European Nitrogen Assessment

Chapter 16: Integrating nitrogen fluxes at the European scale

Supplementary Material: Section C - Accounting of nitrogen use in chemical products

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The motivation for the invention of the Haber-Bosch process to synthesize reactive nitrogen (ammonia) from atmospheric molecular nitrogen was urgent need for nitrogen to enable sufficient agricultural food production and the provision of raw material for explosives (Erisman *et al.*, 2008). Today, about 48% of living humans (estimate for the year 2008, Erisman *et al.*, 2008) depend on about 80% of the nitrogen synthesized globally with the Haber-Bosch process (121 Tg N). About 24 Tg N is used in various industrial processes and the production on non-fertilizer products, or 21 Tg N when excluding ammonia used in caprolactam processing and returned as co-product ammonium sulphate (IFA Statistics, 2010). Several ammonia-based products are used as fertilizers, in industrial processes and in chemical products. Besides some ammonia salts, other ammonia-based industrial products that are not used as fertilizers include nitric acid, adipic acid, hydrogen cyanides, diisocyanates (MDI and TDI used in the manufacture of polyurethanes), acrylonitrile, melamine (produced from urea) and others (Domene & Robert, 2001). It is estimated that about 30% of the N fixed with the Haber-Bosch process is used in Europe for non-agricultural purposes, including about 4.5 Tg N in Western Europe in 2007, 0.7 Tg N in Central Europe, totalling about 5.2 Tg N (see Winiwarter et al., 2011*, Chapter 24*).

Total demand of nitrogen by the industry is about 5250 Gg N yr^{-1} in Western and Central Europe. Demand for industrial urea is about 1930 Gg N yr^{-1}, including 450 Gg N yr^{-1} of urea used for the production of melamine. Demand of ammonia for the production of ammonium nitrate is about 6100 Gg N yr^{-1}; of which 2900 Gg N yr^{-1} was used for the manufacture of fertilizer Calcium Ammonium Nitrate (CAN). The remaining 3100 Gg N yr^{-1} was used as fertilizer and for industrial purposes (IGAN=industrial grade ammonium nitrate) (IFA Statistics, 2010). The remaining nitrogen is used directly or for a range of downstream products, such as acrylonitrile, hydrogen cyanide, methyl methacrylate, methionine**,** animal feed, etc. A brief description of the characteristics of the main substances is given below.

16.SC1 shows the consumption of industrial nitrogen by main product (IFA Statistics, 2010) – as the table indicates, the split of the products over their further use, for example

the use of ammonia for the production of nitric acid other than ammonium nitrate, hydrogen cyanide, etc., is unknown.

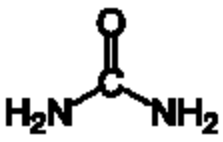
Table 16.SC1. Consumption of industrial nitrogen in Western and Central Europe in 2007 (in kt N)

Substance	Use	CE	WE	Total
Ammonia	Total industrial consumption (excl. caprolactam)[1]	305	2,610	2,915
	Nitric acid for other than AN	*245*	*595*	*840*
	Other uses, including, Ammonium Calcium Nitrate (ACN), Hydrogen Cyanide (HCN), Methylamine (MMA), Methionine	*60*	*2,015*	*2,075*
	Ammonia used for Caprolactam	720	165	885
Urea	Total industrial consumption	295	1,635	1,930
	Industrial use for melamine			*450*
	Other industrial uses			*1,480*
Nitric Acid	Apparent consumption[2]	1,230	3,110	4,340
	Nitric Acid for AN and CAN fertilizers	*940*	*2,085*	*3025*
	Nitric Acid for NPK-NP fertilizers	*-*	*375*	*375*
	Nitric Acid for IGAN	*45*	*55*	*100*
	Nitric acid for other uses	*245*	*595*	*840*
AN products	EGAN consumption	90	110	200

Summary	Industrial nitrogen consumption for non-fertilizer use			
	Total industrial urea	295	1,635	1,930
	Industrial Grade AN (IGAN)	90	110	200
	Other N uses	305	2,610	2,915
	Total	**690**	**4,355**	**5,045**

[1] Caprolactam generates AS that is mainly used as fertilizer.
[2] Underlined data are from IFA data from IFA PIT Service (2010)
[3] SRI Consulting report 2007, Nitric Acid

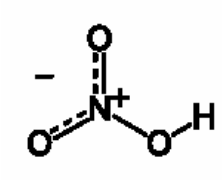
Urea $(NH_2)_2CO$ (46% nitrogen).



The bulk of urea production is used as fertilizer in agriculture, animal feed and urea formaldehyde resins, but it is also used as raw material for chemicals used in plastics, melamine, adhesives and explosives. Urea has the ability to trap many organic compounds in the form of clathrates. The organic compounds are held in channels formed by interpenetrating helices comprising of hydrogen-bonded urea molecules. Industrial uses are estimated to account for roughly 10% of the world urea market in 2007.

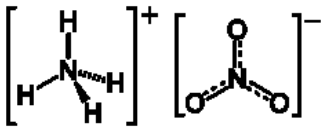
In Europe, the use of industrial urea over its fertilizer use is much larger in proportion than in any other regions with a share of 45% for West Europe and 22% for central Europe, giving a weighted average of about 40% (IFA, 2010). World urea production in 2007 was about 64 million metric tons of nitrogen (Mt), equivalent to about 139 Mt product. Urea production in 2007 was close to 3.4 Mt urea in Central Europe and 4.9 Mt urea in West Europe (IFA Statistics, 2010).

Nitric acid – HNO_3 (22% nitrogen by weight)



Nitric acid[1] is used in many nitro-chemicals for the production of fertilizers, explosives, and other industrial products. Industrial uses include the metal industry (aqua regia), explosives (TNT), dyes, perfumes, fungicides etc. World nitric acid production in 2006 was estimated at about 51 Mt. It is estimated that ammonium nitrate (AN) production accounts for 75% of the world nitric acid market.
The AN market is approximately two-thirds fertilizers and one-third industrial applications[2]. The share of explosive-grade AN (EGAN) is estimated to be about 21%. The industrial use includes the production of pesticides, herbicides, plastics and fibers. Slightly more than half of world nitric acid production occurs in West and Central Europe Apparent consumption of nitric acid in Europe in 2006 was estimated at 19.7 Mt HNO_3, equating to 4.34 Tg N (SRI Consulting, *Nitric Acid*, 2007).

Ammonium nitrate - $(NH_4)(NO_3)$ (27%-34% nitrogen).

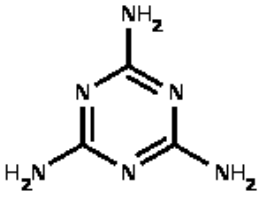


Ammonium nitrate (AN) is formed from ammonia and nitric acid. HNO_3 (aq) + NH_3 (g) → NH_4NO_3 (aq). Although chemically simple, this reaction is technologically challenging and is done using anhydrous ammonia gas and concentrated nitric acid. The reaction is violent and very exothermic. Ammonium nitrate decomposes in temperatures normally well above 200°C. However, the presence of impurities (organic and/or inorganic) will often reduce the temperature point when heat is being generated. Once the AN has started to decompose, then a runaway reaction will normally occur as the heat of decomposition is very large. AN releases so much heat, that this runaway reaction is not normally possible to stop. About 52% of ammonium nitrate production goes to calcium ammonium nitrate (CAN), which is entirely used as a fertiliser. The 48% remaining share of AN production goes for fertilizers (solid AN, UAN, etc) and for industrial-grade AN (or IGAN) (IFA Statistics, 2010). The main use of industrial grade AN is for explosives. Half of the nitrogen is retrieved from nitric acid,

[1] http://www.articlemonkeys.com/Art/3434/217/Nitric-Acid-And-Its-Different-Uses-and-Implications-In-Our-Society.html
[2] http://www.sriconsulting.com/CEH/Public/Reports/757.8000/

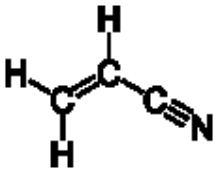
which dedicates about 75% of to the production of AN, while the other half of the nitrogen stems from the direct use of ammonia.

Melamine $C_3H_6N_6$ (66% nitrogen).



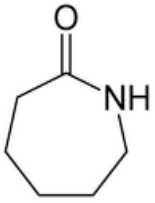
Production of melamine in Europe (incl. Turkey) was about 425 Kt, with 41 Kt net import and a stock adjustment of 12 Kt in 2008[3]. In the production of melamine an equal amount of nitrogen is recovered as ammonia. Melamine is an organic base and a trimer of cyanamide, with a 1,3,5-triazine skeleton. If mixed with resins, it has fire retardant properties due to its release of nitrogen gas when burned or charred, and has several other industrial uses[4]. Urea is the main nitrogen feedstock for producing melamine. Main applications are coatings (for UFC-coated fertilizers), construction industry (e.g. concrete plasticizers), electronics (e.g. computer cases), paper (e.g. bank notes, maps), furniture (laminates), sport articles (skis, snowboards). In Europe, 86% of melamine is used for wood-based panels. About 450 kt N yr^{-1} of nitrogen production through urea is estimated to be used for melamine[3] in Europe.

Acrylonitrile C_3H_3N (36% nitrogen)



According to UK-based consultant Tecnon OrbiChem[5], global ACN capacity in 2008 was just over 6.2 Mt/year. European capacity was 1.25 Mt/year in 2008 with no changes expected to 2015.

Caprolactam - $C_6H_{11}NO$ (12% nitrogen)



The annual global production of caprolactam is about 4 Mt, corresponding to about 480 kt N. Caprolactam is a precurser of Nylon-6, which is used in fibers and plastics. Most processes generate Ammonium Sulphate (AS) as a by-product from caprolactam production. Virtually all this AS is used as fertilizer. Western Europe accounts of about 13% of global nylon production[6].

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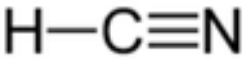
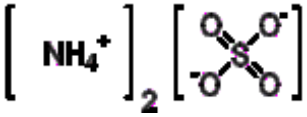
[3] DSM Melamine BV, pers. communication 04.08.2009
[4] http://en.wikipedia.org/wiki/Melamine; http://www.dsm.com/en_US/html/dmm/endmarket.htm
[5] http://www.icis.com/v2/chemicals/9074882/acrylonitrile/uses.html
[6] http://www.yarnsandfibers.com/ir/report/nylon_chain_report2006.html

Hydrogen cyanide HCN (52% nitrogen)



World HCN production is estimated at 1.8 Mt, of which 50% comes from the United States.[7] Production of HCN is generated from either directly or as by-product from the manufacture of acrylonitrile. HCN is mainly used for adiponitrile (for nylon 6/6) and for various other organic compounds and is also partly used for the production of ammonium sulphate. Non-adiponitrile products account for 2/3 of global production and about 1/3 of production in Europe.

Ammonium sulphate - $(NH_4)2SO_4$ (21% nitrogen)



Global production of Ammonium Sulphate was 20.2 Mt in 2007 (IFA Statistics, 2010). Western and Central Europe account for 25% of global production, with a combined total of 1 Mt N, of which 95% is consumed within the region .

Close to 88% of the AS produced in Europe comes from the manufacture of caprolactam; the remaining 12% comes from various industrial processes. However, all this production is used as fertilizers and not in downstream industrial products. No ammonium sulphate is estimated to be used for industrial purposes.

References

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[7] http://www.sriconsulting.com/CEH/Public/Reports/664.5000/; http://www.icis.com/Articles/2005/12/14/642136/chemical-profile-hydrogen-cyanide-hcn.html