

Modeling CO₂ capture processes by chemical absorption: The case of biogas treatment

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Abstract. Our objective through this work is to purify the biogas produced by a methanisation process in order to be valorized in a cogeneration unit. The studied biogas is mainly composed of methane 60% and carbon dioxide 39%. The treatment will increase the quality of the biogas by decreasing the percentage of CO₂, in order to improve the energetic properties of the gas mixture (PCI). Several biogas purification and bio-methane production processes are commercialized. The choice of the technical and economic optimum is strongly linked to the quality and quantity of biogas to be purified, the quality of the desired bio-methane, depends on the type of methanisation, the nature and regularity of the substrate supply, but also on the local conditions of implantation. In this part of our research project, we are interested in the study, dimensioning and modeling of a CO₂ capture unit by chemical absorption, constituted by a packed column. The solvent used is the secondary amines in mixture with the primary amines.

1 Introduction

Biogas is produced from organic waste, through a natural methanisation process in an anaerobic environment, which degrades organic matter through the combined action of several types of micro-organisms. A series of biological reactions leads to the formation of biogas in a bioreactor, while respecting the operating conditions of the adopted process. The essential product of this fermentation is methane, which is considered a renewable energy source, plus other compounds such as carbon dioxide, H₂S substances and water vapor, its composition is essentially determined by the substrates, the fermentation process.

Biogas treatment is a separation task that leads to the production of a methane-rich gas with technical specifications. Taking into account the composition of the raw gas, the separation task consists of the removal of CO₂ (increase in calorific value and Wobbe index) drying of the gas, removal of trace compounds such as oxygen, nitrogen, hydrogen sulphide, ammonia, and compression to a set pressure depending on the end use of the gas [1].

CO₂ capture by chemical absorption requires a separation column in which material transfer is promoted by a large contact surface between the liquid and the gas. Absorption columns are generally tray or packed columns. This is an operation in which a mixture of gases is brought into contact with a liquid solvent in order to solubilize one or more components of the mixture [2].

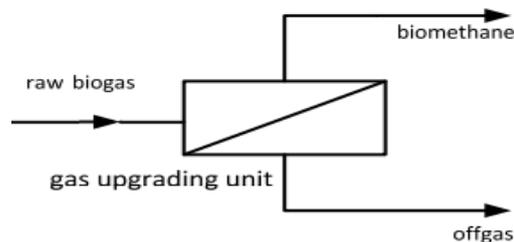


Fig.1. Unitary operation

The solvent is then recycled after being regenerated and reintroduced at the top of the column. Among chemical solvents, alkanolamine solutions are the most commonly used in acid gas absorption processes.

The gas reacts chemically with the liquid absorbent to form more or less weakly bound complexes. MonoEthanolAmine *MEA* and DiGlycolAmine *DGA*, the primary amines, DiEthanolAmine *DEA*, secondary amine, and MethylDiEthanolAmine *MDEA*, tertiary amine are the most commonly used amines. For the simulation of transfer columns, it is necessary to have the required packing diameter and height. The diameter is calculated to operate at a maximum of 80% of the bottleneck within the column, this diameter is therefore calculated so that the gas velocity is 20% lower than the gas velocity at the bottleneck, calculated using the charts provided by the manufacturer [2]. The height is an input data for the technico-economic calculation, which is either fixed by the user or constituted as an optimization parameter.

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A method for estimating the cost of electricity is proposed to quantify the operating and investment expenses related to the installation of such a process. The resulting process simulation and evaluation environment was then coupled with a non-linear optimization method to determine the operating parameters and equipment dimensions that maximize energy and economic performance [2].

2 Principles of chemical absorption

2.1 Chemical absorption

Absorption consists of bringing a mixture of gas and a liquid into contact in order to preferentially solubilize a compound. In the liquid, or solvent, the dissolved compound is called the solute. This operation requires a transfer of material from the gas phase to the liquid phase. The solubility of the gas in the liquid, at a given temperature and pressure, is the concentration of the dissolved gas in the liquid at equilibrium.

In the case of an ideal solution it is written, at equilibrium, that the partial pressure of a compound A , P_A^* is equal to the product of its vapor pressure P_v at the same temperature, by the liquid phase molar fraction x_A , this is Raoult's law [2].

$$P_A^* = P_v x_A \quad (1)$$

In the absorption process a transfer from the gaseous to the liquid phase takes place. It is the potential difference defined as the deviation from equilibrium, expressed as a concentration (in mol.m^{-3}), that creates the material transfer flow at the interface.

It is assumed that the gas and liquid are in equilibrium at the liquid-vapor interface, and that the concentration C_A^* corresponds to equilibrium with partial pressure P_{Ai} . k_L is the transfer coefficient within the liquid, (in m.s^{-1}), k_G is the transfer coefficient within the gas (in $\text{mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$) and ϕ_A is the specific absorption flux per unit of interfacial area [2] :

$$\phi_A = k_G (P_A - P_{Ai}^*) = k_L (C_A^* - C_A) \quad (2)$$

- P_{Ai}^* : partial pressure from A to interface at equilibrium
- C_A^* : dissolved gas concentration A at the equilibrium interface with P_{Ai}^*
- P_A : partial pressure of A in the gas
- C_A : dissolved gas concentration A in the liquid

2.2. Industrial implementation

Chemical absorption requires a separation column in which material transfer is promoted by a large contact surface between the liquid and the gas. Absorption columns are generally tray or packed columns. The trays allow the gas to be divided into small bubbles in a

vertical upward flow. The bubbles are introduced into the liquid phase, which flows horizontally, so that the gas and liquid circulate in a cross-flow [2].

Packed columns divide the liquid flow into thin films through the counter-current flowing gas. The gas to be purified is introduced at the bottom of the absorption column, while the solution is introduced at the top of the column. The solute-rich solution flowing at the bottom of the column is heated in a cross-exchanger with the lean solution, i.e. with the regenerated solution. This rich solution is then introduced into the regeneration column.

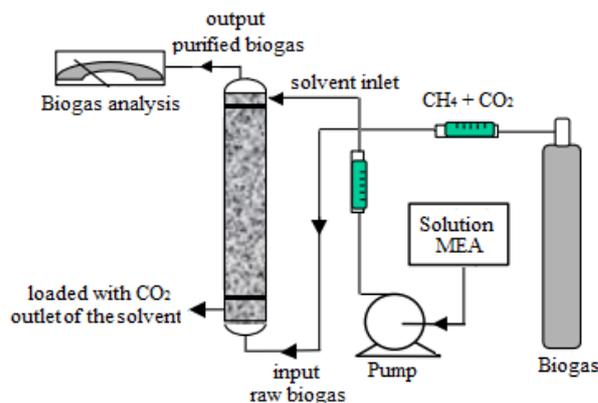


Fig.2. Absorption system

2.3. Chemical Absorbers

Among chemical solvents, alkanolamine solutions are the most commonly used in acid gas absorption processes. The gas reacts chemically with the liquid absorbent to form more or less loosely bound complexes. The molecular structure of alkanolamines contains at least one hydroxyl group (-OH) and one amine group (-N); the hydroxyl group increases the solubility in water and decreases the vapor pressure of the aqueous solution and the amine group provides the alkalinity necessary in aqueous solution to ensure the absorption of acid gases H_2S and CO_2 [2].

MEA is the most reactive amine with an ethanol group bonded to the nitrogen atom; it reacts quickly with acid gases, and allows high quality separations in terms of purities of separate products. However, its capacity to absorb carbon dioxide is relatively low [2].

2.4 Reaction mechanisms

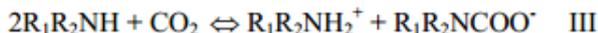
In the following we will note primary and secondary amines in the form $\text{R}_1\text{R}_2\text{NH}$, where $\text{R}_1=\text{H}$ and $\text{R}_2=\text{C}_2\text{H}_4\text{OH}$ for MEA, and $\text{R}_1=\text{R}_2=\text{C}_2\text{H}_4\text{OH}$ for DEA, and tertiary amines in the form $\text{R}_1\text{R}_2\text{R}_3\text{N}$, where $\text{R}_1=\text{R}_2=\text{C}_2\text{H}_4\text{OH}$ and $\text{R}_3=\text{CH}_3$.

The reaction mechanism for the absorption of CO_2 in primary and secondary amines in the presence of H_2O comprises the formation of a zwitterion by reaction I, $\text{R}_1\text{R}_2\text{NH}^+\text{COO}^-$, followed by deprotonation by a base or water molecule to produce a stable carbamate ion $\text{R}_1\text{R}_2\text{NCOO}^-$ and a protonated base. Reaction I is rapid but of finite speed, the proton exchange reaction II is

considered instantaneous. The reactions in the primary and secondary amines therefore lead to degradation by the formation of stable salts, the carbamates [2].



The global reaction is:



The solubility of CO₂ is higher in tertiary amine solutions than in aqueous solutions of primary or secondary amines. It takes one mole of tertiary amine instead of two moles of primary or secondary amine to absorb one mole of carbon dioxide.

The absorption capacity in *MPA* is greater than in *MEA* at 313.15K [3][4]. Its absorptive capacity is comparable to that of *MDEA* [5], and its reaction speed is higher. On the other hand, at higher temperatures its absorption capacity is lower, the CO₂ is therefore easier to desorb.

The enthalpy of reaction of CO₂ in aqueous amine solutions is dependent on the CO₂ loading rate, and to a lesser extent on temperature. It increases from tertiary amines to primary amines, Tables 1 and 2 where it is expressed in KJ per mole of gas absorbed.

Table 1. CO₂ Reaction Enthalpies at Towards Zero Loading Rate, [6]

T(K)	Ammine	Δh(KJ/mol)
313,15	MDEA 30%	49
353,15	MDEA 30%	55
373,15	MDEA 30%	58

Table 2. Enthalpy of CO₂ reaction [7]

Ammine	Δh(KJ/mol)
MEA 30%	84,4
DEA 30%	66,8
DGA 30%	86,7
MDEA	48,5

The addition of primary or secondary amine or piperazine to a tertiary amine solution speeds up the absorption process. Measuring the CO₂ absorption flux in *MEA* and *MDEA* mixtures allows the calculation of the acceleration factor as a function of contact time [8]. The addition of primary amines allows a significant increase in the acceleration factor, even at low contact times and for low concentrations of *MEA*.

The process is more marked with primary amines than with secondary amines: even if *DEA* allows a significant increase in the rate of reaction, it remains lower than that obtained with *MEA*, [8][9]

Table 3. Mixture of *MDEA* and *MEA*, for 313.15 K and 0.94 atm, [8]

Mixture of 30% amines in aqueous solution		Acceleration factor E	
MDEA (% mass)	MEA (% mass)	0,1s	10s
30,0	0,0	2,3	5,9
28,5	1,5	7,5	11,3
27,0	3,0	12,0	17,6
25,5	4,5	15,0	23,0

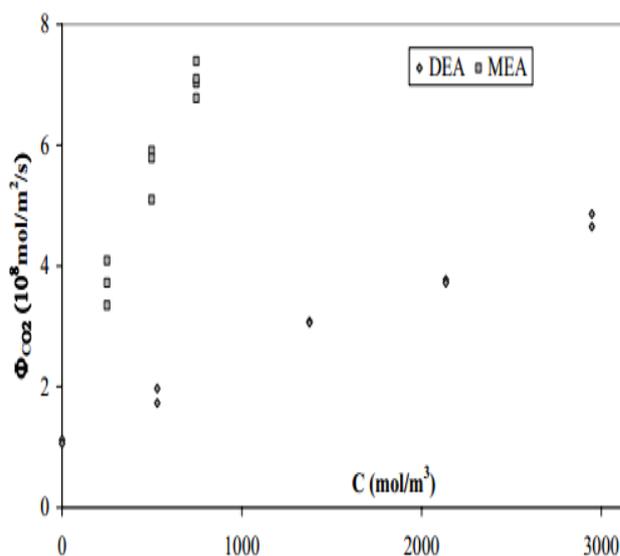


Fig. 3. Influence of the nature of the amine added in mixtures with *MDEA* 30% mass at 298K, [8][9]

2.5 Absorption capacity

While absorption kinetics are improved by replacing a few percent of tertiary amines with a primary or secondary amine, the absorption capacity tends to decrease or increase depending on the loading rate.

The solubility of carbon dioxide varies significantly as the primary amine content in the *MEA-MDEA* mixture is increased for a constant total amine concentration.

The measurement of the absorption capacities of *MEA* and *MDEA* amine mixtures in aqueous solution, for an overall concentration of 30% mass, and for 333K, (see Figure 4), shows a bundle of curves that pass through the same point corresponding to a CO₂ partial pressure of 45KPa and a loading rate, α of about 0.5 [10]. Above this loading rate, the replacement of the *MDEA* by the *MEA* leads to a decrease in absorption capacity.

The mixture of *AMP* and *DEA* has a slightly higher CO₂ absorption capacity, compared to that obtained in the mixture of *MDEA* and *DEA* [11].

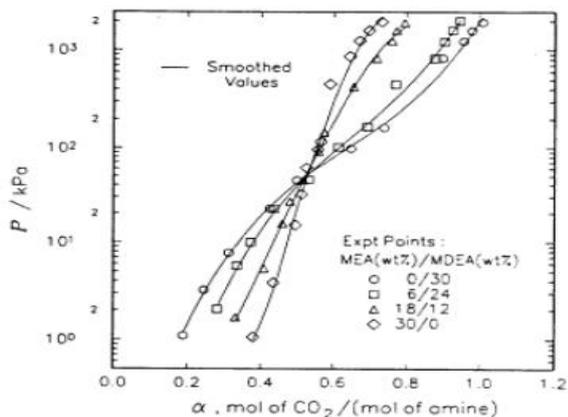


Fig. 4. Solubility of CO₂ in MEA and MDEA mixtures at 333K [10]

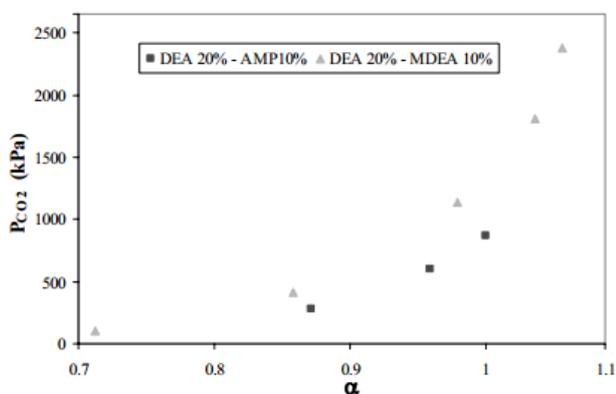


Fig. 5. Solubility of CO₂ in amine mixtures in solution at 313.15K [11]

3 Dimensioning of a packed absorption column

Absorption is the unitary operation whose principle is based on the passage of one or more several constituents of a gaseous phase in a liquid phase. There are exchanges (or transfers) of material between a gaseous phase and a liquid phase whose compositions chemicals are different. This transfer of the material involved takes place within contactors. Gas-liquid in which the two phases are brought into contact to promote exchanges of matter.

3.1. Flow of fluids in packings

Pressure loss: The study of the flow of two fluids in countercurrent through a bed of particles has been the subject of a great deal of work. If, in a packed column, the gas flow rate is gradually increased while leaving the liquid flow rate fixed, the pressure drop ΔP suffered by the gas is growing.

For a zero liquid flow rate, the variation of the head loss ΔP as a function of the gas flow G can be represented by a straight line in logarithmic coordinates. For a given liquid flow rate, the variation has the same rate for fairly low gas flows; although higher than that obtained in the absence of liquid, the pressure drop is

roughly proportional to the square of the gas velocity. It has been observed that under these conditions the retention of the liquid in the filling is more or less independent of G and depends only on the liquid flow rate L . For a certain value of G one observes a change in the curve representing the evolution of ΔP (point A in figure 6); the slope of the line becomes more abrupt. The friction of the gas is then sufficient to hinder the descent of the liquid, causing an increase in liquid retention, which, in turn, reduces the free space available for the gas to flow. This discontinuity, which is sometimes difficult to observe in the evolution of ΔP , corresponds to what is known as the load point of the column.

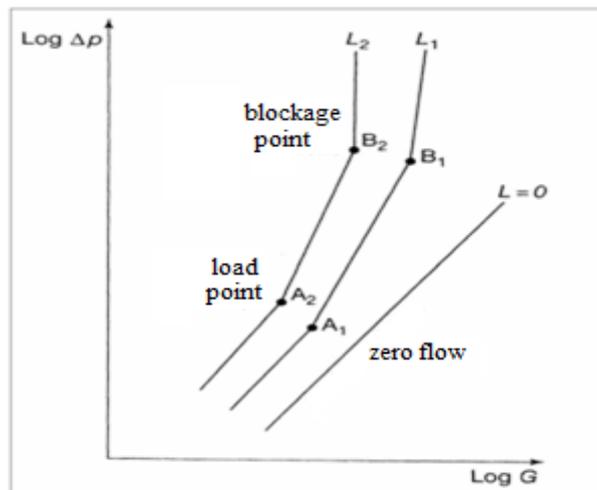


Fig.6. Evolution of the pressure drop as a function of the gas and liquid flow rates in a packed column [12].

The variation in pressure drop below the load point through Raschigou Pall ring beds, or Berlou Intalox saddles can be calculated using the following empirical formula, proposed by Leva (1953) [13] :

$$\Delta P = \alpha \times 10^{\beta L'} \times \frac{G'^2}{\rho_G} \quad (3)$$

In which:

- L' , G' : are the mass flow rates of liquid and gas per unit area of cross-section of the column ($\text{Kg} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$)
- ρ_G : Density of the gas ($\text{Kg} \cdot \text{m}^{-3}$)
- α and β : Characteristic constants of the lining

3.2. Packing capacity

With respect to predicting congestion limits, a number of empirical correlations have been proposed. The most widely used are derived from the correlation established by Sherwood et al. as early as 1938 [14] for bulk ring linings, and taken up by Eckert (1970) [15]. This correlation allows the calculation of the gas velocity at the bottleneck using a graphical relationship between the two groups:

$$A = \frac{U^2 \times a_p \times \psi}{g \epsilon^3} \left(\frac{\rho_G}{\rho_L} \right) \mu_L^{0.2} \quad (4)$$

$$B = \frac{L}{G} \sqrt{\frac{\rho_G}{\rho_L}} \quad (5)$$

In which the terms have the following meanings:

- U : Gas velocity at the bottleneck in the column assumed to be empty ($m.s^{-1}$)
- α_P : Specific surface area of the lining (m^{-1})
- g : Acceleration of gravity ($m.s^{-2}$)
- ε : Vacuum fraction of the filling (-)
- L : Liquid mass flow rate ($kg.s^{-1}$)
- G : Gas mass flow rate ($kg.s^{-1}$)
- μ_L : Viscosity of the liquid (cPo)
- ψ : Corrective term for viscous liquids with a density different from that of water.

3.3 Calculation of the operating point of the column

The dimensioning of a separation column is a delicate problem because of the high investment that such a device represents. As a general rule, first the diameter and then the height of the column are determined. Calculation of the diameter is based on the value of the desired flow rate for the installation. We have seen previously that for a given lining there is a relationship between the maximum flow rates that can flow through the spine without clogging.

The correlations published in the literature in the form of abacus allow us to estimate the gas velocity at bottleneck for a given column. Commonly used best practices adopted, the operating value is a gas velocity of the order of from 50% to 80% of the speed at the bottleneck. Knowing the flow rate and the speed of the gas, it is then easy to deduce the diameter of the column. The calculation of the height of the column is more complex and uses the following concepts of a theoretical tabletop or transfer unit [16].

- **Notion of transfer unit**

To describe how the column works we will make the following simplifying assumptions:

- The solubilities of the diluent in the solvent and the solvent in the diluent are negligible and only the solute (CO_2) is transferred from one phase to the other;
- The steady state flow and material transfer regimes established;
- The transfer operation is isothermal;
- The solutions are highly diluted and therefore the density of each phase can be considered constant.
- The molar flow of the solute Φ entre the two phases results in a variation continuous solute molar fractions (x, y) in each phase throughout the entire the column. Nevertheless, we will consider that we are in the presence of the phases sufficiently diluted and we will assume that the molar flow rates remain constant all the way down the column [17].

$$HUT_G = \frac{G}{A.S.K_G} \quad ; \quad HUT_L = \frac{L}{A.S.K_L} \quad (6)$$

$$NUT_G = \int_{y_s}^{y_e} \frac{dy}{y - y^*} \quad ; \quad NUT_L = \int_{x_e}^{x_s} \frac{dx}{x^* - x}$$

$$L_0 = L_s = cte = L$$

$$G_0 = G_s = cte = G \quad (7)$$

Between the bottom of the column and any section at dimension z the solute balance equation is written:

$$G.y_e + L.x = G.y + L.x_s \quad (8)$$

$$\frac{L}{G} = \frac{y_e - y}{x_s - x} \quad (9)$$

The solute balance on a column element of thickness dz can be obtained by deriving the previous expression:

$$G.dy = L.dx = dN \quad (10)$$

dN : represents the solute flow transferred from one phase to another in the volume range $S.ds$, S represent the area of the right section of the column. These equations could also have been obtained by explicitly writing the balance of the inflows and outflows of this volume element.

The solute flow dN is proportional to the exchange area A between phases (in $m^2.m^{-3}$) and to a difference in titre, which is the driving force of the transfer; the proportionality coefficient is a transfer coefficient, which is a measure of the ease with which the transfer takes place. Thus, if we reason about the gaseous phase [17]:

$$dN = k_G(A.S.dz)(y - y_i) \quad (11)$$

And on the liquid phase:

$$dN = k_L(A.S.dz)(x_i - x) \quad (12)$$

$(y - y_i)$ ($x_i - x$) the driving forces in each of the 2 phases. The products $K_G(A.S.dz)$ and $K_L(A.S.dz)$ are the transfer conductances in the 2 phases. But we don't know the compositions at the interface x_i and y_i . So we reason on all the 2 phases, by posing:

$$dN = K_G(A.S.dz)(y - y^*) \quad (13)$$

$$dN = K_L(A.S.dz)(x^* - x) \quad (14)$$

$x^*(y)$ is the mass fraction of a liquid phase which would be in equilibrium with the gaseous phase of composition; likewise $y^*(x)$ represents the titre of a gaseous phase which would be in equilibrium with the liquid of composition. The differences $(y - y^*)$ and $(x^* - x)$ represent the deviations from the thermodynamic equilibrium evaluated on the whole of the 2 phases [17].

$$dz = \frac{G}{A.S.K_G} \frac{dy}{y - y^*} = \frac{L}{A.S.K_L} \frac{dx}{x^* - x} \quad (15)$$

The height of the column can be expressed as:

$$Z = HUT_G \times NUT_G = HUT_L \times NUT_L \quad (16)$$

4 Conclusion

Our work consisted in dimensioning a packed column that had to be designed to purify a gaseous effluent of a polluting gas (CO₂) responsible for a large part of global warming. This study was limited to determining the diameter of the column and calculating the height of the packing bed for a flow rate of gas to be treated and the required CO₂ concentrations at the inlet and outlet of the column. The numerical values of all the parameters used were taken from a real industrial case. The results obtained allow us to conclude that the calculated diameter of the column is acceptable and meets the manufacturing requirements and that the calculated height of the column is acceptable and meets the manufacturing requirements, and that the calculated height of the column is also admissible and meets international standards.

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