

From Waste to Resource: Avoiding Fouling in Ammonia Recovery

As more organizations look to ammonia recovery to take advantage of recent pricing trends, it is increasingly important to consider the impacts of fouling and other process inefficiencies

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The price of ammonia has increased by 600% from 2020 to 2022 (Figure 1) [1]. In turn, a wide range of ammonia recovery projects that were previously not economical have become attractive. Ammonia recovery technology converts waste ammonia into a useful resource, but fouling can be a significant issue in these processes. Fouling occurs when unwanted substances accumulate on heat-transfer surfaces, reducing the efficiency of the ammonia recovery process. Effective fouling-control strategies are therefore essential to ensure efficient and sustainable ammonia recovery operations.

Common fouling-control strategies include chemical cleaning, mechanical cleaning and filtration. Implementing these strategies early in the design process is important to minimize fouling and maximize ammonia recovery efficiency. Furthermore, an understanding of the different equipment and process-technology configurations during the early design stage can help to reduce the risks for fouling. This article examines various ammonia recovery technologies and discusses design considerations related to fouling.

Ammonia recovery technologies

An engineer may be tasked with recovering ammonia from aqueous streams of varying purity, composition and flowrate. The presence of

particulate solids and other soluble species, as well as the process pH, also present a challenge. To ensure successful ammonia recovery, the engineer must select the appropriate ammonia recovery technology based on the specific characteristics of the aqueous streams. Ammonia may exist in solution in free or fixed forms. Free ammonia readily dissociates upon heating (for example, $\text{NH}_4\text{OH} \leftrightarrow \text{NH}_3 + \text{H}_2\text{O}$) and is readily liberated as a vapor. Fixed ammonia (such as NH_4Cl) requires adjusting the pH into the alkaline range, converting non-volatile ionized ammonia into volatile free ammonia.

There are several technologies commonly used for ammonia recovery including the following, each with its own benefits and challenges in terms of process efficiency and fouling propensity:

- Distillation (stripping) towers
- Dilute acid neutralization and crystallization
- Membrane or reverse osmosis separation

Engineers must carefully consider which technology is best suited for their specific application. Distillation is one of the most common technologies used for ammonia recovery, owing to the relatively low capital cost, ease of use, proven

U.S. Energy Information Administration
U.S. dollar per metric ton

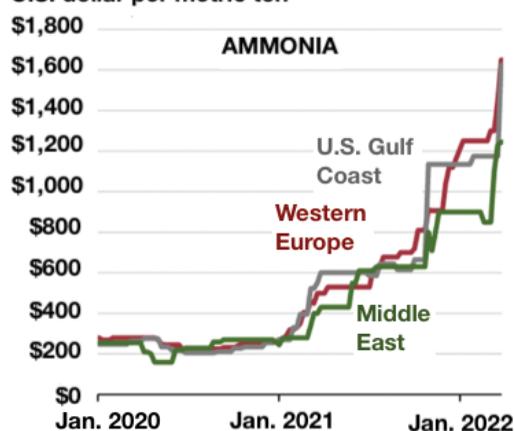


FIGURE 1. As ammonia prices have significantly risen in recent years, many processors are investing in ammonia recovery technologies [1]

technology and operational reliability. Aqueous ammonia-bearing feed material flows down through trays or packing, while steam injected at the lowest point vaporizes the ammonia and carries it out as distillate. Distillation requires no ongoing consumption of chemicals or high pressures, in contrast to crystallizer systems that consume stoichiometric quantities of acid (typically sulfuric acid) or require application of high pressure to force water through a membrane.

Ammonia stripping challenges

Quite commonly there are more species than just water and dilute ammonia present in the feed liquid. Aqueous ammonia generated during biomass processing or fermentation often is mixed with dissolved carbon dioxide, in the form of carbonic acid. Carbonic acid is acidic, while

ammonia is alkaline. One serves as the neutralizing agent for the other. Two salt combinations typically result: ammonium carbonate or ammonium carbamate. Steam stripping of NH_3 will also strip the CO_2 out of the water, and if not correctly designed, the two gas species will recombine in the stripper overhead condenser, leading to fouling with salt deposits. This will eventually reduce performance to below the design production rate. This is because there is a composition gradient from the inlet to the outlet of the condenser. While a simulator may show a completely dissolved solution of ammonium carbonate at the condenser outlet, one must be aware that the condenser feed vapor does not instantly condense and may pass through insoluble regions.

One helpful way to visualize this is to use thermodynamic modeling software that includes a properties package for sour water to calculate equilibrium constants for ammonia and carbon dioxide in water. The portion of the incoming vapor that condenses incrementally increases down the length of the condenser. As 10%, then 20%, and so on up to 100%, of the feed vapor condenses, the residual vapor-phase composition can then be overlaid onto a ternary phase diagram, such as that developed by Sutter and others, shown in Figure 2 [2]. The dark green arrows originate at the inlet composition of the initial vapor phase and progress toward the final residual vapor composition occurring just before the vapor is entirely condensed. The procedure is repeated for many concentrations of CO_2 , expressed as mass ratios to the ammonia. All pathways shown are based on an initial ammonia composition of 17.5 wt.%. At different initial compositions, the thresholds discussed below may be different and need to be reevaluated.

When the mass ratio of $\text{CO}_2:\text{NH}_3$ is low (≤ 0.25 , Figure 2a) the entire green condensing curve, or “pathway” across the ternary diagram, is in regions of liquid and vapor phases only. A standard shell-and-tube condenser is expected to perform satisfactorily in this scenario. When the ratio of $\text{CO}_2:\text{NH}_3$ increases to 0.50 (Figure 2b), the initial and final compositions of the pathway are liquid and vapor, but the intermediate passes through a region containing a partial solid phase containing ammonium carbonate and ammonium carbamate at cold temperatures (10°C). A shell-and-tube condenser is expected to perform satisfactorily, provided the wintertime cooling water temperatures stay warmer than 20°C . If colder cooling-water temperatures cannot be avoided, a shell-and-tube condenser may suffer fouling. This would be further exacerbated at higher ratios of $\text{CO}_2:\text{NH}_3$ (0.75; Figure 2c) where the minimum temperature to avoid the formation of a solid phase is now around 40°C . A shell-and-tube condenser is virtually certain to suffer fouling unless a tempered loop is utilized to keep the cold utility at around 50°C .

When the ratio of $\text{CO}_2:\text{NH}_3$ is high (≥ 1.0 , Figure 2d and 2e), the final condensing vapor composition is in a region where fouling is expected to be the most severe and will

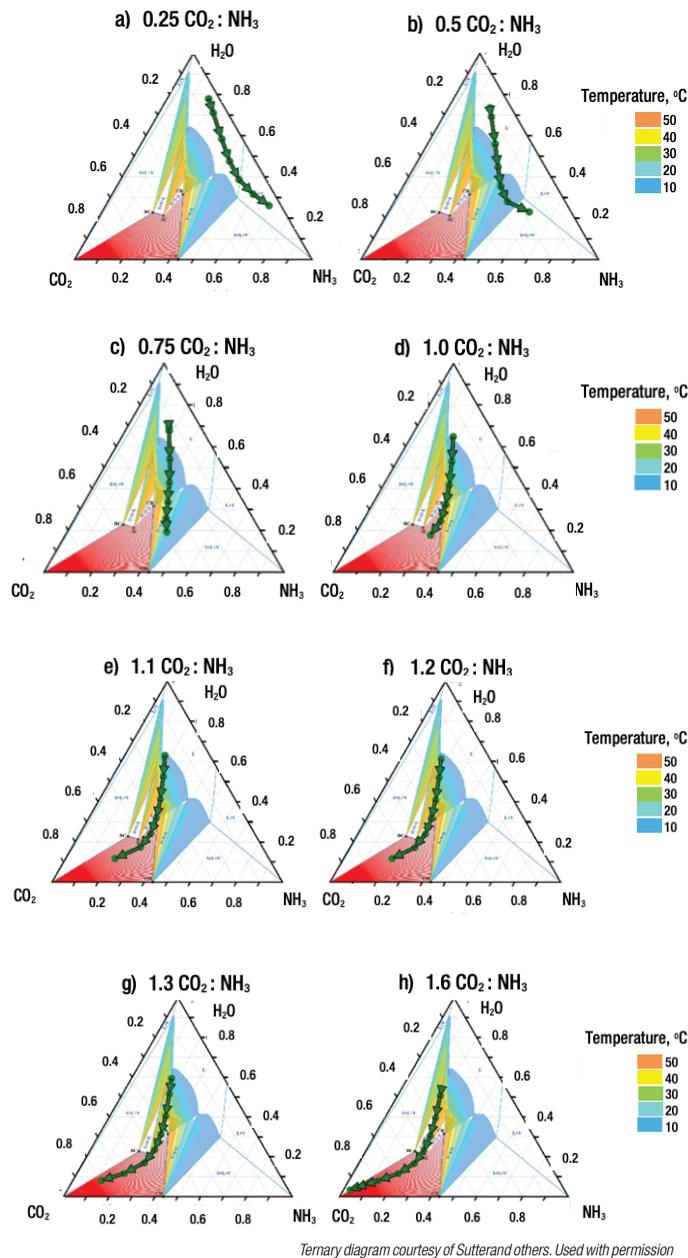


FIGURE 2. Ternary diagrams show the compositional curve pathways in overhead condensers of ammonia stripper towers with various $\text{CO}_2:\text{NH}_3$ ratios. Initial conditions for all curves are based on 17.5 wt.% ammonia [2]

form a variety of ammonium salts. The solid fouling layer is expected to decrease heat transfer rates and force a tower rate reduction. A condenser wash-out would be necessary to (temporarily) restore production rates.

DCC benefits

The design solution for higher $\text{CO}_2:\text{NH}_3$ ratios (≥ 0.75) is to replace the overhead shell-and-tube condenser with a direct contact condenser (DCC; Figure 3). Rather than presenting a metal heat-transfer surface, the DCC sprays a subcooled liquid distillate onto the vapor stream exiting the ammonia stripping tower. The latent heat of vaporization is absorbed as sensible heat into the liquid spray, condensing the vapor. The heated liquid is then cooled via heat exchange in an external recirculation loop before returning to the DCC spray nozzle. A slip-stream is

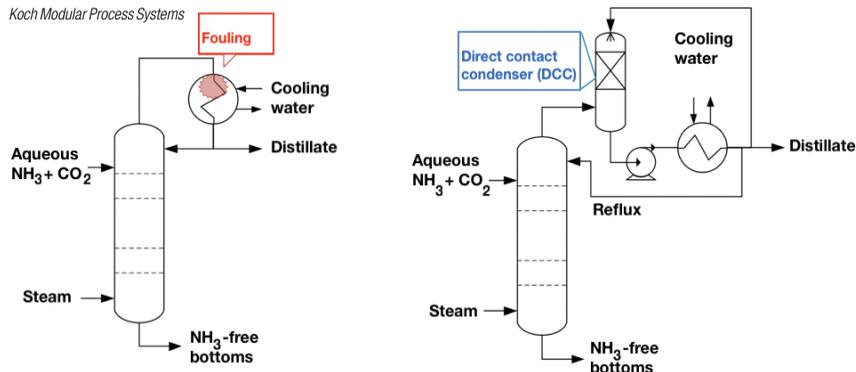


FIGURE 3. A standard ammonia stripper with a shell-and-tube condenser is shown on the left. On the right is an ammonia stripper layout that includes a direct contact condenser (DCC)

withdrawn as product or reflux to ensure the overhead liquid inventory remains constant over time.

The primary advantage conferred by the DCC is compositional control — the mass flowrate of circulated liquid as a ratio to incoming vapor is >10:1 to ensure that there is enough sensible heat to fully condense the incoming stream (except for any non-condensables). Therefore, even small initial amounts of vapor condensation do not materially change the composition of the liquid phase, as it is impossible to enrich the condensed phase in CO_2 and NH_3 when most of the mass comes from the liquid spray, not the vapor feed. A DCC also virtually eliminates dry spots on the condenser, which are prone to solid buildup. Any solids that do form would either be washed away or dissolved in the water-rich wash stream. Viewed on a ternary diagram, the DCC effectively operates on a single point, rather than a pathway, and that point is the initial point of the pathway for the respective CO_2 : NH_3 ratios. The initial point existing in the region of liquid and vapor only avoids solids formation, which would foul or plug the system. Therefore, a DCC-equipped ammonia stripper is tolerant to a much wider range of CO_2 concentrations in the stripper feed than a shell-and-tube condenser.

When the ratio of CO_2 : NH_3 is even higher (≥ 1.2 , Fig. 2f, 2g and 2h), even the initial composition of the condenser (or DCC) would be prone to fouling if it were to reach a low enough temperature, based on the given ratio. If, during the winter months, the cooling water were to

cool the recirculating stream into solid forming regimes, fouling could even form in the DCC and the recirculation cooler. To solve this issue, a tempered loop should be added on the recirculation cooler of the DCC to maintain a temperature above 50°C . When operating at atmospheric pressure, the bubble point temperature of 17.5 wt.% ammonia is around 71°C . If the CO_2 : NH_3 ratio is such that the initial DCC composition is already prone to forming solids, this will require a very large recirculation flow in the DCC, in order to straddle the line between fully condensing the vapor stream and not forming solids in the DCC and recirculation cooler. This would lead to much larger operating equipment. In these circumstances, it is advisable to operate the stripping tower at a higher operating pressure. This will increase the bubble point temperature of the ammonia distillate to give more allowance for a temperature rise in the recirculation fluid, while reducing the required recirculation rate. Unfortunately, increasing the operating pressure also has some downsides since it will lead to increased capital cost and require more steam to strip the same amount of ammonia.

The capital cost for a DCC is higher, owing to the higher equipment footprint and the larger heat exchanger size. The process temperature is dependent on operating pressure and typically subcooling the recirculated fluid by about 50°F is sufficient. A DCC heat exchanger will have a larger surface area to remove the same amount of heat as a conventional overhead condenser, owing to the lower temperature dif-

ferential between the process and utility fluids.

The DCC resembles a miniature stripping tower, often with tower packing inside a cylindrical shell, albeit much shorter than the stripping-tower packed section. The packing ensures sufficient mass-transfer area between the hot condensing vapor and the cooled incoming recirculation liquid. Special consideration must be given to the packing type, particularly in applications with higher liquid loading or rapidly decreasing vapor volume.

It is impossible to avoid co-stripping the CO_2 and NH_3 simultaneously if the ammonia must be recovered. To separate CO_2 from NH_3 , one must utilize sequential stripping towers — a CO_2 stripper followed by an NH_3 stripper. Whether one or two stripping columns are required is dictated by the product specifications the system must achieve. Ultimately, the engineer must carefully evaluate the specific characteristics of their process streams and consider all available options to determine the most appropriate ammonia recovery technology for their application. ■

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References

1. Raghuvver, T. and Wilczewski, W., U.S. ammonia prices rise in response to higher international natural gas prices, *Today in Energy*, U.S. Energy Information Administration, May 2022.
2. Sutter, D., Gazzani, M., and Mazzotti, M., Formation of solids in ammonia-based CO_2 capture processes — Identification of criticalities through thermodynamic analysis of the CO_2 - NH_3 - H_2O system, *Chemical Engineering Science*, Vol. 133, pp. 170–180, September 2015.

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