SNAP CODE: **040520**

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

NOSE CODE: **105.09.76**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Acrylonitrile is made by the catalytic ammoxidation of propylene in the vapour-phase. This process was developed by Standard Oil of Ohio (Sohio).

Some plants still use the older route, namely addition of hydrogen cyanide to acetylene.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of acrylonitrile plants contributes on average <0.01% to the total NMVOC emission in a country.

Table 2.1: 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
Acrylonitrile	040520	-	-	0	-	-	-	-	-

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

Acrylonitrile is produced by reaction of propylene with ammonia and oxygen. For this process a fluid bed reactor with a solid catalyst is used. It is a single pass process meaning that no recycling is used. The propylene conversion is 98%. Operating conditions are: Temperature 400 - 510 °C; p 150 - 300 kPa; the catalyst used is a mix of metal oxides, most commonly bismuth and molybdenum oxides with traces of other metal oxides.

The reactor effluent is quenched with water in a countercurrent absorber and unreacted ammonia is neutralised with sulphuric acid. The resulting ammonium sulphate can be recovered (and used as a fertiliser).

The absorber off-gas containing primarily nitrogen, carbon monoxide, carbon dioxide and unreacted hydrocarbons is vented or passed through an incinerator to combust the hydrocarbons and carbon monoxide and then vented.

The acrylonitrile-containing solution from the absorber is separated in several columns to produce: acrylonitrile, crude hydrogen cyanide, crude acetonitrile and a fraction with heavy impurities. The acetonitrile is either incinerated or purified for use as solvent.

3.2 Definitions

Ammoxidation Oxidative reaction of ammonia with an aliphatic group:
$R\text{-}CH_3 + NH_3 + 1.5\ O_2$ ® $R\text{-}CN + H_2O$
R = aromatic or olefin

3.3 Techniques

Other processes, now obsolete, are:

- ethylene oxide + HCN ® $HOCH_2CH_2CN$ ® $CH_2{=}CH\text{-}CN$

For the first step a base-catalyst is, e.g. diethyl amine; The temperature is 60 °C. For the second step a catalyst of alkali(ne) metal salts of organic acids, e.g. $MgCO_3$ is needed. The temperature is 200 °C.

- CHCH + HCN ® $CH_2{=}CH\text{-}CN$

Cuprous chloride is used as a catalyst.

3.4 Emissions

The major emissions to air are acrylonitrile, ethylene, methane and halogenated hydrocarbons. The halogenated hydrocarbons are released due to cleaning; the acrylonitrile is released in several sections of the plant; methane is released due to leakage; ethylene is released due to combustion.

For the Netherlands the VOC emission due to the acrylonitrile production is 73 ton/y. This emission is related to a production of 166 kton/y and a capacity of 183 kton/y (1992 data).
The VOC emission can be subdivided as follows:

Emission source	**[1]**
leakage losses from appendages, pumps, etc.	62%
flaring, disruptions	35%
losses due to storage and handling	2%
combustion emissions	0.1%
other process emissions	1%

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the acrylonitrile production to estimate total emissions. The amount of emitted VOC is then directly related to the acrylonitrile production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1: Acrylonitrile production in some countries and regions for 1990

Country or Region	kton/y	Source
Western Europe	1200[1]	Kirk-Othmer Vol. 1 ‘91
Mexico	60[1]	Kirk-Othmer Vol. 1 ‘91
Far East	200[1]	Kirk-Othmer Vol. 1 ‘91
U.S.A.	1217	Chem&EngNews 29/6/92
Japan	593	Chem&EngNews 29/6/92

[1] figures for 1988

7 POINT SOURCE CRITERIA

Acrylonitrile production plants can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for acrylonitrile

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [1]	0.44	C
EPA AIRCHIEF 1993 [2]	100	C/D

The proposed emission factor for use in calculating the VOC emission from an acrylonitrile plant is 1 kg/ton.

9 SPECIES PROFILES

Table 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1: The composition of the VOC emissions for the different sources is [1]:

	methane	ethylene	acrylonitrile	HCFC’s	other HC’s
leakage loss	2%	3%	25%	0%	70%
flaring and disruptions	0%	4%	0.2%	0%	96%
storage and handling loss	0%	0%	99.6%	0%	0.4%
combustion	59%	10%	0%	0%	31%
other process emissions	0%	0%	0%	100%	0%

Table 9.2: The overall VOC emission profile for acrylonitrile plants

	TNO ER [1]	EPA [2]
methane	1%	0%
ethylene	3%	0%
acrylonitrile	18%	100%
HCFC’s	1%	0%
other HC’s	77%	0%

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 1 4th edition (1991)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 TNO Emission Registration 1992
2 EPA, AIRCHIEF CD-ROM 1993

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE, AND SOURCE

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Updated with particulate matter details by:
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20 POINT OF ENQUIRY

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