Condensated ammonium water

Technology description

Evaporation technology can be used to remove water or other liquids from liquid-based mixtures. The process of evaporation is already for quite some time used in the food industry to concentrate fruit juice and sugar and to produce milk, whey powder and condensed milk. Recently, the technique is more frequently used on wastewater and even manure of digestate of anaerobic digestion.
In the concentration process, heat is added at a certain temperature and pressure, which vaporises most of the water from a solution and concentrates the nutrients, salts, solids and other non-volatile components.

Increasing pH and/or temperature pushes the equilibrium from water-soluble ammonium (NH_4^+) towards gaseous ammonia (NH_3) and this will volatise during the evaporation process. The water vapour containing volatile components is recovered through condensation as ammonia solution.
To prevent volatilisation of ammonia in temperature ranges from 20°C to 100°C, the pH of the input stream of the evaporator can be adjusted to <5,5.
To use the heat of the evaporator as efficiently as possible, multiple configurations are possible. Vacuum evaporation makes use of lowering the pressure and hereby lowering the boiling point of water, whereas less heat is required. Multiple effect evaporation re-uses the heat of the first evaporator in the following evaporating steps which each have lower pressures, and therefore require less energy to heat up.

Photo 1. Falling film evaporator (France Evaporation ©)

For evaporation of digestate, two types of evaporators are used frequently: falling film evaporation or forced circulation evaporation.
In practice, it has been found that elevating the pH of the digestate, leads to considerable operating costs, which reduces the interest in system deployment, despite its potential efficiency. From this point of view, it will be more reasonable for most biogas plants that have an excess of residual heat from the CHP to raise the temperature to at least 80°C and strip at the existing pH. In theory, the recovery rate of ammoniacal N could be 60 to 75% at this temperature.

Product characteristics

Since ammonium solution is obtained after evaporation and condensation of water and volatile components, it is free of suspended particles, metals and pathogens. Also phosphorus, potassium and other minerals are not volatised.
In theory, it is a solution of anhydrous ammonia dissolved in water. This is a low-pressure solution in which the ammonium ion in solution exists in equilibrium with unionised (free) ammonia, which can volatise.

$$NH_3\,(gas) = NH_3\,(aq) + H_2O = NH_4^+(aq) + OH^-(aq) = NH_4OH(aq)$$

This equilibrium depends on pH and temperature.
From digestate, an ammonium solution of 10-15% ammonium can be obtained.

Table 1. Indicative product characteristics of ammonia solution after evaporation of liquid fraction of digestate

Parameter	Ammonium solution
pH	9-10,5
EC (mS/cm)	11-120
Dry matter (%)	0,02-0,1
Ammonium total (NH4+ and NH3) (g N kg^{-1})	28-200
N mineral/N total (%)	82-90
P_2O_5 (g kg^{-1})	<0-0,5
K_2O (g kg^{-1})	<0-0,06
Sulphur (g kg^{-1})	2
Sulphates (g SO_3 kg^{-1})	4,93

*EC: electrical conductivity

Horizon 2020
The SYSTEMIC project has received funding from the European Union's Horizon 2020 Framework Programme for Research and Innovation under Grant Agreement no. 730400.

Through an additional distillation step, a concentration of 20% ammonium can be reached. By acidifying the ammonium water, the chemical equilibrium is pushed towards ammonium and this stays in solution.

Agronomic aspects

In the USA, aqua ammonia (synthetic), is a popular liquid N fertiliser. It can be injected, but this does not need to be as deeply as NH_3 gas, (which is still used as fertiliser in the USA). It is also frequently added to irrigation water and used in flooded soil conditions.
In field trials performed in England in 1996-1997, injection of aqua ammonia showed that wheat plants gave greener plants than in the control fertilisation, and the apparent N uptake efficiency into the grain and straw was increased with 24%. A study in the USA (2010-2012) confirmed the positive influence on measured N uptake in maize. Additionally, they measured increased biomass with anhydrous ammonia application.
A three-year field experiment (2004-2006) was conducted on a clay soil near Québec City, comparing the fertilising value of Aqueous ammonia, urea ammonium nitrate (UAN) and calcium ammonium nitrate (CAN) on corn (Zea mays L.), no significant difference in grain N content was measured.
Results of field trials in Flanders (Belgium) in 2014 comparing artificial fertilisers and digestate supplemented with ammonia water recovered from digestate showed no significant difference in corn yield.

Environmental aspects

Emissions to the air

In general, based on the widespread use and experiences of aqueous ammonia (pH>10) as a fertiliser in the past and present, surface application is not suitable at any time due to potential ammonia volatilisation at concentrations >10% ammonium at ambient temperatures.

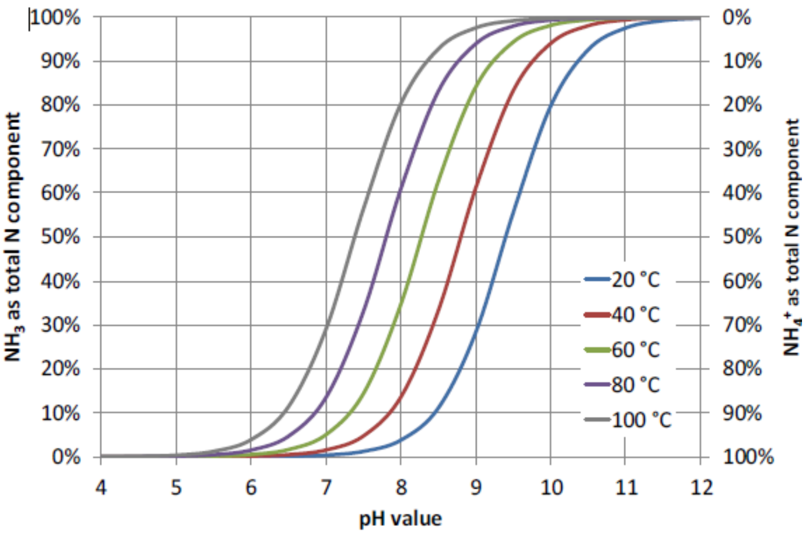

Figure 1. Equilibrium of NH_3 and NH_4^+ in water at different pH and different temperatures

Therefore, reducing the pH to neutral, using solutions with a low ammonium concentration (1-3%) or a mix of ammonium solution with manure or compost can prevent ammonia losses to the air.
However, the volatilisation behaviour of ammonium water in the soil is also influenced by the ammonia saturation and the permeability of the surface soil layers, climate, application and management practices, making it difficult to estimate ammonia emissions, let alone to quantify and monitor them.
When N_2O emissions were calculated, the concentration of NH_4^+ as part of the formulation seemed to produce the greatest N_2O emissions. Several observations in this study indicated that nitrification pathways contributed to the N_2O production, but when N_2O is produced deeper in the soil (by deeper penetration of NO_3^-, or injection in the soil), it had a greater opportunity to be converted to N_2 by de-nitrification before escaping to the surface.

Leaching

Ammonium present in ammonia water will, when injected in the soil, attach to clay and organic matter particles, thus preventing it from leaching away. During the growing season, soil microorganisms convert the ammonium to nitrate (nitrification), which is the main form taken up by plants. The soil conditions that promote nitrification include: a soil pH of 7, moisture at 50% of the soil's water-holding capacity, and a soil temperature of 25°C. Under the following conditions, nitrification will not occur, and ammonium is susceptible for leaching: a pH below 5.5, a waterlogged moisture condition, and temperature under 5°C, i.e. during wet autumns and winters.
In general, both NH_3 and N_2O emissions and NO_3^- leaching can be minimised when the ammonia water is applied by soil injection and incorporation into the soil after application.

Current legal view on condensated ammonium water

Condensated ammonium water (Aqua ammonia) is in principle a regular fertiliser although its position with the Nitrates Directive has to be clarified. Bio-based fertilising products based on capturing ammonia in water (or in an acid) however, might not meet regulatory requirements for these regulatory liquid fertilisers. In the EU, a minimum 15% N (C.1.1. Annex 1 of EC 2003/2003) for liquid N fertilisers is required, otherwise national legal requirements are in force. If the national regulations do not specifically describe ammonium solution or aqua ammonium, the EU Regulation rules.
If fatty acids are present in the ammonium solution, the % of organic carbon (from fatty acids) should be determined to conclude if it falls under the criteria of an inorganic fertiliser (European Commission 2018).
However, in some EU countries, it is possible to ask a national derogation for application of any bio-derived fertiliser for a specific application area or time period ('pilot status'), taking into account additional criteria or conditions that maybe imposed.

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