

Capturing CO₂ and Recovering NH₃ by Producing Ammonium Bicarbonate Through Stripping Batch Process at Lab Scale

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A sustainable environment is a critical necessity in today's world, as it addresses the urgent need to conserve energy, reduce pollution, and support economic stability. Researchers are developing various sustainable waste management practices to mitigate air and water pollution. Key industrial sectors such as cement production, chemical processing, and power plants are among the largest sources of CO₂ emissions. Ammonia-based absorption technologies offer a promising approach to significantly reduce these emissions and enhance the cleanliness of industrial processes. One such technology is the stripping process, which captures CO₂ by removing ammonia from the water. This process not only facilitates CO₂ capture but also produces ammonium bicarbonate (NH₄HCO₃), a valuable chemical used in various industries and as a fertilizer. This study focuses on a lab-scale stripping process for ammonia recovery and CO₂ capture under different experimental conditions, an area not extensively explored in previous research. The precipitated product was analyzed using various characterization techniques, including Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) and X-ray Diffraction (XRD). The results indicate that variations in absorption times, CO₂ flow rates, and solution concentrations significantly impact the quantity of the product. The research identifies the optimal conditions for maximizing NH₄HCO₃ production as 110 minutes of absorption time, a CO₂ gas flow rate of 0.5 L/min, and a 15% NH₄OH solution.

Keywords: Ammonium Bicarbonate, Ammonium Hydroxide, Carbon dioxide, Stripping Batch Process, and Recovering.



Introduction:

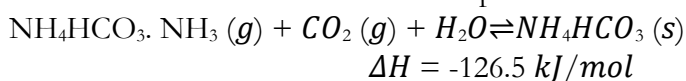
Pre- and post-combustion are currently the two primary CO₂ capture strategies under investigation [1]. Among the various absorbents and absorption methods, the monoethanolamine (MEA) process, which utilizes potassium carbonate solution, is the most widely employed, with nearly a thousand units in operation, equivalent to roughly 700 plants. However, the MEA process has several drawbacks, including low CO₂ loading, limited absorption efficiency, high energy requirements for regeneration, and container corrosion issues. Due to the large volume and potential for pH fluctuations, the absorbed CO₂ in MEA absorbents remains in the liquid phase, which can lead to its release.

To address these challenges, aqueous ammonia has been explored as an effective alternative for CO₂ absorption. It offers several advantages, including high absorption capacity, lower energy requirements for regeneration, reduced corrosiveness, lower costs, and increased removal efficiency [2][3]. Additionally, aqueous ammonia facilitates the crystallization of ammonium bicarbonate, although it can also lead to container corrosion [2][3].

While capturing CO₂ in MEA involves storing it in a liquid state, which might release CO₂ gas, some studies have replaced MEA with aqueous ammonia for CO₂ absorption [4][5]. This method produces ammonium bicarbonate crystals by using a scrubber to absorb CO₂ with aqueous ammonia. This technology effectively captures CO₂ and yields ammonium bicarbonate, a valuable byproduct used in the food and agricultural industries. The crystallization process is considered a viable and environmentally friendly method for CO₂ capture and utilization due to its energy efficiency [6].

Ammonium carbonate molecules, particularly ammonium bicarbonate, play a crucial role in capturing, storing, and recycling important nutrients like carbon and nitrogen back into the environment. Despite the advantages of recovered ammonium (bi)carbonate, its practical application depends on its stability in the environment to avoid the drawbacks of inherent reactivity [7].

The chemical formula for ammonium bicarbonate is NH₄HCO₃. It is a colorless to white solid that rapidly decomposes into ammonia and carbon dioxide. It has a density of 1.58 g/cm³ and a molecular weight of 79.06. Unlike other ammonium compounds, ammonium bicarbonate dissolves in water without decomposition. Exothermic reactions produce



Chinese farmers continue to use ammonium bicarbonate as a fertilizer despite its lower nitrogen content (18%) compared to urea (46%). Significant technological and economic advancements in the production of fertilizers, particularly ammonium bicarbonate, have been reported in China, as highlighted by Zhuang et al. [8]. The production scale showcases highly integrated and efficient technology, utilizing between 3,000 to 12,000 tons of ammonia annually. Nitrogen (N), an essential component for plant growth, is absorbed from the soil in the form of either ammonium (NH₄⁺) or nitrate (NO₃⁻) [9]. Ammonium bicarbonate decomposes in a manner that leaves no solid residue, with NH₃, CO₂, and H₂O all entering the gas phase. For example, heating ten grams of NH₄HCO₃ to 150°C at standard temperature and pressure (STP) produces thirteen liters of gas. These properties make ammonium bicarbonate useful not only in agriculture but also in the food industry as a leavening agent in baked goods and in industrial applications, such as dissolving thin calcium sulfate layers in heat exchanger tubes to remove deposits.

In 2016, ammonium bicarbonate's global sales were dominated by agricultural use, which accounted for 83% of consumption, followed by food-grade (10.5%) and technological applications (6.5%). The substance is also widely used in the leather and rubber industries for softening leather. While its standard parameters are comparable to those of other fertilizers,

the nitrogen content of ammonium bicarbonate typically remains at 17% or less [10]. Other researchers have explored gas-liquid absorption by varying NH_3 solution concentrations and have discussed factors that can enhance the nucleation of NH_4CO_3 crystals [11].

The rapid increase in global CO_2 emissions is causing temperatures to rise at an alarming rate, leading to severe environmental consequences. Reducing CO_2 emissions, particularly from steel and coal-fired power plants, has therefore become a critical priority. This study aims to optimize the parameters and characterize the products obtained from CO_2 capture using ammonium bicarbonate.

Materials and Methods

Materials and Chemicals:

- Ammonium Hydroxide solution (NH_4OH , 32%)
- De-ionized water
- Ice
- Carbon dioxide (CO_2 , 100% pure) gas cylinder
- HI 8424 pH meter
- SHIMADZU weight balance
- Lovibond Multimeter
- E-instruments CO_2/CO COMFORT-4 gas analyzer

Experimental Setup:

The experimental setup, illustrated in Figures 1 and 2, consists of a pure carbon dioxide gas cylinder, flow meter, reactor, water bath, scrubber, and gas analyzer. The gas from the cylinder enters the reactor at room temperature. A diffuser fixed at the outlet of the tube entering the reactor causes the gas to bubble. The reactor contains liquid ammonium hydroxide solutions of varying concentrations: 15%, 10%, and 5%. As the gas is bubbled into the reactor, the reactions, as detailed below, begin to occur. The remaining gas exits the reactor, and a gas analyzer is used to detect the CO_2 at 5-minute intervals. The temperature was maintained using chilled water, with all reactions conducted at temperatures $>5^\circ\text{C}$. The reaction durations were set at 60, 90, 120, and 140 minutes, while CO_2 flow rates were varied at 0.2, 0.3, 0.4, and 0.5 liters per minute. All experimental steps are detailed in Figure 1.

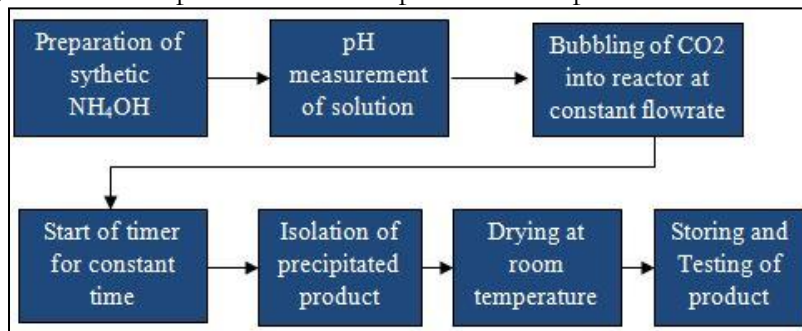


Figure 1: Experimental procedure for the proposed ammonia-based carbon capture and Ammonium bicarbonate production unit.

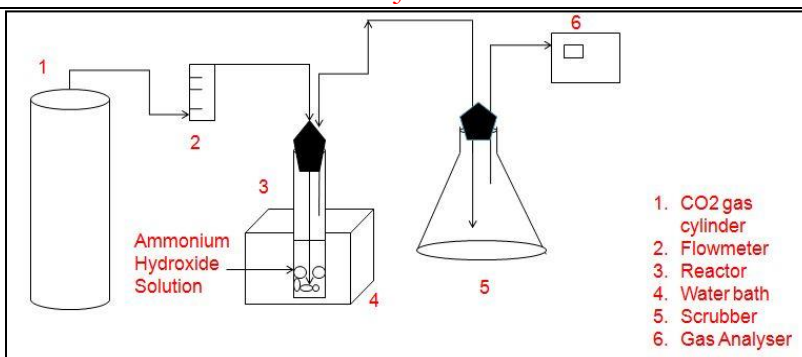


Figure 2: Schematic diagram of the experimental setup

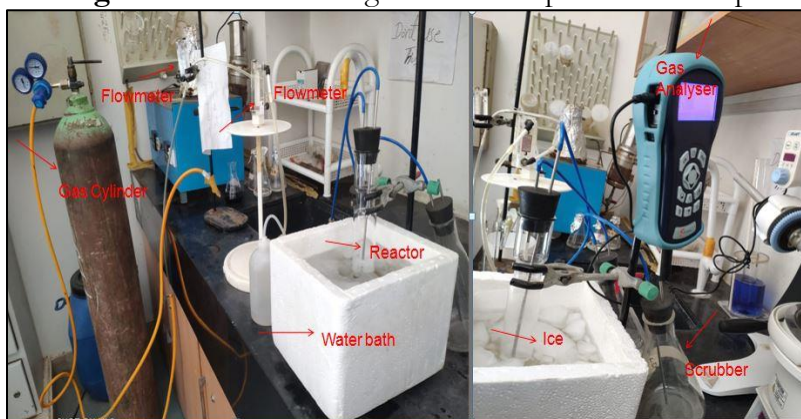
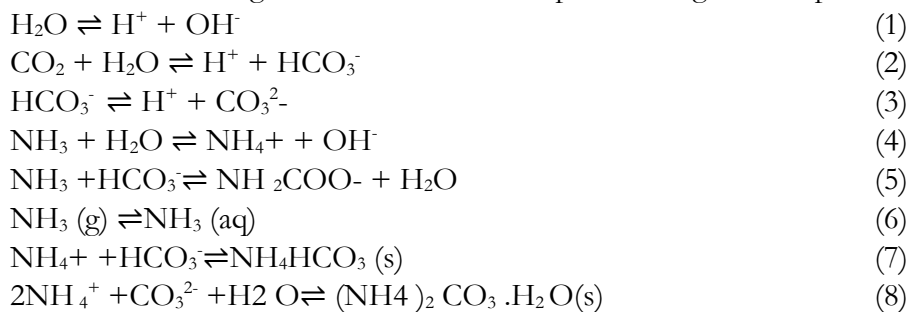


Figure 3: Experimental setup

Result and Discussions:

When the gas bubbled during experiments the formation of crystals started occurring at 60 mins. Figure 4 (a) and 2(b) show the white crystalline product obtained at the bottom of the reactor. The pH was measured before and after each reaction.

It is expected that the following reactions will be taken place during these experiments



Ammonium bicarbonate: NH_4HCO_3 Ammonium carbonate: $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$



(a)



(b)

Figure 4 (a). The precipitated product, **(b).** The Dried product

Effect of Reaction Time:

As shown in Figure 5, the quantity of product increases with reaction time. However, beyond 110 minutes, there is no significant change in the product amount. The most substantial increase in product quantity occurs between 90 and 110 minutes. The reaction reaches equilibrium by 140 minutes, at which point the CO₂ concentrations at the outlet and inlet are equal.

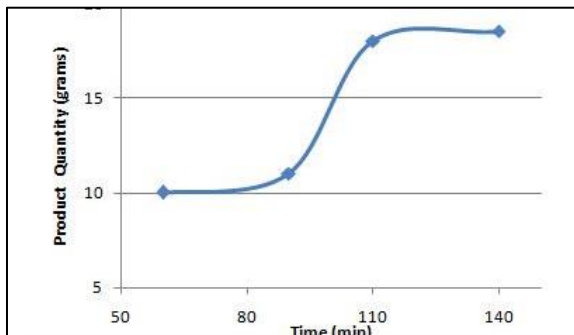


Figure 5: Effect of Time on Yield at constant condition 15% NH₄OH, Ph: 13 flowrate CO₂: 0.5l/min, Temp <5C

Effect of CO₂ Flowrate:

It can be observed from the experiments that the flow rate of CO₂ gas has a clear impact on product quantity. Product quantity increases as the flow rate increases in Figure 6. Higher flow rates provide higher formations of carbonates and bicarbonate ions HCO₃⁻. Pao Chi Chen et al. also found an increased absorption rate at increased CO₂ flow rates at different experimental conditions [6].

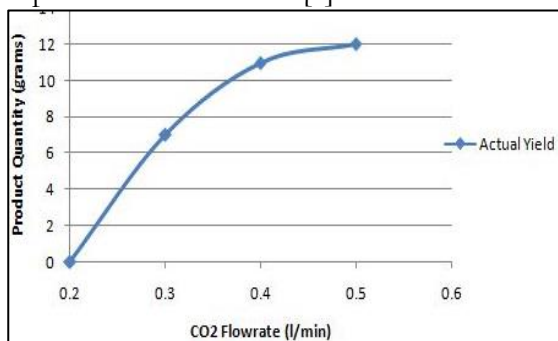


Figure 6: Effect of CO₂ Flowrate at constant condition 15% NH₄OH, Ph: 13, Time: 90 min, Temp <5C

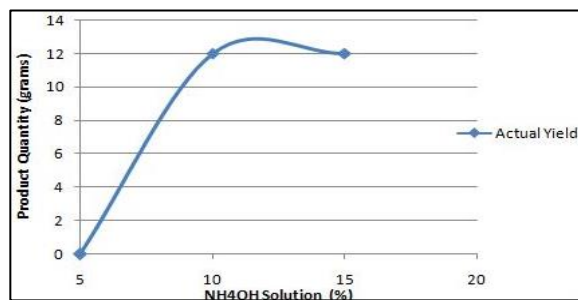


Figure 7: Effect of Ammonium Hydroxide solution concentration at constant condition 15% NH₄OH, pH 13, Time: 90 min, Temp <5C, CO₂ flowrate

Effect of NH₄OH Solution Concentration:

Various scholars and researchers have investigated different conditions affecting CO₂ absorption. For instance, Asmaa S found that lower concentrations of NH₄OH yield maximum absorption [12]. However, this research indicates that at a constant temperature below 5°C and a reaction time of 90 minutes, higher concentrations of NH₄OH result in increased product quantity, as shown in Figure 7. It is important to note that higher concentration solutions require more time to precipitate compared to lower concentrations. The higher pH in more concentrated solutions necessitates additional time for the reaction to reach the desired pH range of 8.5–10 for effective precipitation. Other studies have also observed the effects of varying ammonium hydroxide concentrations under different experimental conditions [10].

Characterization of the Products: The products were identified using XRD, microscopy, FTIR, SEM, and pH measurements, as depicted in Figures 4, 5, 6, 7, and 8. FTIR analysis, shown in Figure 4, confirmed the presence of CO₃²⁻ and N-H bonding, correlating with the data provided in [13]. XRD analysis, illustrated in Figure 9, confirmed the formation of

ammonium bicarbonate (NH_4HCO_3). The XRD pattern aligns perfectly with the reference card pattern for pure ammonium bicarbonate crystals (00-009-0415), with key peaks at $2\theta = 16.3^\circ, 29^\circ,$ and 42.5° . Similar results were reported in other studies [11]. Microscopic analysis, shown in Figure 10, revealed the orthorhombic shape of the crystals, characteristic of NH_4HCO_3 . Additionally, Figure 11 presents the SEM image of the crystals, providing further detail on their morphology.

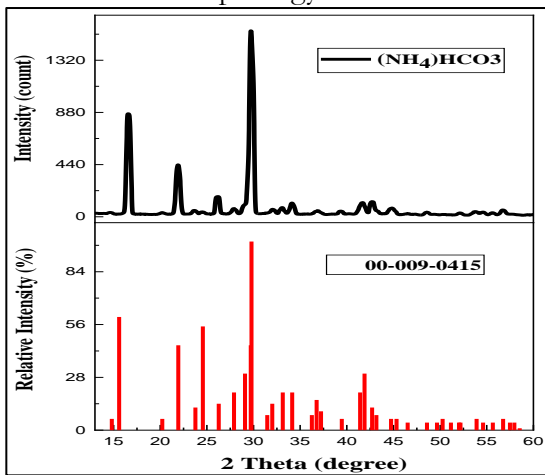


Figure 8: FTIR Characterization

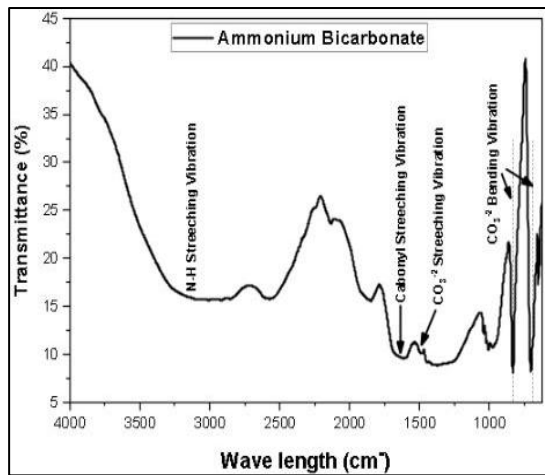


Figure 9: XRD Characterization

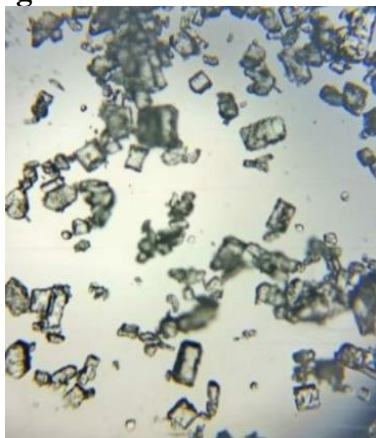


Figure 10: Microscopic Analysis

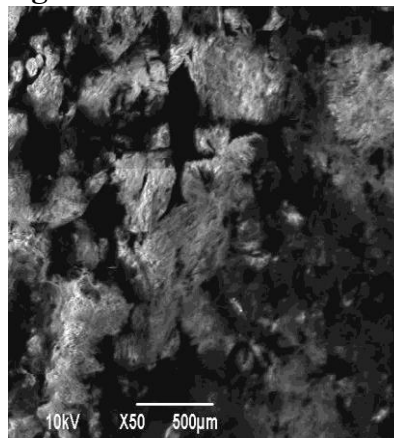


Figure 11: SEM Image

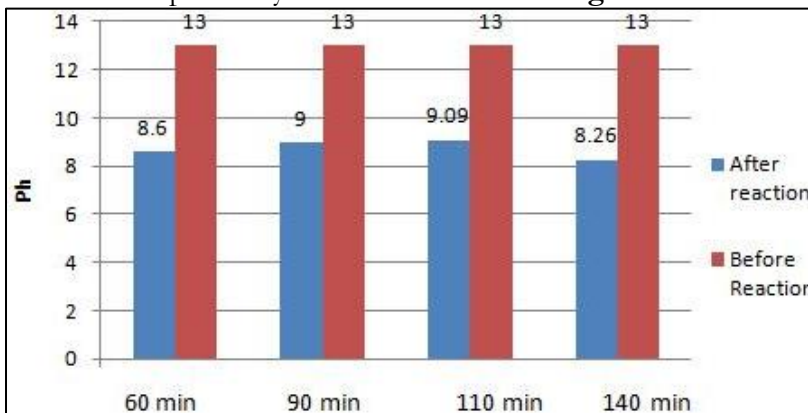


Figure 12 (a): pH of the solutions before and after reactions at different times

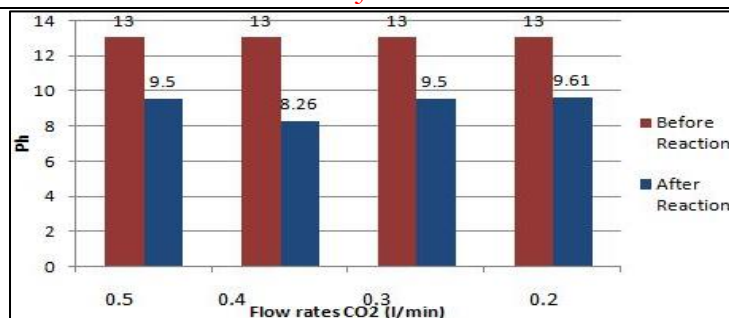


Figure 12 (b): pH of the solutions before and after reactions at CO₂ flowrates

Figure 8 indicates that the pH values, which range between 8 and 10, are consistent with the formation of ammonium bicarbonate. This range aligns with the findings of Chin et al. [6][14], who reported that ammonium bicarbonate forms at pH levels between 8 and 10. Additionally, FTIR spectroscopy, a valuable technique for characterizing crystals, reveals the presence of specific chemical bonds, providing further confirmation of ammonium bicarbonate formation.

Discussion:

Several studies have explored the effect of time on absorption. For instance, increased absorption with time was noted, with reaction completion typically observed after 30 minutes, as reported by [12]. However, in our study, product precipitation was observed after 90 minutes due to differing experimental conditions. Similarly, Pao Chi Chen et al. found that higher CO₂ flow rates enhance absorption rates under various experimental settings [6]. This trend was also observed in our study.

The production of more product is associated with higher concentrations of NH₄OH solutions. However, the higher pH in these concentrated solutions results in a longer time required for product production. Other researchers have also utilized Fourier Transform Infrared Spectroscopy (FTIR) to demonstrate the formation of CO₃²⁻ and N-H bonds, as shown in Figure 4. This is corroborated by the graph provided in [13]. XRD analysis further supports these findings, with similar results observed in other studies [11]. The pH readings in Figure 8, falling between 8 and 10, corroborate the findings of Chin et al., indicating the formation of ammonium bicarbonate [6][14].

Conclusion:

This research demonstrates that a CO₂ flow rate of 0.5 L/min yields the maximum product mass. Higher CO₂ flow rates lead to greater product formation when absorbed in an NH₄OH solution. The concentration of the NH₄OH solution also affects product mass. Specifically, a 15% NH₄OH solution results in a higher product quantity when the absorption time is extended. At 90 minutes, the product mass is similar for 10% and 15% NH₄OH solutions, approximately 12 grams. The high pH of the 15% solution, initially around 13, necessitates a longer time to reach the optimal pH range of 8-10 for product precipitation at constant CO₂ flow rates. Therefore, higher concentration solutions require more time to produce higher yields, or higher CO₂ flow rates if solution concentrations are increased. Otherwise, no significant change in product quantity is observed if other parameters remain constant. Additionally, increasing absorption time continues to increase product mass until equilibrium is reached. The final products obtained are ammonium bicarbonate (NH₄HCO₃) and ammonium carbonate (NH₄CO₃).

Recommendations: This labwork can be further studied at various flow rates and other parameters including temperature. Apart from this, it can be implemented in textile, steel, and other industries where CO₂ and NH₃ are pollutants.

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