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Development of a Decarbonation System for a Confined Space

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The objective of this work was to develop a compact decarbonation system for a confined space and to evaluate the post-combustion capture performance of selected solvents: MEA (Monoethanolamine), MDEA (N-methyl-diethanolamine) and K_2CO_3 (potassium carbonate). Dimensioning of the absorption columns for each solvent was performed by integrating the appropriate kinetic schemes into Aspen Plus™ in order to proceed with a detailed optimization of the decarbonation system, especially in terms of CO_2 percentage, energy requirements and system compactness. The results have shown that high solvent flow rates lead to energy overconsumption and low lean loading rates lead to high power consumption. In consequence, the CO_2 capture method using a high lean loading rate appears to be the best solution. The concentration of the solvent at the outlet of the washing column has shown to be negligible. From a system efficiency point of view, the MEA seems to be the best solution for a decarbonation system in the case of a confined space.

1. Introduction

In order to ensure the elimination of CO_2 accumulated in a confined space, essentially produced by the breathing of personnel, a decarbonation system must be deployed. The objective is to maintain a maximum of 0.5 % CO_2 in the atmosphere of the place of confinement. There are several constraints to consider for such purpose imposing the use of products and processes that have no impact on health. For instance, the carcinogenic, mutagen reprotoxic products shall be avoided - where eventually a leak detection system must be installed in addition to an output condenser system acting as a second barrier. The systems must be compact because of the limited space with limited energy sources.

The most widely used method for CO_2 capture is chemical absorption (Gonzalez-Garza et al., 2009). Plenty of research has been conducted either to minimize the cost of the capture process (Toro-Molina and Bouallou, 2013), or to recover the captured CO_2 in other forms such as methanol (Van-Dal and Bouallou, 2012) or ethanol (El Fouih and Bouallou, 2013).These solvents are also required to generate the least possible degrading products, especially when these products are toxic (Boulmal et al., 2017). The objective was therefore to develop a compact confined space decarbonation system and to evaluate the post-combustion capture performance of the selected solvents.

CO_2 absorption by a chemical solvent is based on the formation of a new component by reacting the CO_2 with the solvent. The solvent is thereafter regenerated in a regeneration column in which the reaction between the CO_2 and the solvent is reversed by supplying heat. Monoethanolamine (MEA) and methyldiethanolamine (MDEA) are the two main amines used. The first one allows faster CO_2 reaction kinetics and the second has a high absorption capacity (1 mole of absorbed CO_2 per mole of MDEA). There are other separation methods by using carbonate solutions such as potassium carbonate (K_2CO_3).

The effectiveness of any amine for absorbing CO_2 is mainly due to its alkalinity, although a number of chemical reactions can occur in solution. The degree of substitution of the nitrogen atom in the alkanolamine also has an impact on its physicochemical properties. For example, the vapor pressure of alkanolamines decreases as the degree of substitution of nitrogen increases. However, a high vapor pressure leads to significant losses by evaporation. On the other hand, amine's basicity also plays a role. The primary alkanolamines, such as MEA, are the strongest bases and therefore the most reactive with CO_2. Primary alkanolamines are also the most difficult to regenerate because of their high reactivity. Indeed, the heat of reaction between the acid gases and

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the primary alkanolamines is 25 times higher than the one with the secondary alkanolamines, resulting in significant energy expenditure for regenerating the solution. The chemical stability of the alkanolamine is also an important point. It characterizes the ability of the compound to resist chemical degradation especially caused by oxygen.

As a result, the overall properties required for a solvent to be used for CO_2 absorption are: high solubility, low saturated-vapor pressure which limits solvent losses, high selectivity, chemical stability, low viscosity limiting the pressure drop in the system, low corrosivity, non-toxicity, non-flammability, low price and ease of supply, and high loading (Boulmal et al., 2017). The loading refers to the amount in moles of CO_2 absorbed (n_{CO2}) per mole of solvent solution ($\propto_{CO_2} = \frac{n_{co_2}}{n_{solvent}}$).

Zhao et al. (2009) studied the CO_2 absorption with K_2CO_3 solutions, the choice was justified by its great solubility in water compared to Na_2CO_3. K_2CO_3 solubility in water allows the use of high solvent concentrations, leading to a better absorption capacity without precipitation problems. A solution concentration of 2.77 mol.L^{-1} (i.e. 30 wt %) of K_2CO_3, which is the typical concentration used for CO_2 absorption was used. It was determined that K_2CO_3 absorbs NOx, shows a substantial reduction in CO_3^{2-} and results in an increase in HCO_3^- concentration. The implication of this phenomenon for CO_2 capture results in a substantial reduction in CO_2 absorption capacity.

The solvents used in this work are MEA, MDEA and K_2CO_3. These solvents were established due to their absorption capacity, their low carbon reaction rate and, their low toxicity. The objective was to study the decarbonation of CO_2 from the air contained in a confined space. The maximum allowed CO_2 concentration in air was set to 0.5 %.

2. Simulation of the decarbonation process

A series of simulations of the CO_2 capture process using MEA, MDEA and K_2CO_3 solvents was conducted. The simulations were performed using Aspen Plus™ software which is built around a sequential modular architecture.

2.1 Thermodynamic model

The choice of the appropriate thermodynamic model was a decisive decision in the accuracy of simulation results. The chosen model was used to evaluate the thermodynamic and transport properties which include enthalpy, entropy, Gibbs free energy and viscosity, diffusion coefficient, and surface tension (Chen and Evans, 1986). Thermodynamic models are based on equations-of-state, which are represented using a mathematical expression that shows the relationship between temperature and pressure conditions, the volume occupied and the amount of material for a pure compound or mixture. For acid gas absorption, like CO_2, the recommended thermodynamic model is the NRTL electrolyte model (Chen and Song, 2004). This model was chosen to represent the CO_2-solvent-H_2O system considering the presence of polar molecules (as for the case of water) and electrolytes.

2.2 Description of the decarbonation process

The airflow in the studied confined space is represented as a feed stream AIREIN in Figure 1. AIREIN is compressed to a pressure of 1.2 bar in a first step (COMP1), in order to limit the losses in the absorption process. This stream is then passed upward through the absorption column (ABSORBER), in counter current to the solvent stream fed at the top of the column. The CO_2-enriched solvent leaving the bottom of the absorption column is pumped out there from PUMP and sent to an economizer exchanger (B2). This heat exchanger allows heating-up the rich solvent solution to the temperature of the regeneration column, between 363 and 373 K; while cooling-down the lean solvent leaving the bottom of the regeneration column. The purified air, leaving the absorber, is thereafter washed with water for removing any solvent residue. On the other hand, the solvent is regenerated in the regeneration column (STRIPP) by supplying heat (regeneration pressure of 2.1 bar). This regeneration step allows lowering the loading rate to a poor loading rate value (α_{poor}) and to return the solvent to the absorption column. The lower the loading rate is set, the more expensive the regeneration is in terms of steam needed. The stream recovered at the top of the regeneration column (CO_2 + H_2O + solvent) is cooled-down and sent to a phase separator (FLASH). The recovered liquid stream is returned to the regeneration column, while the gas mainly composed of CO_2 is then compressed to 50 bar (5 MPa) in a compressor (COMP2) and finally removed from the confined space.

Two case studies are reported in this article. A first case (Case 1) of 40 people where the air volume of the place of confinement is between 1,000 m^3 and 1,500 m^3 and, a second case (Case 2) of 130 people where the air volume is between 7,000 m^3 and 8,000 m^3. On average, a person uses 15 m^3 of air-per-day.

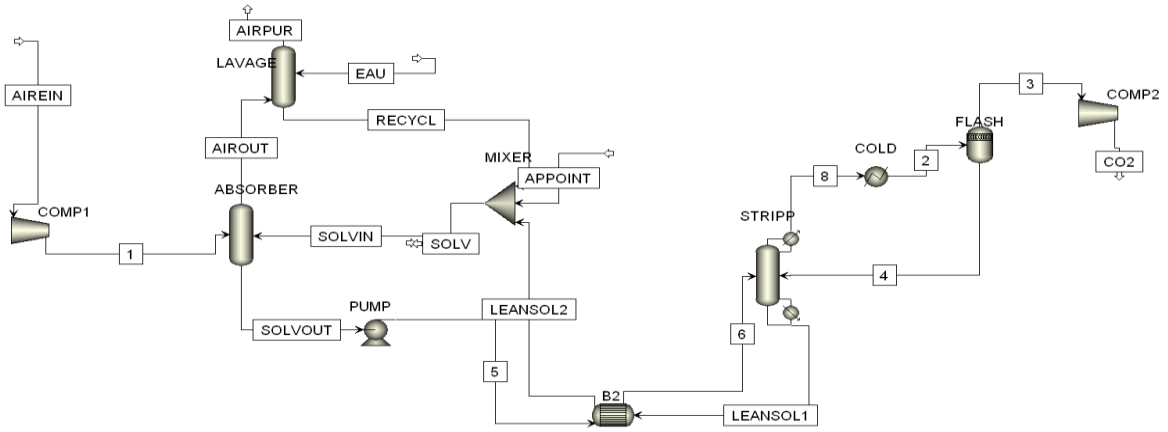

Figure 1: Diagram of the decarbonation process

The characteristics of the inhaled and exhaled air as well as the characteristics of the air entering the decarbonation system are presented in Table 1.

Table 1: Characteristics of inspired and expired air (Case 1)

		Composition of inhaled air	Composition of the exhaled air	Confined space (case 1)
Composition in mol %	H_2O	1.4	1.4	1.4
	CO_2	0.038	4.0	0.5
	O_2	20.7	17.5	21
	N_2	77.9	77.1	77.1
Pressure (bar)			1	1
Temperature (K)			298	298
Flow rate ($m^3.s^{-1}$)			0.01	0.05

3. Results

The influence of pollutants on the CO_2 absorption was examined. Table 2 presents the pollutants existing in the confined space. The concentrations of pollutants in the air were increased from 10 to 1,000 % in order to evaluate the possibility of disturbances in the decarbonation process. The CO_2 absorption shows no significant change with the introduction of pollutants. The pollutants do not react with any tested solvent (MEA, MDEA and K_2CO_3). Moreover, the energy demand of the process does not vary. A sensitivity analysis was performed to optimize the decarbonation process. Increasing the flow rate leads to an increase of the amount of CO_2. A flow rate of 8.33 x 10^{-6} $m^3.s^{-1}$ was selected in the case of the MEA, 41.67 x 10^{-6} $m^3.s^{-1}$ for the MDEA and 44.44 x 10^{-6} $m^3.s^{-1}$ for the K_2CO_3.

Table 2: Pollutants found in the confined space

Compound	Concentration (10^{-6} $kg.m^{-3}$)	Molar Mass ($kg.mol^{-1}$)	Concentration (ppmv)	Mole % ($mol.mol^{-1}$)
Freon R134a	20	0.10204	5	0.0005
Ethanol	20	0.04607	10	0.001
Methanol	1	0.03204	1	0.0001
Phenol	0.5	0.09411	0.13	0.000013
Acetone	2	0.05808	0.83	0.000083
1, 3, 5 -trimethylbenzene	1.0	0.12019	0.2	0.00002
Ethyl acetate	1.0	0.88105	0.275	0.0000275
Cyclohexane	3	0.84160	0.86	0.000086

For Case 1 - confined space, the determined optimal loading rates were used for Case 2. Thus, for the process using MEA, a poor loading rate of 0.2 was used for the solvent, a loading rate of 0.05 for the case with MDEA and, a loading rate of 0.3 for K_2CO_3.

Table 3: Configuring Absorption and Regeneration Columns

absorption column		
MEA	MDEA	K_2CO_3
Structured packing IMTP # 40	Glitsch Ballast Tray	Mellapak 350Y Packing
Diameter 0.2 m	Diameter 0.2 m	Diameter 0.2 m
Height 1 m	Height 1 m	Height 1 m
regeneration column		
Structured packing IMTP	Structured packing IMTP	Structured packing IMTP
Diameter 0.1 m	Diamètre 0.1 m	Diameter 0.1 m
Height 0.5 m	Height 0.5 m	Height 0.5 m

It was important to define the amount of solvent to be used for the decarbonation system in order to predict the size of the recovery tank for the future removal of the solvent. The amount of solvent needed was estimated, taking into account the residence time of the liquid in the absorption column. For predicting the residence time, it was necessary to determine the liquid velocity in the absorption column and the packing height of the column. The established residence time is multiplied by the amount of solvent flow rate. A tank of at least 50 x 10^{-3} m^3 is required to store the solvent. Table 4 presents the results obtained for the 3 solvents in Case study 1.

Table 4: Simulation results Case 1 confined space

Solvent	MEA	MDEA	K_2CO_3
Solvent Concentration (wt %)	30	50	30
Poor loading (mol CO_2 /mol solvent)	0.2	0.05	0.3
Solvent flow rate (10^{-6} $m^3.s^{-1}$)	8.33	41.67	44.44
Solvent Concentration in the air	Traces	Traces	-
Air Compressor (W)	1299	1299	1299
Pump (W)	0.85	12.25	13.42
Condenser (W)	2,036	340.35	570.66
Power required to regenerate the solvent (W)	3,362.05	1,968.56	3550

Increasing the flow rate leads to higher amount of CO_2 absorbed. Nevertheless, high flow rates also increase the thermal power required for the solvent regeneration. A compromise must be made to absorb an optimal amount of CO_2 without increasing energy consumption. This compromise corresponds to a flow rate of 67 $kg.h^{-1}$ (18.05 x 10^{-6} $m^3.s^{-1}$). Similarly, even though an increase in the MDEA or K_2CO_3 solvent flow rates are beneficial for the CO_2 absorption, the amounts of solvent to be used in the case of MDEA and K_2CO_3 are greater than in the case of MEA solvent because of the low reactivity of these two solvents. The solvent flow rates required to absorb CO_2 are 310 $kg.h^{-1}$ (83.33 x 10^{-6} $m^3.s^{-1}$) for MDEA and 350 $kg.h^{-1}$ (93.05 x 10^{-6} $m^3.s^{-1}$) for K_2CO_3.

Table 5: Influence of the loading rate

	MEA		
Solvent concentration (wt %)		30 wt %	
Poor loading (mol CO_2 /mol solvent)	0.15	0.2	0.25
Solvent flow rate (10^{-6} $m^3.s^{-1}$)	14.72	18.06	22.22
Power required for solvent regeneration (W)	11,691.37	7,341.75	5,562.94

The effects of the low loading rate on the solvent flow rate and the regeneration heat were evaluated. The conclusions, relating to the MEA case, can be applied to the MDEA and K_2CO_3 cases. Various sensitivity studies have demonstrated that the solvent flow rate decreases as the loading rate does. This is explained by the fact that the absorption capacity of the solvent increases (rich rate - poor rate). On the other hand, the power required to regenerate the solvent increases with a decrease in the low CO_2 loading rate (Table 5).

For the process using MEA, a lean loading rate of 0.2 was retained. This optimum value corresponds to a compromise between the solvent flow rate and the energy expenditure necessary for the regeneration. For the MDEA solvent, the value of the used loading rate is 0.05, while for the K_2CO_3 it is 0.3.

Furthermore, increasing the packing height of the absorption column was identified to be beneficial for the process. The CO_2 molar fraction decreases with the height of the packing. However, from a certain height, the variation becomes negligible. A packing height of 1.6 m for the MEA-based solvent and 1.7 m for the MDEA-based solvent and the K_2CO_3 solvent were selected. The amount of solvent leaving the washing column was

reduced to traces. Table 6 shows the different configurations used for each solvent in order to model the absorption column.

Table 6: Configuring Absorption and Regeneration Columns Case 2 confined space

Absorption Column		
MEA	MDEA	K_2CO_3
Structured packing IMTP # 40	Glitsch Ballast Tray	Mellapak 350Y packing
Diameter 0.35 m	Diameter 0.30 m	Diameter 0.30 m
Height 1.6 m	Height 1.8 m	Height 1.8 m
Regeneration Column		
Structured packing IMTP	Structured packing IMTP	
Diameter 0.10 m	Diameter 0.10 m	
Height 0.7 m	Height 0.7 m	

The amount of solvent to be used in the Case 2 is greater than that of Case 1. A container of at least 41.67 x 10^{-6} $m^3.s^{-1}$ is required to store the solvent. Table 7 presents the results obtained using the 3 solvents for the Case 2.

Table 7: Simulation Results for the case study 2 - confined space

Solvent	MEA	MDEA	K_2CO_3
Solvent concentration (wt %)	30	50	30
Poor loading (mol CO_2 /mol solvent)	0.2	0.05	0.3
Solvent flow rate (10^{-6} $m^3.s^{-1}$)	18.5	83.33	93.05
Solvent concentration in the air	Traces	Traces	-
Compressor (W)	4,331	4,331	4,331
Pump (W)	1.84	140.19	30.16
Condenser (W)	3,474	3,074	3,067
Power required to regenerate the solvent (W)	7,341.75	4,562.57	7,380

Table 8: Results of MEA simulations for the case study 1 - confined space

Solvent	MEA		
Solvent concentration (wt %)	30 wt %		
Poor loading rate (mol CO_2 /mol solvent)	0.15	0.2	0.25
Solvent flow (10^{-6} $m^3.s^{-1}$)	8.05	8.88	9.72
Make-up solvent flow rate (10^{-3} m^3/year)	< 2		
Energy consumption			
Compressor (W)	180.44	180.44	180.44
Pump (W)	2.5	2.7	2.98
Heat Exchanger (W)	1,276	1,513	1,526
Reboiler (W)	6,596	3,964	2,677
Condenser (W)	4,900	1,900	710
Total energy consumption (W)	12,954.94	7,560	5,096
Total optimized energy consumption (W)	11,678.94	6,047	3,570

For Case 1 (40 people) the CO_2 concentration at the inlet of the decarbonation system has been increased. The air characteristics of the confined space are those of exhaled air (Table 2). The results of the simulations are given in Tables 8 and 9. These simulations are shown as a matter of example, in order to evaluate the energy consumption and the flow rates of the solvents tested. For the safety of people in the confined space, the CO_2 concentration cannot increase beyond 0.5 % volumetric or molar.

Table 9: Results of MDEA and K_2CO_3 simulations Case 1 confined space

Solvent	MDEA			K_2CO_3
Solvent concentration		50 wt %		25 kg.m^{-3}
Poor loading (mol CO_2 /mol solvent)	0.05	0.07	0.09	0.3
Solvent flow (10^{-6} m^3.s^{-1})	41.67	41.67	41.67	36.11
Make-up Solvent flow rate (10^{-3} m^3/year)		1.49		
Energy consumption				
Air Compressor (W)	220.07	220.07	220.07	135.00
Pump (W)	11.2	11.2	11.2	11.03
Heat Exchanger (W)	8,388	9,647	7,823	8,172.87
Reboiler (W)	3,184.2	1,087.8	1,994.31	3,550.00
Cold Heat Exchanger (W)	413.83	461	239.62	569.20
CO_2 Compressor (W)	201.5	180.42	155.32	100.00
Total energy consumption (W)	12,418.7	11,607.49	10,443.52	12,538.1
Total optimized energy consumption (W)	4,009.69	2,960.49	2,620.52	4,365.23

As shown in Tables 8 and 9, the energy consumption for all solvents has been optimized. The energy optimization is performed by heating-up the cold stream leaving the bottom of the absorption column with the hot stream leaving the bottom of the regeneration column. MEA is the solvent that uses the lowest flow rate, whereas MDEA is the solvent that consumes the least energy. MEA solvent is the best solvent to be used in a confined space. Although its solvent losses are higher compared to other solvents, the recovery of the solution with a washing column has shown to be effective. Moreover, due to the low solvent flow rate used, the size of the column is smaller than if MDEA or K_2CO_3 solvents are used instead. The great disadvantage of the K_2CO_3 solvent is the risk of crystallization. During the reaction between the solvent and CO_2 a salt is produced (potassium bicarbonate) which can solidify. The possible formation of crystals may cause the obstruction of the absorption ducts thus renders the decarbonation system inoperable. In case that MEA solvent is not used, it is recommended to work with the MDEA solvent, because the energy consumption for its regeneration is low.

4. Conclusions

The aim of this work was to model and simulate a CO_2 capture process in a confined space for keeping the CO_2 concentration in the air below 0.5 %. Three types of solvents were used in the study: MEA, MDEA and K_2CO_3. The different simulations have shown that a high solvent flow rate leads to energy overconsumption. Furthermore, if the low loading rate is low, the power consumption will be higher. As a result, the CO_2 capture method using a high lean loading rate appears to be the best solution. The concentration of the solvent at the outlet of the washing column is reduced to traces. From a system efficiency point of view, the MEA seems to be the best solution for a decarbonation system in the case of a confined space.

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