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CHILLED AMMONIA PROCESS EVALUATION FOR CO_2 SEPARATION

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In this study, the chilled ammonia technology was analyzed for diminishing CO_2. Thus, the temperature in the absorption stage of the chilled ammonia method was varied, observing its influences on the CO_2 capture performance and on the thermal heat consumption for solvent regeneration. The number stages of the absorption column are another factor that has an impact on the CO_2 capture method performance. Also, the ratio between the flue gases amount and aqueous ammonia amount was varied for determining the optimal ratio of the technical point of view. It is observed that the optimal solvent temperature was 10 °C for which a minimum energy consumption was obtained.

Keywords: CO_2 capture, chilled ammonia, energy systems, heat duty

1. Introduction

In the context of climate changes, due to the increases of CO_2 concentration in the atmosphere, the Carbon Capture and Storage (CCS) attracts a special analysis. CCS is view as one of the promising ways for reducing CO_2 pollutant [1-3]. Correlate to the International Energy Agency (IEA), fossil fuel combustion provides over 80% of total energy demand worldwide, 29 % of primary energy consumption is represented by coal. Thus, the coal combustion process generates almost 44% of total global CO_2 emissions [4]. Therefore, the CO_2 capture technologies integration into coal-fired energy generation processes is necessary to assure the reduction of CO_2 emissions for minimizing the global warming rate [5, 6].

In this paper, we treated only the capture processes and for that, we assumed that the CO_2 stream respects the conditions for transporting and storing it. There are many capture technologies that were developed for CO_2 separation split into three families according to the place they are integrated: before and after the combustion processes [7,8]. The CO_2 capture using the chemical solutions before the combustion method is ready to be used in the power plants and it is

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considered the most feasible technology for CO_2 separation from the big energy processes [8, 9]. Nevertheless, the main drawback of the CO_2 separation by using amines is the high thermal needs for solution regeneration, which represents over 60% of the whole energy requirements of the CO_2 separation process [10-12]. In the case of energy processes, the thermal energy needs for solvent regeneration reduces the overall power plant performance with 25-40% and consequently to an increase in electricity cost with 70-100% [13,14].

The CO_2 capture process is not only an option for power plants, also it can be integrated in different industrial processes like cement (CO_2 content in flue gases is > 30 mol %) or glass factories. The chilled ammonia process could be easily integrated in the existing power plants but from technical point of view there is 2 major concerns: one is related to the value of the CO_2 certificate and the second is referred to parameters of the flue gases/syngas (CO_2 concentration, temperature and pressure).

Therefore, for reducing the energy consumption associated with the CO_2 capture method, in this paper, the chilled ammonia method was analyzed. The scope of the paper was to determine the energy requested by the ammonia process and to compare it with that one obtained in the chemical absorption method using MEA (30 wt.%).

2. Description of the ammonia method

The aqueous ammonia (NH_3) is considered another possible solvent for CO_2 absorption [15,16]. Compared with monoethanolamine (MEA), the aqueous ammonia has many advantages [15]. The first advantage consists in its higher absorption capacity of CO_2, with a theoretical ratio of 1 mole NH_3/mole CO_2, compared with monoethanolamine which the ratio is 2 mole MEA/mole CO_2. The solvent regeneration in the method with NH_3 uses less heat than in the case of amine-based solvent [16,17]. In the case of NH_3, the thermal energy requirement is based on the CO_2 absorption enthalpy which is 60-80 kJ/mole, smaller than in the MEA case: 80-90 kJ/mole. Another reason for the lower thermal energy demand is that the NH_3 regeneration can be achieved at high pressures, which reduces the heat of water vaporization [17]. Another advantage of NH_3 is its behavior against thermal and oxidative degradation due to the simplicity of its composition and chemical structure between nitrogen and hydrogen. The NH_3 process can simultaneously capture different pollutants, acid gases such as SO_x and NO_x [18]. The CO_2 capture technology based NH_3 has an opportunity to reduce the complexity of the pilot installation by reducing more pollutants (SO_x and NO_x) from the exhaust gases. The main drawback of the NH_3 process consists in its loss during the absorption column considering the high volatility. Although the NH_3 process needs less thermal energy for regeneration than the benchmark case (ethanolamine utilization), the total heat demand associated with the whole NH_3 method makes its implementation inaccessible at commercial scale [19].

The CO_2 absorption process based aqueous ammonia implies physical and chemical phenomena. The reactions that take place in the absorption and desorption column are presented in Table 1.

Table 1

Chemical reactions of the chilled method [15]

Reaction in the absorption column	
Carbamate formation	$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4$
Bicarbonate formation from carbamate hydrolysis	$NH_2COONH_4 + H_2O \leftrightarrow NH_4HCO_3 + NH_3$
Reaction NH_3 with H_2O	$NH_3 + H_2O \leftrightarrow NH_4OH$
Carbonate formation	$NH_4HCO_3 + NH_4OH \leftrightarrow (NH_4)_2 CO_3 + H_2O$
Bicarbonate formation by CO_2 absorption by $(NH_4)_2CO_3$	$(NH_4)_2 CO_3 + H_2O + CO_2 \leftrightarrow 2NH_4HCO_3$
Solids formation	$NH_2COONH_4(aq) \leftrightarrow NH_2COONCH_4(s)$ $NH_4HCO_3(aq) \leftrightarrow NH_4HCO_3(s)$ $(NH_4)_2 CO_3(aq) \leftrightarrow (NH_4)CO_3(s)$
The general reaction of CO_2 separation with ammonia	$NH_3 + CO_2 + H_2O \leftrightarrow NH_4HCO_3 + NH_2COOONH_4$
Mechanism of zwitterion reaction	$NH_3 + CO_2 \xrightarrow{k_1} NH_3^- COO^+$ $NH_3^+ COO^- + CO_2 \xrightarrow{k_{-1}} NH_3 + CO_2$ $NH_3^+ COO^- + B \xrightarrow{k_2} NH_2COO^- + BH^+$ $NH_2COO^- + BH^+ \xrightarrow{k_{-2}} NH_3^+ COO^- + B$
Reaction rate between CO_2 and NH_3	$r_{NH_3-CO_2} = \frac{[CO_2][NH_3]}{(1/k_1) + (k_{-1}/k_1)\left(1/\sum k_8 [B]\right)}$
Reaction rate between CO_2 and OH^-	$r_{OH^- - CO_2} = k_3 [OH][CO_2]$
General reaction rate at CO_2 absorption by NH_3	$r_{general} = r_{NH_3-CO_2} + r_{OH^- - CO_2}$
Reaction in the desorption column	
$2NH_4 + 2HCO_3^- \leftrightarrow 2NH_4^+ + CO_3^{2-} + CO_2 + H_2O$	$\Delta H = 26.88\ kJ/mol$
$NH_4^+ + HCO_3^- \leftrightarrow NH_3 + CO_2 + H_2O$	$\Delta H = 64.26\ kJ/mol$
$NH_4^+ + NH_2COO^- \leftrightarrow 2NH_3 + CO_2$	$\Delta H = 72.32\ kJ/mol$
$2NH_4^+ + CO_3^{2-} \leftrightarrow 2NH_3 + CO_2 + H_2O$	$\Delta H = 101.22\ kJ/mol$

The ammonia method was patented in 2006 by Eli Gal [20]. Firstly, the purpose of this method is to separate the CO_2 at a low temperature. It is mentioned an interval of temperature values from 0°C to 20°C, and usually from 0°C to

10°C. Therefore, flue gases cooling is required before entering into the CO_2 absorption method. The CO_2 capture performance of the chilled ammonia process depends on the flue gases temperature and on the aqueous ammonia temperature. The flue gases could be cooled using water in a closed circuit. The water flow required for cooling flue gases (10 ^{o}C) is 200 kg/h. In this case the water temperature outlet of the heat exchangers is 57 ^{o}C. For reducing the water temperature from 57 to 5 ^{o}C a refrigeration fluid (e.g. r410a.mix) is required. Thus, a mechanical compression in a single stage allow to reduce the water temperature with an efficiency of 4.7. The power of the piston compressor is 2.44 kW. However, the energy required for flue gases cooling wasn't take into consideration in this study. After cooling, the exhaust gases enter in the absorption unit, and as for chemical absorption method using amines, the CO_2 absorption takes place at atmospheric pressure. After CO_2 absorption, the clean flue gases leaves the column on the top and the CO_2 rich solution on the bottom. In the desorption column, the rich solution is regenerated at about 110°C, the CO_2 lean solution is recirculated and cooled before enters in the absorption column. The pure CO_2 leaves desorption column at the top. The diagram of the chilled ammonia process is shown in Fig. 1.

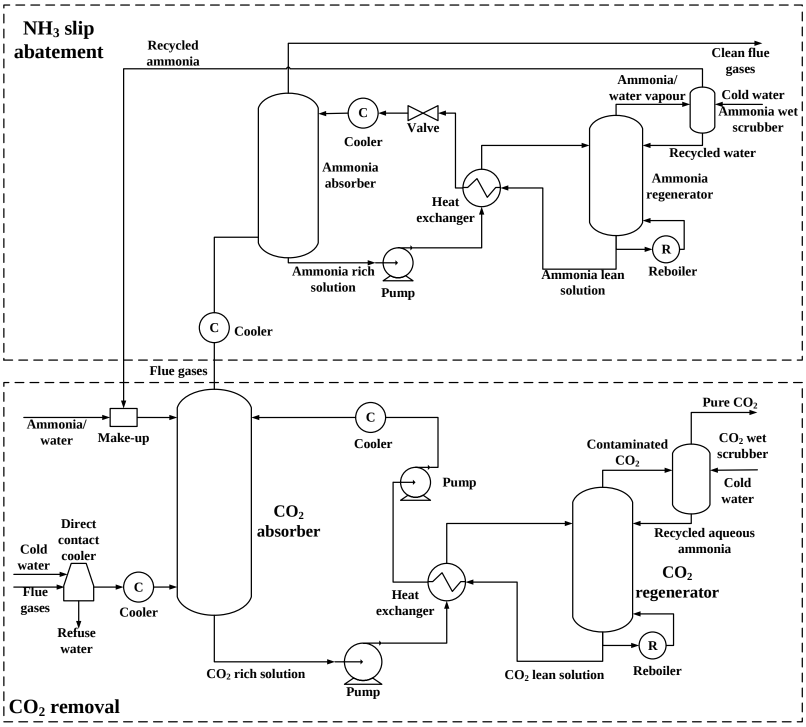

Fig. 1. Schematic diagram of the ammonia method [22]

To maintain a specifically CO_2 capture performance it requires a fresh amount of aqueous ammonia because in the absorption and the desorption methods there are losses. The schematic diagram of the chilled method is divided into two parts: CO_2 removal and NH_3 slip abatement. In this study, we analyzed only the CO_2 removal part. The aim of the NH_3 slip abatement part is to recover the ammonia evaporated in the absorption method.

The CO_2 capture process based on NH_3 was simulated in Aspen HYSYS. The flue gases to be treated are provided from a lignite power plant. The mass composition of the lignite and the composition of the exhaust gases are presented in Table 2. The data used in the simulation are shown in Table 3.

Table 2

Lignite and exhaust gases composition, (wt. %)

Mass composition of coal							
C, [%]	H, [%]	S, [%]	O, [%]	N, [%]	W, [%]	A, [%]	LHV, [kJ/kg]
23	1	1	1.6	1.5	35.5	36.4	7913

Mass composition of exhaust gases		
	Dry flue gases	*Wet flue gases*
CO_2, [%]	12.3	10.4
SO_2, [%]	0.2	0.17
N_2, [%]	80	70
O_2, [%]	7.5	6.6
H_2O, [%]	-	12.93

Table 3

Main data for CO_2 capture process simulation

Parameter	*Value*	*U.M*
Flue gases flow	100	kg/h
Flue gases temperature	10	°C
Flue gases pressure	300	kPa
Aqueous ammonia flow	55...100	kg/h
Ammonia concentration	20	%
Aqueous ammonia temperature	-10...10	°C
Aqueous ammonia pressure	300	kPa
Stages number of absorber	5...11	-
Stages number of stripper	6	-
CO_2 rich solvent temperature at heat exchanger outlet	50...80	°C
CO_2 lean loading solvent	0.26	mol_{CO2}/mol_{NH3}

3. Results and discussion

In this assessment, the CO_2 capture method based on ammonia according to different parameters was analyzed. The CO_2 capture performance depends on the ratio between aqueous ammonia amount and flue gases amount, thus the CO_2 capture performance increased with L/G measure. In Fig. 2 is presented the variation of CO_2 capture performance correlate to the L/G ratio, it is noticed that for an L/G ratio of 1 $mol_{solvent}/mol_{flue\_gases}$ a CO_2 capture performance of 100% was obtained due to the higher amount of solvent available for the same flue gases flow. For smaller L/G, the CO_2 capture performance could be improved by changing the absorption column in order to increase the surface between the liquid and gas interface. However, an increase of the absorber column height generates an increase of the investment cost. In Fig. 3, the influence of the surface in the column on the energy consumption and the lean loading solvent is presented. In this assessment, the energy consumption was determined as the sum of the heat energy and electricity required for cooling the CO_2 lean solvent before of the absorption column. Considering the CO_2 capture process performance constant, a higher surface in the absorber column led to reducing the energy consumption due to the smaller amount of solvent flow. For comparing the thermal energy consumption, it is assumed that the lean solvent has approximately the same CO_2 concentration. To keep constant the CO_2 concentration in the regenerated solvent, the thermal energy was varied. The lean loading solvent is considered approximately 0.26 mol_{CO2}/mol_{NH3} [21]. A smaller value of the CO_2 concentration in the regenerated solvent allows to increase the heat consumption while a higher value permits to increase the amount of the solvent flow for maintaining the same CO_2 capture process performance.

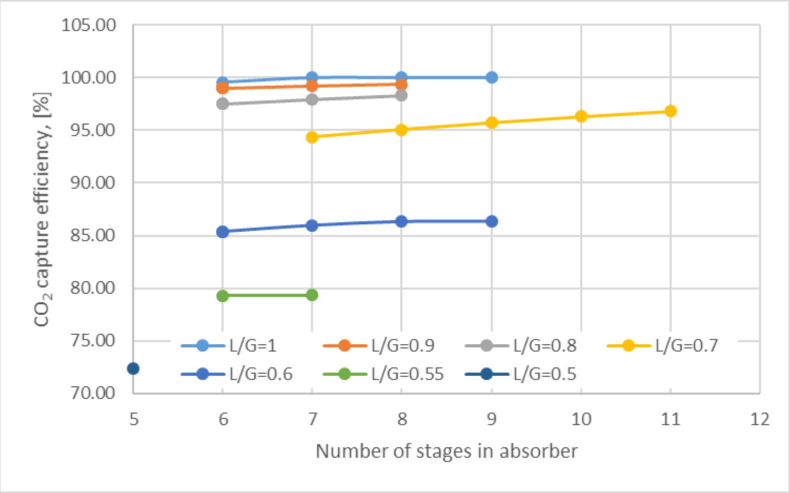

Fig. 2. CO_2 capture performance according to the absorber surface and L/G measure

The CO_2 rich solvent temperature at the inlet in the stripper unit has a sensible impact on the chilled ammonia method energy consumption. The heat exchanger optimization (see Fig. 4) has a huge benefit for minimizing the thermal energy consumption, taking into account that the lean solvent temperature at the absorption column inlet is low (-10…10°C). According to the solvents temperature at the exit of the stripper column and absorption column respectively, the maximum temperature of the solvent at the heat exchanger outlet was 80°C. In the present study, the heat energy consumption was reduced from 4.5 to 3.1 GJ/tCO_2.

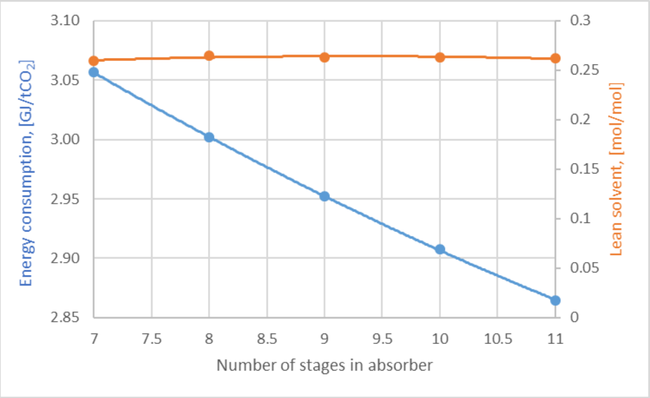

Fig. 3. Heat energy according to the absorber surface

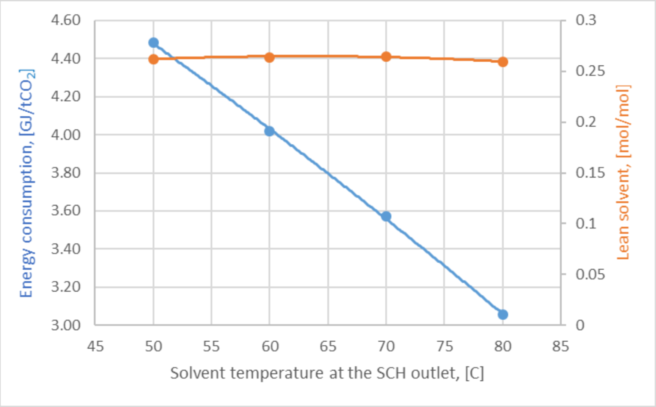

Fig. 4. Energy consumption according to the solvent temperature at the HEx outlet

The aqueous ammonia temperature in the absorption method influences both the CO_2 capture performance and the energy consumption of the method. We analyzed three cases considering three temperatures for the aqueous ammonia: -10, 0 and 10°C. In Fig. 5 and 6 there are presented the results obtained for CO_2 capture performance and energy consumption. For higher L/G (>1), the CO_2 capture process performance tends to 100% irrespective the lean solvent temperature due to the high amount of solvent compared with the amount of flue gases. For L/G ratio smaller than 1 the CO_2 capture process performance decreases, faster for the solvents with a higher temperature at the inlet in the absorber column.

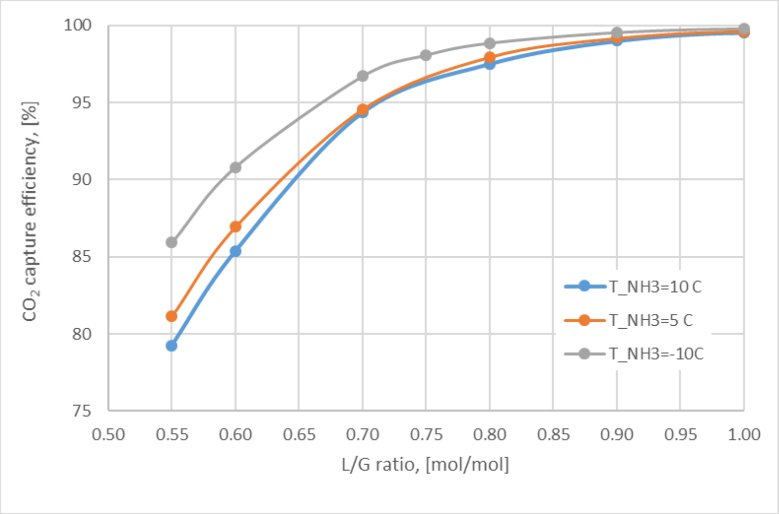

Fig. 5. CO_2 capture performance correlate with L/G and temperature of NH_3

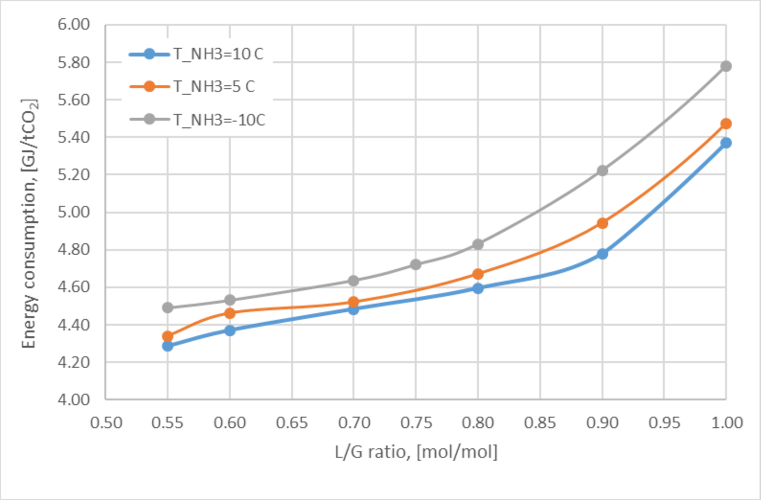

Fig. 6. Energy consumption correlate with L/G

As regarding the energy consumption (see Fig. 6), a lower value for the solvent temperature at the inlet absorber column led to increases the energy consumption due to the heat needs for cooling the solvent before the absorption column. In this context, an optimization of the heat exchanger is required for establishing the solvent temperature at the outlet of the HEx. Thus, two cases were analyzed: considering 50 and 80°C. For the first case, a lower electricity is required for cooling the NH_3 solution before the absorption column while in the second case a lower energy consumption is needed for heating the solution before the stripper unit. In Figure 6, the energy consumption evaluation is presented for the solvent temperature at the outlet from HEx of 50°C. Figure 4 is noticed that the energy consumption is reduced from 4.4 to 3.1 when the solvent temperature at the outlet from HEx is increased from 50 to 80°C.

4. Conclusions

The chilled ammonia process for CO_2 separation can be an alternative solution for chemical absorption process based on alkanolamines. The aqueous ammonia is characterized by a higher value for acid gases absorption and lower values for heat and electricity consumption according with the ethanolamine method. The streams temperature in the process influences both the CO_2 capture performance and the electricity and heat used. In addition, the column surface and the temperature of the CO_2 solvent at the heat exchanger outlet have an impact both on the CO_2 capture performance and energy consumption. Consequently, more researches should be done to find the optimal solution for CO_2 capture post-combustion and its integration at large-scale, also an economic analysis is required.

In this study we have used the software Aspen Hysys for process simulation. Thus, we simulated only the chilled ammonia process and not the its integration in an energy process. We have chosen not to study the energy integration of the chilled ammonia due to the fact that this process could be used both in the post- and pre- combustion processes where the syngas pressure could have the required values. For this reason, we do not take into consideration the electricity required for flue gases compression. In terms of energy balance for our case, the energy consumption for compression represents 15% (16 MJ/h) from the all energy required by the all equipment in the chilled ammonia process: cooling (39 MJ/h) and solvent regeneration (50 MJ/h).

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