SNAP CODE: **040521**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Adipic Acid

NOSE CODE: **105.09.72**

NFR CODE: **2 B 3**

1 ACTIVITIES INCLUDED

This chapter covers emissions from the bulk production of adipic acid using the intermediates cyclohexanol and cyclohexanone. The mixture of these intermediates is sometimes known as KA.

2 CONTRIBUTION TO TOTAL EMISSIONS

There is uncertainty in national emission estimates for N_2O and it is not possible to give an accurate figure for the contribution of adipic acid production to total emissions.

It has been estimated that the increase in the concentration of N_2O in the earth's atmosphere is 0.2% and that growing adipic acid production accounts for up to 10% of this increase (Theimans and Trogler, 1991). From this it is not clear if adipic acid production is considered a major contributor to national emissions, compared with natural and other anthropogenic sources.

Global adipic acid production is estimated to be 2.2 x 10^9 kg, and that just under one mole of N_20 is emitted for every mole of adipic acid produced (Theimans and Trogler, 1991), suggesting that global emissions of N_2O from adipic acid production is of the order of 0.5 x 10^9 kg.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Adipic Acid	040521	-	0	-	-	-	-	12.4	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Adipic acid is a colourless, odourless, sour tasting crystalline solid. Little of this dicarboxylic acid occurs naturally. Aqueous solutions of the acid are corrosive. Adipic acid is produced from cyclohexane. Cyclohexane is used to produce KA, a mixture of cyclohexanol and cyclohexanone. KA is then oxidised with nitric acid to produce adipic acid. Adipic acid is primarily used for the manufacturing of 6.6-nylon.

3.2 Definitions

3.3 Techniques

The first reaction stage is the production of the intermediates cyclohexanone and cyclohexanol (usually abbreviated to KA, KA oil, ol-one or anone-anol). The KA, after separation from unreacted cyclohexane and reaction by-products, is then converted to adipic acid by oxidation with nitric acid via nitrolic acid intermediates.

All current industrial adipic acid production processes use nitric acid in the final oxidation stage. Growing concern with air quality may exert further pressure for alternative routes as manufacturers seek to avoid NO_x abatement costs, a necessary part of processes that use nitric acid.

There are variations of the cyclohexane oxidation process. However, the process is still fundamentally the same as originally developed in the early 1940s. Cyclohexane is oxidised with 40-60% nitric acid in the presence of copper and vanadium catalysts. The reaction is exothermic and produces the following major by-products: dicarboxylic acids, glutaric, succinic acids and CO_2. Nitric acid is reduced to a combination of NO_2, NO, N_2O and N_2.

The most industrially significant reaction of adipic acid is with diamines, specifically 1,6-hexanediamine. A water soluble polymeric salt is formed initially upon mixing solutions of the two materials; then heating with removal of water produces the polyamide, nylon-6,6.

3.4 Emissions

The principle emissions of concern from these processes are related to nitric acid, either as the various oxides of nitrogen or as a very dilute solution of the acid itself.

Nitrous oxide is produced during the conversion of cyclohexanol to the ketone, and also upon oxidation of aldehyde and alcohol impurities usually accompanying the KA and arising in the cyclohexane oxidation step. This oxidation step has an associated emission factor (for unabated emissions) of 300g N_2O/kg adipic acid produced.

Of all the intermediates the nitrolic acid is the only one of sufficient stability to be insoluble under very mild conditions. It is hydrolysed to adipic acid in one of the slowest steps in the sequence. Nitrous oxide is formed by further reaction of the nitrogen-containing products of nitrolic acid hydrolysis. The NO and NO_2 are reabsorbed and converted back to nitric acid, but N_2O cannot be recovered in this way, and thus is the major nitric acid derived by-product of the process.

About 20% of the reaction occurs by the vanadium oxidation of 1,2-dioxygenated intermediates; this path does not produce the non-recoverable nitrous oxide.

The nitric acid oxidation step produces three major waste streams: an off-gas containing oxides of nitrogen and CO_2, water containing traces of nitric acid and organics from the water removal column; and a dibasic acid purge stream containing adipic, glutaric and succinic acids.
Adipic acid may also be dispersed as a dust when it is subject to normal dust explosion hazards. The material is also an irritant, especially upon contact with the mucus membranes.

3.5 Controls

Off gases may be treated in a reductive furnace to reduce NO_X emissions, this treatment also destroys N_2O.

Nitric acid may be removed by distillation, the copper and vanadium catalyst are recovered by ion-exchange treatment.

4 SIMPLER METHODOLOGY

The simpler methodology involves multiplying the national production data for adipic acid with an emission factor.

5 DETAILED METHODOLOGY

The detailed methodology involves gaining site specific data on the production of adipic acid and emissions of N_2O, other oxides of nitrogen and compounds such as CO_2.

6 RELEVANT ACTIVITY STATISTICS

The relevant activity statistic is the national production of adipic acid in metric units (eg kg, metric tons). There was an adipic acid demand of nearly two billion metric tons per year world-wide in 1989. World-wide production in 1986 reached 1.6×10^6 metric tons (3.5×10^9 lb) and in 1989 was estimated at more than 1.9×10^6 metric tons. Adipic acid is a large volume organic chemical. It is one of the top fifty chemicals produced in the United States in terms of volume, with 1989 production estimated at 745 000 metric tons.

7 POINT SOURCE CRITERIA

There are relatively few adipic acid manufacturing plants and they should be treated as point sources when plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Emission Factor	Quality Code	Reference	Comments
300g/kg N_2O produced	C	Thiemans and Trogler 1991	Based on laboratory experiments designed to simulate industrial production

9 SPECIES PROFILES

For the simpler methodology, it is assumed that the emission profile is 100% N_2O. For the detailed methodology, the emissions profile is obtained directly from site measurement data. Note, other compounds believed to be emitted include CO_2 and possibly NO and NO_2.

10 UNCERTAINTY ESTIMATES

The range of production of N_2O from the laboratory measurements was between 0.7 and 1.06 moles per mole of adipic acid produced. This suggests the uncertainty in the emission factor is about ±20%. However, it is not clear how representative of the possible range in emissions the laboratory measurements are and so an absolute uncertainty cannot be stated.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The simple methodology relies on one emission factor, no account is taken of slightly differing processes, abatement equipment etc. The more detailed methodology requires measurement data from the plant, but this is not widespread practice.

Improving the emission factors requires measurements to be taken from a range of representative industrial plants.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant as plants are to be considered point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

Unless further information is available, it is assumed that emissions are constant, both on a diurnal and seasonal basis.

14 ADDITIONAL COMMENTS

During the late 1980's and early 1990's adipic acid production continued to increase globally, particularly in the Far East, as demand for nylon increased.

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

Verification procedures are through site specific measurements. With few emission factors available, comparison with other countries is likely to show up differences in production statistics rather than in actual emissions.

17 REFERENCES

IPCC Guidelines for National Greenhouse Gas Inventories. Greenhouse Gas Inventory Manual. Vol. 3, 1995.

Kirk-Othmer 1991 Encyclopaedia of Chemical Technology. Fourth Edition. Pub. Wiley Interscience.

Thiemans M.H., Trogler W.C. 1991. Nylon Production: An Unknown Source of Atmospheric Nitrous Oxide, Science Volume 251 pp 932 - 934.

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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