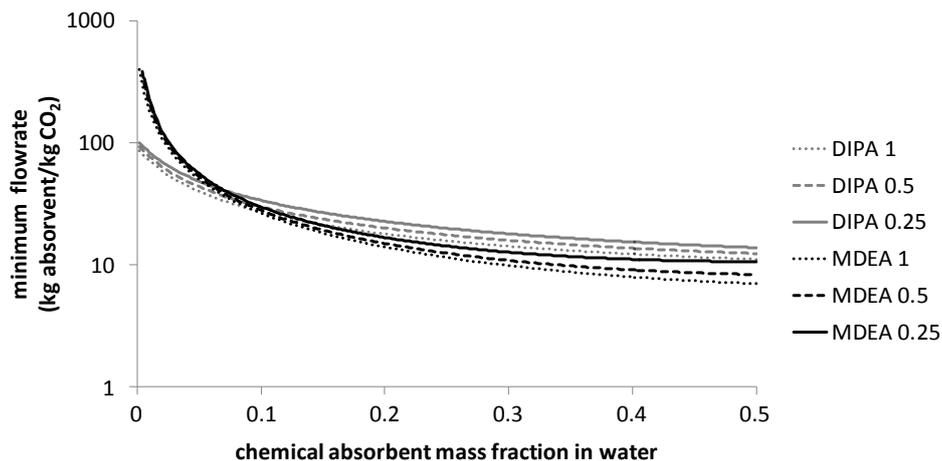


Figure 6: Pressure influence on chemical absorption for components with high minimum flowrate

Finally, Figure 7 compares physical and chemical absorption from the CO₂ load point of view. The minimum flowrates of absorbent calculated for the chemical absorption are always lower than for the physical absorption. Ammonia and MEA are used to delimitate the chemical absorption region and water and methanol are used to delimitate the physical absorption region. MEA and ammonia are chosen because their CO₂ load is not affected by pressure variation. Therefore, it can be concluded that, in general, at low and moderate pressures, the CO₂ load for the chemical absorption is lower than for the physical absorption. Nevertheless, from this result cannot be concluded that chemical absorption is always better than physical absorption. Besides the energy costs of absorbent pumping and absorption column diameter, the energy cost for absorbent recovery is also a very important parameter to take into account. Furthermore, the limits are defined by the above mentioned compounds, but for some other compounds the limits are less clear.

The simplified method presented so far is useful to compare the minimum CO₂ load for different absorption media. In this paper, for illustration purposes, the method is applied to well-known and widely used compounds, but it can be used for fast evaluation of novel alternative absorption media.

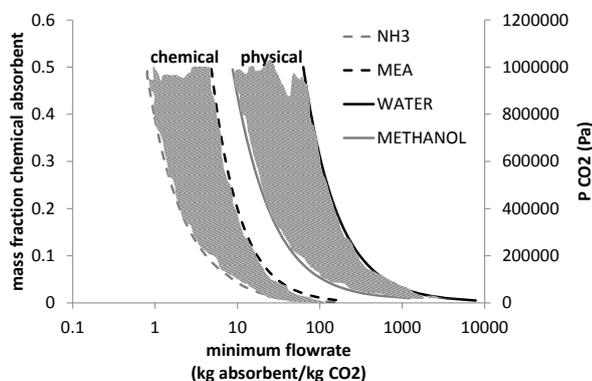


Figure 7: Comparison between physical and chemical absorption

4. Conclusions

CO₂ load and energy required to recover the solvent are two parameters of great importance when the suitability of a solvent is evaluated. Experimental determination of the mass transfer coefficients and solving the model by the simulation of an absorption column are not straightforward. However, the model can be simplified assuming an infinite number of transfer units and the model thus obtained can be easily solved using only basic thermodynamic data. Therefore, the present paper provides a simplified model that can be used to determine the minimum absorbent flow rate as a measure of the minimum limit of the CO₂ loading capacity. The CO₂ loading capacity in water can be more effectively increased when adding a chemical absorption compound than increasing the pressure of the gas stream. Water is commonly used as physical absorber, but some other compounds readily available can be used instead, providing a higher absorption capacity. For instance, methanol has a higher CO₂ load capacity than the other absorbents evaluated in the present paper. On the other hand, the highest load capacity for the chemical absorption is using ammonia. The alkanolamines can be used as concentrated solutions without being evaporated a large quantity. The MEA and AMP present the highest CO₂ load capacity between alkanolamines, because its basicity is higher. The DIPA presents the highest CO₂ load at low concentration and is less corrosive.

As future work, a more complete simplified method will be provided to determine the other main parameter needed to evaluate the suitability of a solvent. Therefore, the minimum energy requirements will be calculated according to the analysis of the entropy and enthalpy variation between input and output streams of the unit operations in the process flowsheet. This will allow the recovery of the absorbent by distillation or temperature-swing.

Acknowledgements

The authors would like to thank the financial support of POSCCE project ID 652 (Structural Funds for Development and Cohesion).

References

- Chremos A., Forte E., Papaioannou V., Galindo A., Jackson G., Adjiman C., 2013, Modelling the fluid phase behaviour of multifunctional alkanolamines and carbon dioxide using the soft- γ approach, *Chemical Engineering Transactions*, 35, 427-432, DOI:10.3303/CET1335071.
- Gatti M., Marechal F., Martelli E., Consonni S., 2013, Thermodynamic analysis, energy integration and flowsheet improvement of a methanol absorption acid gas removal process, *Chemical Engineering Transactions*, 35, 211-216, DOI: 10.3303/CET1335035.
- Niesner J., Jecha D., Stehlik P., 2013, Biogas upgrading techniques: state of art review in european region, *Chemical Engineering Transactions*, 35, 517-522 DOI:10.3303/CET1335086.
- Nonthanasin T., Henni A., Saiwan C., 2013, Solubility of carbon dioxide in five promising ionic liquids, *Chemical Engineering Transactions*, 35, 1417-1422, DOI:10.3303/CET1335236.
- Pleșu V., Bonet Ruiz A.E., Bonet J., Llorens J., Iancu P., 2013, Minimum number of transfer units and reboiler duty for multicomponent distillation columns, *Applied Thermal Engineering*, 61(1), 67-79.
- Suppaibulsuka P., Saiwan C., Supap T., 2013, Effect of organic solvents on separation of heat stable salts (hss) generated during carbon dioxide absorption using amine solution, *Chemical Engineering Transactions*, 35, 409-414, DOI:10.3303/CET1335068.
- Yazgi M., Kenig E., 2013, Hydrodynamic-analogy-based modelling of CO₂ capture by aqueous monoethanolamine, *Chemical Engineering Transactions*, 35, 349-354, DOI:10.3303/CET1335058.