SYSTEMIC

Fact sheet

Recovery of nutrients and resources from digestate

2021

Market opportunities for advanced bio-refinery products from digestate

Ammonia as hydrogen carrier

Extract from D 3.4 Market study for biobased fertilising products from digestate within a European context

Ammonia as a hydrogen carrier

There is a demand for ammonia as a hydrogen carrier (reductant) in emerging emission control (DeNOx) technologies in industrial and automotive applications.
Selective (non-)catalytic reduction for flue gas cleaning of NOx is used in a wide range of capacities in all kinds of combustion installations in sectors like waste incineration, energy plants, metal industry and greenhouse horticulture. The scrubbing process is also used to remove NOx from NOx rich gases produced in a relatively small amount at metal-dissolving, nitric acid and chemical plants, etc. (emis/vito.be).
Selective (Non-)Catalytic Reduction reduces NOx (the oxides of nitrogen) to N_2 and H_2O by adding NH3 or urea according to the following this reaction diagram:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$

Selective non-catalytic reduction (SNCR)

In SNCR, a mixture of steam and the reducing agent is injected in the flue gas of an incineration process, to the furnace. If ammonia is used as reducing agent, the optimal temperature is 930 to 980°C. If urea ($(NH_2)CO$) is used, the temperature needs to be even higher (950-1050°C) because it needs to be thermally cracked to NH3, which can then react as the reducing agent.
NOx removal efficiencies in SNCR range from 40 to 70% (Anon n.d.) .

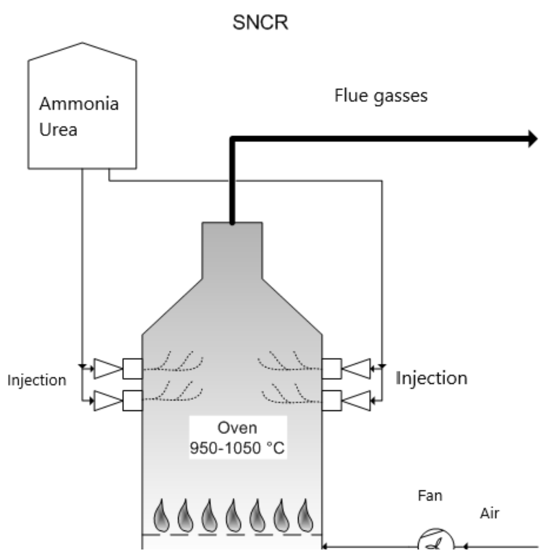

*Figure **Fout! Geen tekst met de opgegeven stijl in het document.**-1. Scheme SNCR (Emis: energie- en milieu-informatiesysteem voor het Vlaamse Gewest n.d.)*

Example

An incineration plant that processes 25 tonnes of waste an hour, emits 25 to 40 kg NOx/h. To reduce the NOx below the limit of 120 mg NOx/Nm³ this would require 100 L of ammonia solution (25% chemical grade). At a cost of 150€/ tonne of ammonia solution this would mean a yearly cost of 14.000€. A larger incineration plant claimed to use 1000 tons ammonia solution (25% chemical grade) per year, costing them 150.000€/year.
Recovered ammonia water (10-20%) is perfectly suited to replace urea.

There are already waste incineration companies using only recovered ammonia water in their DeNOx process and have not had any problems with it. Lower concentrated ammonia water (10%) can also be used, because different concentrations of recovered ammonia water can be blended in one storage tank before usage.
Impurities in the recovered ammonia water are no issue for SNCR since there is no catalyst present which could be fouled.
In general, most incineration plants are not inclined to use the recovered N alternative, because this cost of contaminant free 25% urea solution is only marginal for them.
They could be persuaded to use (lower quality) ammonia water for their flue gas cleaning (SNCR), if they can obtain it for a low price.
If only transport costs are taken into account, both parties (the biogas plant and the incineration plant) are reducing their costs.

Selective catalytic reduction (SCR)

SCR is using a catalyst to accelerate the deNOx process and improve the efficiency. The optimum process temperature lies between 320 – 500 °C depending on the catalyst (oxides of vanadium, wolfram, molybdenum or other metals).

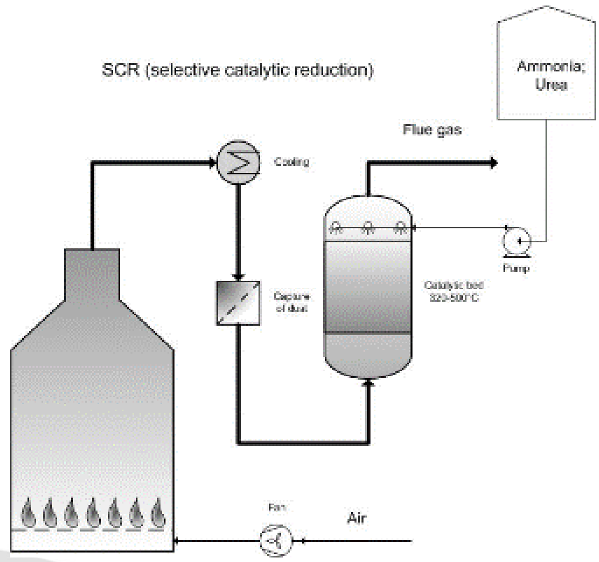

*Figure **Fout! Geen tekst met de opgegeven stijl in het document.**-2. Scheme SCR (Emis: energie- en milieu-informatiesysteem voor het Vlaamse Gewest n.d.)*

NOx removal efficiencies with SCR range from 80-95% (Anon n.d.) with incoming concentrations of NOx of some g/Nm³ up to 1 000 000 Nm3/h. This is a higher NOx reduction yield compared to SNCR. Smaller installations (<5MWth) have a lower yield (80-85%).

The SCR installation can be placed immediately after the boiler ("high-dust" switching) or after the dust filters or scrubbers ("low-dust" switching). This requires the flue gas to be heated to reaction level. The ammonia source is injected into the exhaust gases prior to their passing into the SCR (Chironna and Altshuler 2001).

The use of recovered ammonia water as a reducing agent would also be possible in SCR but requires a higher purity because of the presence of the catalyst. The following components must not be present in that the recovered ammonia water:

- SO_3 and Cl, since they react with ammonium and water to form ammonium sulphate, ammonium bisulphate and ammonium chloride. These condensed ammonium salts can cause reversible deactivation of the catalyst, by lowering the active surface of the catalyst and hereby reducing its separation efficiency. They are emitted as aerosols that are difficult to separate.
- Dust, because it contains potassium and sodium, which can precipitate on the catalyst causing poisoning or irreversible deactivation of the catalyst.

Some ammonia solutions recovered from bio-waste can already meet these quality specifications (personal communication, 2018). Yet, plants using SCR are reluctant on using recovered ammonia water because, the flue gas cleaning process is far from their core business, and the reduced costs related to the recovered ammonia solution are relatively small compared to the risk they would take by poisoning their catalysts.

The use of recovered ammonia water could also help contribute to the green image of the plant and reduce the costs of buying chemical grade ammonia. If the whole chain (biogas plant, provinces, incineration plants of municipal waste) could be involved, this could facilitate the logistic and supply aspect and raise more public awareness about recycling.

SCR as deNOx for exhaust gasses from combustion engines

In the European Union emissions of nitrogen oxides (NOx), must be limited by EU exhaust emissions standards and Real Driving Emissions legislation. One in two new cars registered in Western Europe is a diesel vehicle, which means the number of cars with SCR technology is set to rise.
The SCR reaction is the same as described above, the reducing agent is called “Diesel exhaust fluid (DEF)” better known under the commercial name “AdBlue®” or AUS32 under the ISO 22241. DEF is an aqueous urea solution made with 32.5% urea and 67.5% deionized water.

ISO 22241 lists strict requirements for maintaining concentration and purity of ingredients critical to the proper functioning and longevity of the SCR system. It also contains a description on the methods to be used for determining these parameters and reproducibility of the results.

An important phrase in the ISO 22241 states that AUS 32 is an aqueous urea solution, manufactured from technically pure urea – with no addition of any other substances – and pure water. Technically pure urea is industrially produced grade of urea with traces of biuret, ammonia and water only. The specifications of AUS 32 are listed in Table Fout***! Geen tekst met de opgegeven stijl in het document.****-1*.

*Table **Fout! Geen tekst met de opgegeven stijl in het document.**-1. Specifications for AUS32 in ISO22241*

Characteristics	Unit	Min	Max
Urea content	% (m/m)	31.8	33.2
Density at 20°C	Kg/m³	1087.0	1093.0
Refractive index at 20°C		1.3814	1.3843
Alkalinity as NH3	%(m/m)		0.2
Biuret	%(m/m)		0.3
Aldehydes	Mg/kg		5
Insoluble matter	Mg/kg		20
Phosphate (PO4)	Mg/kg		0.5
Calcium	Mg/kg		0.5
Iron	Mg/kg		0.5
Copper	Mg/kg		0.2
Zinc	Mg/kg		0.2
Chromium	Mg/kg		0.2
Nickel	Mg/kg		0.2
Aluminium	Mg/kg		0.5
Magnesium	Mg/kg		0.5
Sodium	Mg/kg		0.5
Potassium	Mg/kg		0.5

The strict requirements of the composition and purity of AUS 32 described in the ISO 22241 make it practically impossible for recovered ammonia water to be used as such as AUS 32. Even if a purity similar to AUS 32 could be reached by upgrading, ammonia water would still not contain urea (but ammonium).

It would also not be possible to sell it under the name "AdBlue®" and suppliers of SCR systems would not want to use this product in their systems, since it does not meet the ISO22241 specifications and therefore they cannot give guaranties on its performance. However, the European Emission Standards do not mandate the use of specific technologies (and products) to meet the standards.

So, there is a prospect for recovered ammonia water being used as DEF, but only if it is proven to work with a certain SCR technology and could pass all safety requirements for quality, handling, testing, transportation storage, and refilling.

Furthermore, it would be very difficult to be competitive in the AUS 32 market, since AdBlue® is produced in large quantities and sold with a profit margin of only a few €cents per litre (personal communication, 2018). This makes it even for the large manufacturers difficult to produce a competitive product and they can sometimes only achieve this by having the do this by having their producing facilities on the most opportune locations. The easiest way to use recovered ammonia as AUS 32 would be by supplying it to a producer of AUS 32 as secondary raw material.

Gas engines on natural gas or other fuels (e.g. biogas) are used more frequently as emergency power supply. The NOx emission limit for gas engines on natural gas and biogas is 190mg NOx/Nm³ (https://www.amps.org.uk/eu-emissions-update). NOx excess can again be removed with an SCR gas cleaning system using a urea solution as reductant.

To be an eligible alternative reductant for SCR, the purity of the products needs to be proven before it can be used. Also, a file needs to be made to get a resource declaration from the ruling authorities for this specific product application. The file should scientifically substantiate that the product is suited for this application. It should also describe the composition and purity required to guaranty the safety for the SCR process.

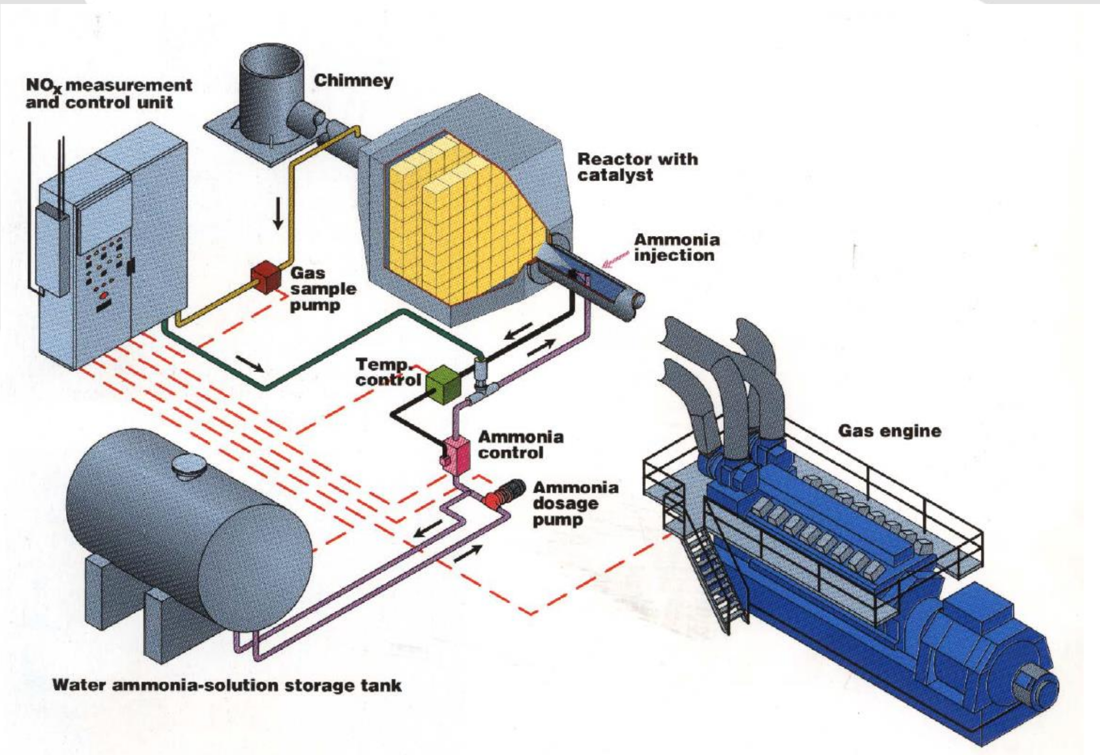

*Figure **Fout! Geen tekst met de opgegeven stijl in het document.**-3.SCR in gas engine.*

References

Anon. n.d. “Emis: Energie- En Milieu-Informatiesysteem Voor Het Vlaamse Gewest.” Retrieved (https://emis.vito.be/).

Chironna, Robert, and Boris Altshuler. 2001. “The Chemical Aspect of NOx Scrubbing.” *CR Clean Air Group, LCC*, 6.