Energy Proceedings
Vol 33, 2023
ISSN 2004-2965

A low energy consumption ammonia based CO_2 capture process with bipolar membrane electrodialysis

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ABSTRACT

Post combustion capture using chemical absorption is one of the most mature technologies, which can effectively reduce CO_2 emissions from plants. But it usually comes with the cost of high energy consumption. Aiming to reduce the regeneration energy consumption of post combustion CO_2 capture technology, a novel ammonia based CO_2 capture process with bipolar membrane electrodialysis(BMED) and CO_2 regeneration reactor is designed. In the CO_2 regeneration reactor, the CO_2 loaded by rich solvent is completely released and collected due to the reactions between the rich solvent and strong acid. After that, energy consumption of the BMED unit is effectively reduced because there is no bubble formation in the cell during the electrodialysis process. The performance of conventional amine based process and the novel process is evaluated by simulation and calculation. Result shows that the CO_2 regeneration energy consumption of the novel process is as low as 1.80MJ/kgCO_2, which is much lower than that of the conventional process(3.91MJ/kgCO_2). Given the volatilization of the NH_3, the treatments of escaped NH_3 in the novel process is discussed. When the value-added products is considered, sent the escaped NH_3 washing solution to the desulfurization part as absorbent may be a better choice than recovering NH_3 with heating. With the development of the membrane technology, the energy consumption of the novel process will be further reduced. If combined with renewable energy technology, it is expected to be a new CO_2 capture technology.

Keywords: CO_2 capture, aqueous ammonia, bipolar membrane, energy consumption

NONMENCLATURE

Abbreviations	
MEA	Monoethanolamine
BMED	*Bipolar membrane electrodialysis*

1. INTRODUCTION

The rising emission of greenhouse gases, mainly CO_2, has caused climate change and environmental problems. CCUS(Carbon capture, utilization and storage) technologies have been receiving increasing attention. Post combustion CO_2 captured by chemical absorption is considered as the most practical and effective capture technology at present. Monoethanolamine(MEA), K_2CO_3 and aqueous ammonia are the most commonly CO_2 absorbents. Compared to conventional amine based CO_2 capture solvent, aqueous ammonia possesses many advantages, such as low material cost, resistance to thermal degradation and oxidation degradation, and most importantly lower regeneration energy (about 3MJ/kgCO_2)[1].

The main drawback of the ammonia based CO_2 capture process is the high volatility of the NH_3, which leads to the ammonia concentration in the purified flue gas is much higher than the emission standard. Extra equipment and energy consumption are required to recover the escaped NH_3, making ammonia based process has no obvious advantages in energy consumption compared with amine based process (about 4MJ/kgCO_2). Therefore，for the ammonia based CO_2 capture process, two aspects should be considered to reduce energy consumption: regeneration part and escaped NH_3 recovery. For the regeneration part, in addition to the process optimization of conventional

This is a paper for International CCUS Conference 2023 (ICCUSC2023), April 14-15, 2023, Beijing, China.

thermal regeneration, it is also very important to find new schemes with energy saving potential. Bipolar membrane electrodialysis(BMED) is recently considered as an alternative scheme for absorbent regeneration after CO_2 capture[2]. Previous study has shown that direct electrodialysis NH_4HCO_3 solution has low CO_2 recovery and very high energy consumption[3]. Valluri S et al[4] believed that the bubbles existence during electrodialysis in cells is the reason of high energy consumption and designed a process which eliminated the bubble. Results shows that reagent regeneration energy of the new scheme was reduced as low as 1.18MJ/kgCO_2, which is very competitive compared to thermal regeneration. But there are few reports on the energy saving of BMED in ammonia based process. For the escaped NH_3 recovery, water is usually used to capture NH_3 and there are two treatments for washing solution. One is recovering escaped NH_3 by heating the solution[5,6], the other is sending solution to SO_2 scrubbing unit and producing ammonium sulfate fertilizer co-product[7]. However, the compassion of the two treatments are rarely reported, It is necessary to evaluate the two methods so that the escaped NH_3 can be treated more economically.

This paper aims to design a novel ammonia based CO_2 capture process with low energy consumption. The BMED unit and CO_2 regeneration reactor are set for the regeneration part of the process. Simulation and calculation are carried out to compare the conventional amine based process and the novel process. In addition, considering the NH_3 volatilization, treatments of the escaped NH_3 in the novel process are also discussed and compared.

2. PROCESS DESCRIPTION AND MODEL

The flue gas data are shown in the Tbl. 1 , which is derived from the desulfurized flue gas of a catalytic unit in Hebei, China. The SO_2 content of the flue gas is less than 50mg/m^3 so that SO_2 component is ignored in the simulation.

Tbl. 1 Flow rate and composition of desulfurized wet flue gas

Flow rate ($kg \cdot h^{-1}$)	Temperature(K)	Mole fraction of components(%)			
		N_2	H_2O	CO_2	O_2
109430	323.15	75.10	9.00	12.46	3.44

2.1 Process description

Fig. 1 shows the flowsheet of conventional amine based process. The flue gas was introduced into

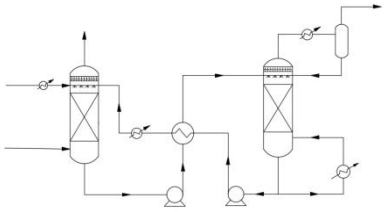
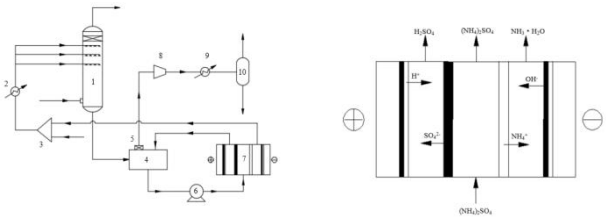


Fig. 1. Flowsheet of conventional amine based process

absorber and most of the CO_2 component was captured. The rich solvent was introduced into stripper by passing the heat exchanger to be regenerated to lean solvent and CO_2 product. The lean solvent was then circulated back to the absorber.

Flowsheet of the novel process is shown in Fig. 2. The BMED unit was set as the regeneration scheme of ammonia based process. Aiming to reduce the regeneration energy consumption, a CO_2 regeneration reactor was set between the absorber and BMED unit of the novel process. The process was initialized by introducing desulphurized flue gas into CO_2 absorber, the flue gas made contact with aqueous ammonia and CO_2 was captured. The vent flue gas was then washed with fresh water to recover the escaped ammonia and discharged into the atmosphere after it was heated. The rich solvent from CO_2 absorber was introduced into the CO_2 regeneration reactor and reacted with strong acid. Through the reactions, CO_2 would be regenerated effectively and rapidly regenerated from the rich solvent, and corresponding strong acid ammonium salt would be generated. The ammonium salt solution discharged from CO_2 regeneration reactor was then sent to BMED unit, in which salt solution would be regenerated into strong acid and aqueous ammonia under the action of electric field. The produced strong acid was recirculated back to CO_2 regeneration reactor and aqueous ammonia was recirculated back to CO_2



(a) (b)

Fig. 2. Flowsheet of the novel process and schematic diagram of BMED unit with three compartments (a)flowsheet of the novel process (b) BMED unit (1)CO_2 absorber, (2,9)cooler, (3)mixer, (5)demister, (6)pump, (7)BMED unit, (8)compressor, (10)separator,

absorber.

2.2 Model validation

Simulation and calculation were performed to evaluate the feasibility of the novel process and its energy saving potential was compared with amine based process with Aspen Plus. Equilibrium model was used in simulation. For the amine based process, Electrolyte NRTL method was used to calculate the liquid phase properties and the Redlich-Kwong equation was used to calculate the fugacity coefficient of vapor phase. The N_2, O_2 and CO_2 were set as Henry's law components. As shown in Fig. 3, the methods are validated against VLE(vapor and liquid equilibrium) data from literatures[8-10]. For the novel process, Pitzer method and Redlich-Kwong equation were used to calculate the VLE data. The N_2, O_2, CO_2 and NH_3 were set as Henry's law components. The reliability of the methods in predicting the thermodynamic properties of the NH_3-H_2O-CO_2 system has been verified in the literature[11].

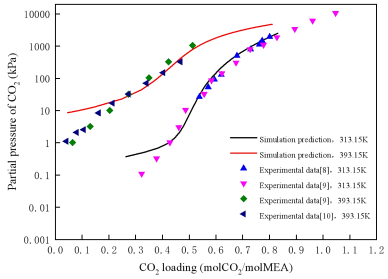


Fig. 3. Model validation of thermodynamic methods for MEA process

3. RESULTS AND DISCUSSION

The amine based process was taken as the basic case, while the CO_2 removal efficiency and regeneration energy consumption were taken as evaluation criteria for process. The original operation condition parameters of the basic case were shown in Tbl. 2. In order to inhibit NH3 volatilization, the concentration and temperature of aqueous ammonia are lower.

Tbl. 2 Original operation parameters of cases

Parameter	Unit	MEA process	The novel process
Concentration of solvent	wt%	25	6
Flow rate of solvent	kg/h	300000	300000
Temperature of solvent	K	313.15	288.15

3.1 Amine based process

3.1.1 MEA concentration

The influence of MEA concentration on CO_2 removal efficiency and regeneration energy consumption is shown in Fig. 4. With the MEA concentration increasing, the CO_2 removal efficiency increases and the energy consumption decreases, which means better system performance. But the oxidation, degradation and corrosion of amine solvent are much more severe with the increase of concentration. Therefore, the concentration of MEA solvent is limited under 30wt.%.

3.1.2 Flow rate of the solvent

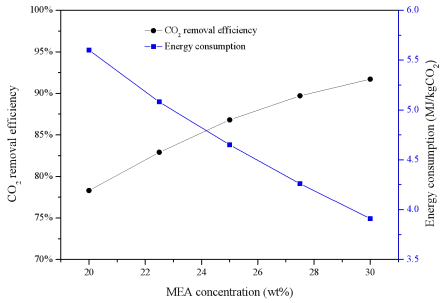


Fig. 4. CO_2 removal efficiency and regeneration energy as a function of MEA concentrarion

The influence of solvent flow rate on CO_2 removal efficiency and regeneration energy consumption is shown in Fig. 5. With the solvent flow rate increasing, the CO_2 removal efficiency increases, and the regeneration energy consumption first decreases and then increases. The minimum regeneration energy consumption of 3.91MJ/kgCO_2 and CO_2 removal efficiency of 91.7% appears when the solvent flow rate is 3.0×10^5kg/h. The solvent flow rate not only affects the performance of the process but also affects the operation of pump and geometric size of the absorption and regeneration equipment[1]. Therefore, the solvent flow rate corresponding to the lower CO_2 regeneration energy consumption is considered as optimized condition and used in following sections.

3.2 Regeneration energy consumption of the novel

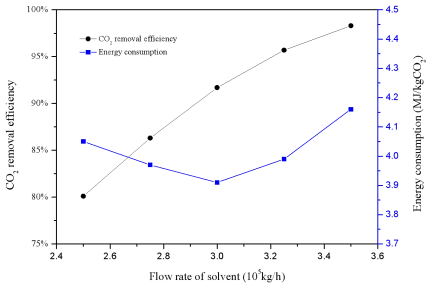


Fig. 5. CO_2 removal efficiency and regeneration energy as a function ofsolvent flow rate

process

Due to the lack of BMED unit module in Aspen Plus, the regeneration energy consumption of the novel process is calculated by combining literatures data with process simulation. The electrodialysis energy consumption of ammonium salts is shown in Tbl. 3. As can be seen from the Tbl., the experimental equipment size, membrane material and operating condition of different ammonium salt electrodialysis research are different. Therefore, the minimum energy consumption data reported in the literatures are used to calculate the BMED unit in novel process. The original unit of energy consumption in Tbl. 3 can be converted to MJ/kgCO_2 by material conservation of strong acid and CO_2 in the CO_2 regeneration reactor. The calculation results show that the energy consumption of direct electrodialysis NH_4HCO_3 is the highest, folllowed by NH_4NO_3, NH_4Cl, and $(NH_4)_2SO_4$ is the lowest. Therefore, H_2SO_4 is set as the strong acid which reacts with rich solvent to regenerate CO_2 in the novel process.

Tbl. 3. Electrodialysis energy consumption of ammonium salt

Salt solution type	BMED configuration	Operation condition	Energy consumption	Ref
NH_4HCO_3	Three compartment	Current density:100A/m^2 NH_4HCO_3 concentration:0.75mol/L	2.21 kW·h/kgCO_2	[3]
NH_4Cl	Three compartment	Current density:80mA/cm^2 NH_4Cl concentration:1mol/L	1.19kW·h/kgHCl	[12]
$(NH_4)_2SO_4$	Three compartment	Current density:15.8mA/cm^2 $(NH_4)_2SO_4$ concentration:0.758mol/L	0.208kW·h/kg$(NH_4)_2SO_4$	[13]
NH_4NO_3	Three compartment	Current density:50mA/cm^2 NH_4NO_3 concentration:2.02mol/L	1kW·h/kgHNO_3	[14]

The rich solvent contains $(NH_4)_2CO_3$, NH_4HCO_3, residual ammonia and intermediate of the absorption recation(mainly NH_2COONH_4, which will react with H_2O and form NH_4HCO_3 and NH_3). These reaction products associated with ammonia need to be fully reacted with H_2SO_4 in the regeneration reactor to ensure the complete recovery of CO_2. Therefore, the energy consumption of the BMED unit in the novel process can be calculated by the ratio of the final constant substance between SO_4^{2-} and NH_4^+,combined with Tbl. 3. Flow rate of NH_4^+-related are provided by process simulation. Fig. 6 shows the CO_2 removal efficiency and escaped NH_3 as a function of 6wt% ammonia solvent. Considering the influence of aqueous ammonia flow rate on pump work, equipment size and ammonia escape amount, the flow rate of solvent in novel process is selected at 2.55×10^{5}kg/h and the flow rate of NH_4^+-related component can be determined by simulation and shown in Tbl. 4.

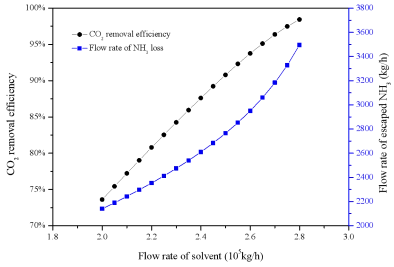


Fig. 6. CO_2 removal efficiency and NH_3 escaping as a function of 6wt% ammonia solvent

Tbl. 4. Flow rate of ammonia-associated component in rich solvent

Component name	Unit	Value
NH_3	kmol·h^{-1}	104.7
NH_4^+	kmol·h^{-1}	456.9
NH_2COO^-	kmol·h^{-1}	126.4

The comparison of the MEA process and the novel process is shown in Tbl. 5. Compared with MEA process, the CO_2 removal efficiency of the novel process is similar, but the CO_2 regeneration energy consumption is significantly reduced, only 46% of the MEA process, which indicated that the novel process shows competitiveness and development potential in energy saving.

Tbl. 5. Comparison of novel process and MEA process

Process	CO_2 removal efficiency	Regeneration energy consumption(MJ/kgCO_2)
MEA process	91.7%	3.91
Novel process	92.3%	1.80

3.3 Economic comparison of escaped ammonia treatment

As mentioned above, there are usually two ways to treat the NH_3 washing solution: recovering NH_3 by heating the solution or using it as desulphurization absorbent. In this section, the former one is set to be scheme No.1 and the latter one is set to be scheme No.2. Both schemes will be evaluated and compared

For the scheme No.1, water at 283.15K is used to wash the flue gas and the NH_3 content in the flue gas after washing is controlled at less than 50ppm. Heat exchanger is set between washing column and NH_3

regenerator to reduce energy consumption. Simulation results show that 1.15×10^5kg/h water is required to absorb the escaped NH_3 and additional energy consumption is 1.52MJ/kgCO_2. The washing solution cannot be directly returned to CO_2 absorber because the concentration is too low to meet the requirement.

For the scheme No.2, the novel process requires continuous supply of aqueous ammonia to keep the CO_2 removal efficiency, which brings additional costs. However, the desulfurization product $(NH_4)_2SO_4$ is valuable, which can make up part of cost caused by aqueous supplement. Tbl. 6 shows the recent prices of related chemical products, combined with simulation results, the economic performance of the two treatments can be evaluated and compared.

Tbl. 6 Recent prices of related chemical products

Chemical substance	Product status	Cost (¥/tons of product)
H_2O	0.4MPa saturated steam	180-220
$NH_3{\cdot}H_2O$	20wt% aqueous ammonia	800-1200
$(NH_4)_2SO_4$	Crystal	1500

The calculation results are converted to the cost of capturing one ton of CO_2. The cost of recovering NH_3 is 143.2¥/tCO_2, the cost of aqueous ammonia supplement is 752.9¥/tCO_2 and the income of $(NH_4)_2SO_4$ product is 828.6¥/tCO_2, which means recovering NH_3 shows much economy than that of aqueous ammonia supplement. However, the $(NH_4)_2SO_4$ product can effectively reduce the gap between the two ways. If 73.7 percent of NH_3 can be converted to $(NH_4)_2SO_4$, the scheme No.2 may be a better choice.

4. CONCLUSION

In order to reduce the regeneration energy consumption of CO_2 capture process , a novel ammonia-base process with bipolar membrane electrodialysis was designed. The simulation and calculation results showed that the regeneration energy of the novel process can be as low as 1.80MJ/kgCO_2, which is much lower than that of amine-base process. The economy of escaped NH_3 treatment ways was also discussed. Given the value of ammonia desulfurization products, it may be a better choice to send washing solution for escaped NH_3 to desulfurization part and continuously supply aqueous ammonia than to regenerate NH_3 with heating.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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