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Recent Trends in the Use of Amine Solvents for Carbon Dioxide Scrubbing Process

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Abstract:
Though carbon dioxide is crucial for life on earth, its extensive release causes a lot of problems like global warming and greenhouse effect. To avoid this, its release into the environment needs to be controlled. Besides this, carbon dioxide has many industrial uses. Hence the process of carbon dioxide scrubbing was brought into picture, in which the carbon dioxide present in the flue gases is scrubbed with the help of liquid solvents. Aqueous amine solvents are commonly used for this process, with primary and secondary amines as the most common choice among the industries. However, due to the large regeneration energy requirements, studies are being carried out on the use of tertiary amines and sterically hindered amines for this process. This work focuses on these solvents, with their merits and demerits, related to the process. From the comparison carried out in this work, it can be seen that the tertiary amines, blended with activators, prove to be a better choice with respect to energy requirements than the pure primary amines.
Keywords: *Carbon dioxide, Amine solvents, Primary, Secondary, Tertiary, Sterically hindered*

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I. Introduction

Energy production, in most places, requires the burning of fossil fuels, which create a huge amount of flue gases. Many of those extraneous emissions are greenhouse gases that contribute to the greenhouse effect. Even though carbon dioxide usually makes up no more than 15 percent of a power plant's emissions by volume, it's responsible for 60% of the greenhouse gas effect. In order to prevent the CO_2 from escaping into the atmosphere, post-combustion carbon capture, also known as carbon dioxide scrubbing works by isolating CO_2 from the other flue gases after combustion. Once the flue gases have been removed, or scrubbed, they're released into the air[1]. Currently, the solvents commonly used are aqueous amines.

Chemical absorption of carbon dioxide (CO_2) into aqueous alkanolamine solutions provide a reversible process for its separation from gaseous streams. CO_2 capture helps in mitigation of greenhouse gas emissions. It is also useful as a flooding agent in enhanced oil recovery. Some other applications are in coal gasification, natural gas processing, ammonia production and urea manufacture[2].
In this work, we studied the various types of amines used for carbon dioxide scrubbing, along with their advantages and disadvantages for the process.

II. Process Description of Carbon Dioxide Scrubbing

Figure 1 illustrates the amine-based carbon dioxide capture process from the flue gas. The flue gas entering the process at close to atmospheric pressure and at the required operation temperature is bubbled through a packed absorber column (amine scrubber) containing a 25 – 30 % aqueous amine solution at high pressures. Amine absorbs carbon dioxide to form a carbamate species, in the case of primary and secondary amines and bicarbonates in the case of tertiary amines. Flue gas exiting the top of the absorber is water washed to reduce the entrained solvent droplets and then vented to atmosphere. Following the absorption process, the rich solvent (high content of carbon dioxide reaction product) passes through a stripping column operating at higher temperature than the absorber in order to release the carbon dioxide in high purity (over 99 %) which may be later compressed for commercial utilization or storage[3].

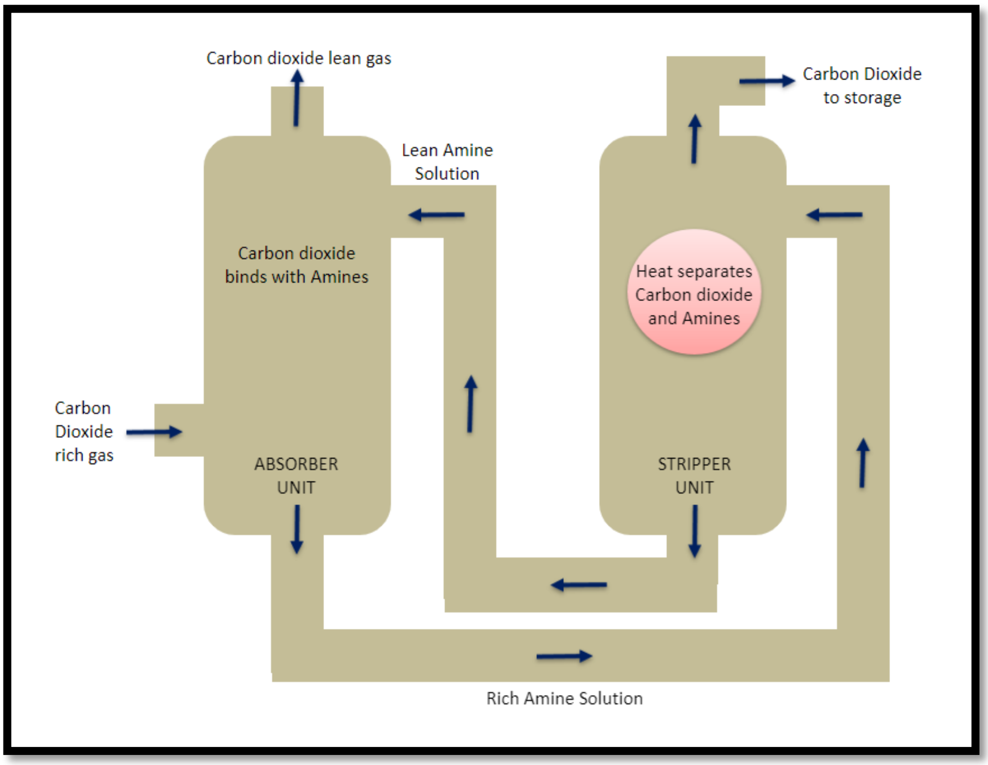

Fig. 1 Carbon Dioxide Scrubbing

III. Amine Solvents for Carbon Dioxide Scrubbing

Aqueous solutions of primary amines, secondary amines, tertiary amines and sterically hindered amines are the solutions used for the chemisorption of CO_2. Studies are still carried out on using aqueous solutions of blended amines, to increase the efficiency of the solvents. They are industrially important and are discussed here.

3.1 Primary Amines

Primary Amines are the ones in which an alkyl or aromatic group replaces one of the three hydrogens of ammonia. The most commonly used primary amine, for the chemisorption of CO_2 is monoethanolamine (MEA).

The MEA process has been considered as the most suitable technique for post-combustion CO_2 capture due to its high reactivity for even low concentrations of CO_2 , such as in flue gases. However, here the CO_2 loading capacity is limited to 0.5 mol/mol of amine[2] and this MEA process consumes a lot of heat energy for solvent regeneration because the MEA solvent is aqueous based. The reboiler heat energy occupies about 80% of the entire energy consumption for CO_2 capture process. In order to reduce the reboiler heat requirement, an advanced configuration of MEA process was suggested which consists of split flow and a phase separation heat exchanger. The split flow permits to reduce the reflux ratio in the stripper and the phase separation heat exchanger permits to alleviate preheating duty loss. As a result, the regeneration energy of the advanced process is reduced[4].

3.2 Secondary Amines

Secondary Amines are the ones in which the alkyl or aromatic group replaces two of the three hydrogens of ammonia. The most commonly used secondary amine, for the chemisorption of CO_2 is Diethanolamine (DEA).

DEA is the most popular secondary alkanolamine used for CO_2 removal. It has several advantages, including high reactivity, low solvent cost, and reasonable thermal stability[5]. DEA is an inexpensive solvent due to its wide use in many industries, and it is especially used for removing CO_2 and H_2S in natural gas, where the selectivity is high and for the reversible reaction process at the absorber column. One of the most common disadvantages is the presence of SO_2 and O_2 in the flue gas, causing solvent degradation. The presence of O_2 in flue gas causes the oxidation of DEA and leads to increased degradation[6]. Also DEA possess the same CO_2 loading capacity as MEA and also consumes a lot of heat energy for solvent regeneration.

3.3 Tertiary Amines

Tertiary Amines are the ones in which the alkyl or aromatic groups replace all three hydrogens of ammonia. The most commonly used tertiary amine, for the chemisorption of CO_2 is methyldiethanolamine (MDEA).

MDEA needs low energy for regeneration due to the acidic gas reaction having a low enthalpy and the high capacity for the absorption of CO_2, which is nearly 1 mol CO_2/mol amine. Also, it is less aggressive, requires a low heat for the reaction with CO_2, is less corrosive, can be used in higher concentrations and has lower circulation rates. However it has slow reaction with carbon dioxide and low absorption capacity when the concentration of carbon dioxide is low[6]. In order to overcome the drawback of low absorption capacity, MDEA is blended with activators, which have affinity towards carbon dioxide. Many a times, these activators are primary and secondary amines which have high absorption capacity, at low concentrations of carbon dioxide. The commonly used activators are MEA, DEA and piperazine (PZ)[2].

Another tertiary amine, which is currently being tested for use in the chemisorption of CO_2, is N, N'-diethylethanolamine (DEEA). It has the same advantages and drawbacks as those of MDEA. Hence, the aqueous blends of this amine with promoters like piperazine, N-ethylethanolamine, hexamethylene diamine, N-(2-aminoethyl)ethanolamine and ethylene diamine have been tested. Of these blends, the DEEA/PZ blends proves to be superior. Two new polyamines, (methylamino)propylamine (MAPA) and diethylene triamine (DETA)are also studied by researchers. Even they have proved to be excellent activators, with DETA being more reactive than MAPA[2].

3.4 Sterically Hindered Amines

A new class of amines with regeneration costs lower than those of conventional primary and secondary amines – sterically hindered amines – has recently received considerable attention. A sterically hindered amine is a primary amine in which the amino group is attached to a tertiary carbon atom, or a secondary amine in which the amino group is attached to a secondary or tertiary carbon atom. 2-Amino-2-methyl-1-propanol (AMP) ($C_4H_{11}NO$) and 2-piperidineethanol (PE) ($C_7H_{15}NO$) are examples of sterically hindered primary and secondary amines, respectively. Due to a large group attached to the nitrogen atom, these amines form carbamates of low stability, thereby resulting in a CO_2 capacity of 1 mol of CO_2 per mol of amine[7].

The amino group of 2-Amino-2-methyl-1-propanol is attached to a tertiary carbon atom. Two additional methyl groups occupy the space around the amino group, in comparison with MEA. The absorption heat of CO_2 with AMP in aqueous solution is lower than that of CO_2 with MEA. AMP is more stable and resistant to solvent degradation and corrosion than MEA. As a result of the steric hindrance, AMP suffers from slow kinetics in comparison with MEA. Even so, the kinetics of CO_2 absorption is faster than for MDEA.

2- Piperidineethanol or PE (C7H15NO) is a sterically hindered secondary amine with a naphthenic group attached to the amino group. It is a promising candidate absorbent for CO_2 capture in terms of both absorption capacity and kinetics. The CO_2 reaction with PE is faster than that with MDEA[8].

IV. Conclusion

Carbon dioxide, if present in excess, proves to be harmful, but at the same time, if recovered from flue gases, it has a lot of commercial uses. Thus, we can see that studies are still carried out to obtain amine solvents which have low regeneration cost, but high CO_2 absorption capacity. From the studies that have been carried out till now, it can be seen that aqueous tertiary amines, blended with activators prove to be the best, among all the amine solvents. The information on sterically hindered amines is scarce; hence it is still a subject for further studies.

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