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Carbon dioxide removal from air - A state of the art review

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Abstract
Atmospheric air is an important part of human habitat. Because of the inventions in advanced technologies in many areas certain impacts on environment are observed. One of the concerned impacts is air pollution. The atmospheric air constitutes many elements, one of that is CO2. It is introduced in air from many sources like power plants, automobiles etc. and we are aware about the fact that CO2 is undesirable and harmful to all human beings.
In this paper, an attempt is done to focus the lamp on the work done to remove hazardous gases like CO2, SO2, and NOx from atmospheric air. Different investigators worked on different methods for removal of these gases and these techniques are also discussed. The MEA (mono-ethylene-amine) process is also studies along with its drawbacks. Investigators are now switching from MEA process to aqueous ammonia process. The process parameters in ammonia process and its result analysis are also discussed here. Still the research community is facing many problems in developing efficient and effective process which establishes the way to new future work in this area.

Keywords: CO2 capture, CO2 sequestration, MEA process, aqueous ammonia, falling film reactor, NH3 slippage

Introduction
We know that air is one of the most important elements for human beings to survive. Continuous breathing of fresh air keeps a man away from many diseases. Hence it is our prime duty that everyone should receive healthy clean air. The civilization is always in search of new inventions which are needed to make human life more easy and comfortable. But at the same time, it is observed that, these inventions are making few impacts over its surroundings also. We can call it as side-effects.

We are making numerous types of appliances, devices and machines like household refrigerator, motors, pumps, entertainment gadgets etc. all are run by electricity. It generates the necessity of making electricity on the large scale. Numbers of power plants are developed to fulfill this enlarged requirement of energy. On the other side, increased population and enhanced life-style results in the extensive use of automobiles. Though there is a consistent development of new techniques in automobile sector such as alternative fuels, techniques to assist complete combustion of fuel, reuse of exhaust gases etc., still the problems exists in fulfilling the emission norms.

In this paper, the study of techniques to remove the harmful gases like CO_2, SO_2, and NOx from the exhaust gases is discussed. Few literature papers are available and they are mainly concentrated on the study of exhaust gases from power plants. Researchers were using MEA process initially to remove these exhaust gases. But later on they developed the aqueous ammonia process. In this work the small focus is given on comparison on both of these processes. Also the aqueous ammonia process is having certain advantages and disadvantages during its working which are also discussed in current work.

Power plants and invention of idea

In china many fertilizers are used in farming. One of the important fertilizers is ammonium bicarbonate i.e. NH_4HCO_3 or it is also called as synthetic ammonia. The production process of ammonium bicarbonate includes one process which is known as carbonization. From this carbonization process, Zhang Yun et al. got the idea for CO_2 capture.

In carbonization process the input raw gas contains some impurities like CO_2, CO and others. Hence it is important to remove these impurities. For this aqueous ammonia is used which reacts with CO_2. Thus aqueous ammonia removes such kind of impurities and makes the gas pure. When ammonia reacts with CO_2 then ammonium bicarbonate (ABC) is formed as a by-product. Like this Zhang Yun et al. found a way for CO_2 removal by aqueous ammonia.

Zhang Yun et al. had done experimental study for capturing CO_2 at National Power Plant Combustion Engineering Technology Research Center (NPCC) China. They had focused on CO produced from fossil fuels used in power generation. They had dealt with capturing and sequestering of CO_2. They had developed an experimental facility at NPCC in existing coal-fired system to study the use of aqueous ammonia in CO_2 absorption. They had performed a series of experiments for not only capturing CO_2 but also sulfur dioxide (SO_2) and nitrogen oxides (NO_x). They had conducted the experiments in a pilot scale absorption tower using a spray of aqueous ammonia.

In this study, they have drawn three main conclusions. First one is that whether the spray of aqueous ammonia into actual flue gas produced from coal combustion is capable of capturing CO_2, SO_2, and NOx. They also studied the relationship between absorption efficiency of CO_2 with NH_3/CO_2 molar ratio. In third conclusion they found the by-products of aqueous ammonia after absorption. It is found that, after absorption aqueous ammonia generates ammonium bicarbonate [NH_4HCO_3], ammonium sulfate [$(NH_4)_2SO_4$] and ammonium nitrate [NH_4NO_3]. These compounds can be utilized in fertilizers.

Zhang Yun et al. receive very positive responses from their experimentation. They found that the spray of aqueous ammonia in the actual flow of flue gas is capturing CO_2, SO_2, and NOx as well.

They observed that if reaction condition between ammonia and flue gas from coal-fired facility varies, then absorption efficiency of CO_2 also varies. They establish the relation as, if the concentration of aqueous ammonia increases, then absorption efficiency for CO_2 and SO_2, also increases. If the molar ratio NH_3/CO_2 falls in the range of 1.25 to 1.40 then the CO_2 capture efficiency was measure in the range of 76. 4% to 91.7% at 35°C.

After absorption it has been observed by Zhang Yun et al. that the aqueous ammonia solution contain mixed ammonium bicarbonates ammonium sulfate and ammonium nitrate. They are the constituents of compound fertilizers.

When ammonia solution absorbs CO_2 then it takes the form of HCO_3^- and $[CO_3]^{-2}$. Zhang Yun et al. stated that when the molar ratio NH_3/CO_2 is at particular value, then there is a balanced concentration of HCO_3^- and $[CO_3]^{-2}$ in ammonia. But when same ammonia solution is again sprayed in flue gas having CO_2 then concentration of HCO_3^- increases which subsequently increases NH_4HCO_3.

Falling film reactor

Budzianowaski (2011) had worked on NH_3 slippage effect in NH_3 based CO_2 capturing process. He agreed upon the fact that the emissions from coal-fired power plants without NH_3 and with NH_3 are different. The emission without NH_3 containsSO_2, NOx and particulate matter. While with NH_3 it comprises of different elements. Budzianowaski (2011) had presented experimental and 2-d modeling work of CO_2 absorption from flue gases into aqueous ammonia using falling film reactor. He had analyzed the effect of pH, pressure and temperature on CO_2 absorption and NH_3 slippage.

In this paper, Budzianowaski (2011), concluded that, elevated operating temperatures, optimized value of pH, and increased value of pressure are factors to limit the NH_3 slippage. He has illustrated the simulation and experimental data for NH_3 slippage in CO_2 capture conditions and air stripping conditions. In this paper, Budzianowaski (2011) focused on modeling analysis of CO_2 separation from flue gases by aqueous ammonia solution using falling film reactor. He had handled the parameters like mass transfer chemical reactions electrochemistry and hydrodynamics in simple but realistic way.

Budzianowaski (2011) explained a falling film reactor as simple and suitable geometry to pursue detailed kinetic studies. In falling film reactor, aqueous ammonia and flue gas flows in opposite directions. He also stated that CO_2 separation process can approach equilibrium conditions.

Conventional ‘MEA’ and new aqueous ammonia processes

MEA stands for “mono-ethanol-amine”. On one side MEA has advantage like it is a promising method for control on CO_2 recovery. But on other side it has disadvantages also like expensive processes, slow absorption rate, low solvent capacity, high equipment corrosion rates, and high energy consumption during solvent regeneration. Apart from this, in MEA process, SO_2 and NOx must be removed before CO_2 absorption. But in case of ammonia solution, all above three elements are separated simultaneously. Also, in case of ammonia solution, the by-products obtained can be used as fertilizers for certain crops. But here, there is one problem. These ammonia salts are highly soluble in water. To separate them, processes have to be performed like crystallization, filtration, sedimentation etc. As compared to MEA, ammonia is having high absorption rate of CO_2. For ammonia it is 1.2 kg of CO_2 per kg of NH_3. While for MEA it is just

0.4 kg of CO_2 per kg of NH_3. Yet ammonia has few drawbacks also, one of that is volatility. This causes contamination of flue gases. Hence Budzianowaski (2011) has focused in his paper how to reduce this NH_3 emissions i.e. NH_3 slippage in NH_3 – based CO_2 capture systems. He has investigated the effects of ammonia volatility, falling film reactor, pH, elevated pressure and temperature etc. on NH_3process.Budzianowaski (2011) stated that as the pressure increases CO_2 absorption also increases and NH_3 slippage decreases. Thus increase in a pressure is favorable condition and can be achieved in practical situation. Regarding temperature Budzianowaski (2011) has an observation that as temperature increases, NH_3 solubility in water decreases and thus it decreases NH_3 slippage.

Semi-continuous reactor systems

Resnik et al. (2004) had also compared the traditional mono-ethanol-amine (MEA) process with ammonia process. He had agreed upon that the experimental research work on removal of CO_2 and other harmful gases from the flue gases of coal-fired power plants is going on large institutes like US DOE, NETL, and NPCC etc. It is found that aqueous ammonia process can remove CO_2, SO_2, NOx, HCL, and HF simultaneously.

Resnik et al. (2004) had presented the test results of ammonia and CO_2 reaction conducted in semi-continuous reactor system. They have also discussed the effects of sparger design, reaction temperature and ammonia concentration on absorption rates. Resnik et al has worked on regeneration of solution and its recycling during absorption.

Resnik et al. (2004) had conducted the experiments in semi-continuous reactor at controlled temperatures of 60, 80 and 100^{o}F. Sintered metal gas sparger is used to support the gas-liquid mixing. The flue gas contains 15% CO_2 and 85 % N_2 of the total volume. While the ammonia concentration was 7%, 14%, and 21% by weight.

From the previous work we know that, three fertilizers are obtained as a by-product in the use of aqueous ammonia. Out of these, ammonium bicarbonate has only certain fertilizing value and this value is less than other ammonia compound fertilizers. China has developed additives which are added into ammonium carbonate. Then they achieve modified ammonium bicarbonate (MAB). On these additives, they have taken a patent (Chinese patent: ZL901050125).

Ammonium bicarbonate is not only used in fertilizers, but it is also used in baking industries. Also to remove calcium sulphate scales on heat exchanger tubes, ammonium bicarbonate is used. Strong oxidizers are used for oxidation of nitric oxide to NO_2. One oxidation process uses hydrogen peroxide. Here, the liquid hydrogen peroxide is injected into flue gas, then H_2O_2vaporizes and dissociates into hydroxyl radicals. These radicals then oxidize the NO into NO_2.

Resnik et al. (2004) agreed upon the fact that, very few research reports in the usage of ammonia for CO_2 capture exists. Some of the notable papers are Bai and Yeh (1997). Bai and Yeh (1997) had two papers. In one paper, they had focused on sparging of CO_2 into ammonium hydroxide solution. While in other paper, they had focused on comparison between MEA process and ammonium hydroxide process. In second paper, Bai and Yeh (2000) reported that CO_2 removal by ammonia reached up to 99% while by MEA it is up to 94 % under same test conditions. Bai and Yeh (2000) in their paper, said that the purchase price of industrial grade NH_3 solution is approximately $1/6^{th}$ of that the MEA absorbent on the same weight basis in the world market.

Resnik et al. (2004) list out the positive points of ammonia as follows.

1) Aqueous ammonia has high loading capacity.
2) Aqueous ammonia does not cause a corrosion problem.
3) There is no absorbent degradation problem, thus reducing absorbent make-up rate.
4) The energy requirement for absorbent regeneration is predicted to be much lower than in the MEA process.

Resnik et al. (2004), has stated about the thermal energy consumption also. He has estimated that, the thermal energy consumption in case of aqueous ammonia is around 75% less as that of MEA process. But the authors are unaware about the users of ammonium bicarbonate fertilizers. Hence they suggested a way of recycling of ammonia for CO_2 sequestration.

In the experimental work, the flue gas is simulated as 15% CO_2 and 85%N_2 by volume. The main absorber of CO_2 is nothing but a glass container of 3-litre capacity and contains 1.5 liters of aqueous ammonia solution. The pressure is almost atmospheric and the temperature is maintained at 80^oF.

Resnik et al. (2004) has done a great work of analyzing effect of parameters like NH_3 concentration, reaction temperature on CO_2 absorption rate. It has been clearly stated that, as ammonia concentration increases, CO_2 absorption rate are found to be higher. Hence it is advantageous to use higher concentration ammonia solution as CO_2absorbent. These conclusions are found consistent for all three reaction temperatures. In his work, he focused on comparison between clean and plugged cylinder also. Clean cylinder allowed normal flow of CO_2in to reactor while plugged cylinder offers hindrance to CO_2 entrance by the crystals of NH_4HCO_3 by- product. Because of this, a sudden drop in reaction rates has been observed during switching over from clean to plugged cylinder. The reaction temperatures taken under study, by Resnik et al. (2004), are 60^{o}F, 80^{o}F, and 100^o F. The decomposition a temperature of NH_4HCO_3 is around

140^{o}F, hence reactor temperatures are not kept above 100^o F. He mentioned the effect that as reaction temperature increases the amount of CO_2 absorbed decreases. The conclusions have found good agreement to results by Bai and Yeh (2000). Hence it is expected to carry out experimental work at low temperatures.

Resnik et al. (2004) has focused on results what he obtained regarding loading capacity i.e. absorption capacity and regeneration cycles. The initial absorption was carried out at 80^{o}F. Then the resultant solution is thermally regenerated at 180^{o}F. The absorption/regeneration cycle was repeated for three cycles and the results of CO_2 loading in 3 cycles are shown graphically.

The graph shows that for first cycle, higher CO_2 absorption occurs. But in 2nd there is a sudden drop of loading capacity with respect to 1st cycle, and afterwards it almost remains constant for 3rd cycle. It is also found that, out of the total solution ammonia vapor loss occurs which causes CO2 loading capacity. Resnik et al. (2004) has given quantitative analysis also. The initial 198 g. of ammonia in solution, 85.4 g was lost in vent lines because of vaporization. This lost occurs at the end of 3rd cycle, while after 1st cycle, it is observed to be only 71.5 g.

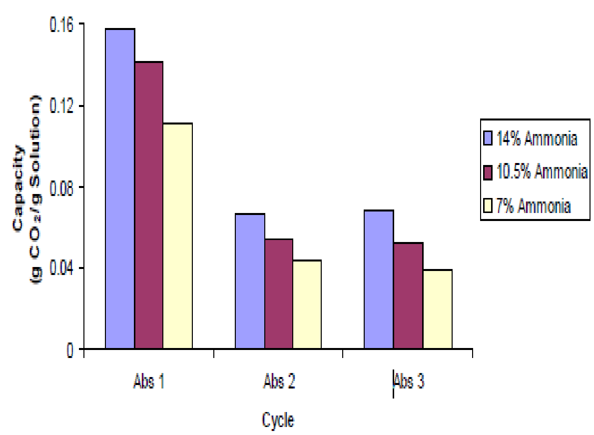

Fig. 1: Absorption rate with loading capacity.

Conclusion

Removal of carbon dioxide and other harmful gases is very important as far as human health is considered. The valuable and potential work has been carried out by researchers and investigators. The processes introduced in this direction are MEA and aqueous ammonia process, which are studies in this work. The drawbacks of MEA processes can be overcome by aqueous ammonia process. The simultaneous removal of three major constituents like CO_2, SO_2, and NOx can be achieved which is not possible by MEA process. Along with it, the falling film reactor and semi-continuous reactor systems are adding more advantages into it. Researchers have focused on very minute details also like absorption rate, loading capacity and concentration of ammonia; reaction temperatures etc. higher concentration of ammonia solution is always preferable for higher co2 absorption rate. In this work, we studied that the by-products of aqueous ammonia process are useful as fertilizers in many countries. These by-products such as ammonium bicarbonate are useful in baking industries as well. Thus, a single step towards removal of carbon dioxide from power plants initiates many new positive impacts over environment and human health.

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