

SNAP CODE: 040505

SOURCE ACTIVITY TITLE: PROCESSES IN ORGANIC CHEMICAL INDUSTRIES
(BULK PRODUCTION)
1,2 Dichloroethane + Vinylchloride (Balanced Process)

NOSE CODE: 105.09.59

NFR CODE: 2 B 5

1 ACTIVITIES INCLUDED

This chapter only includes the vinylchloride produced in the balanced process. For other vinylchloride production processes see chapter B454.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of vinylchloride plants contributes on average 0.02% 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 ₂ O	NH ₃
1,2 Dichloroeth. + Vinylchl. (balanced process)	040505	-	-	0	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

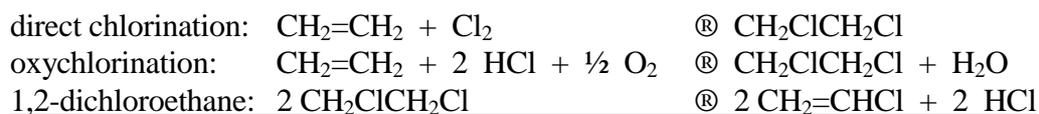
- = no emissions are reported

3 GENERAL

3.1 Description

Vinylchloride is mainly produced by the balanced process.

The balanced process consists of two routes operated simultaneously; in the direct chlorination route, chlorine is added to ethylene to form 1,2-dichloroethane; in the oxychlorination route, ethylene reacts with hydrogen chloride under oxidative conditions (presence of oxygen) also to form 1,2-dichloroethane. The reaction equations are:



- Direct chlorination:
Ethylene and chlorine are dissolved in 1,2-dichloroethane with FeCl_3 . The reaction is limited by ethylene absorption. The selectivity to 1,2-dichloroethane is >99%. The formation of 1,1,2-trichloroethane by-product is suppressed by using oxygen or DMF as inhibitor.

The reactor can be operated in two ways:

- reactor temperature 50 - 65 °C; after the reactor the 1,2-dichloroethane is washed with water to remove FeCl_3 or the FeCl_3 is adsorbed on a solid, e.g. activated carbon.
 - reactor temperature is equal to the boiling temperature of 1,2-dichloroethane; the evaporation of 1,2-dichloroethane removes the heat of reaction from the reactor. The reactor effluent, crude 1,2-dichloroethane, contains no FeCl_3 , so no washing is needed.
- Oxychlorination:
This is a vapour phase process using CuCl_2 with additives on porous support, e.g. alumina, as catalyst. Both dry air and dry oxygen are in use. The use of pure oxygen has the advantage of reducing purge streams and it allows the use of reduced (reaction) temperatures. Good temperature control is necessary because the reaction is highly exothermic.

Operation conditions for fluid beds are: T: 220 - 235 °C; p: 250 - 600 kPa.

Operation conditions for fixed beds are: T: 230 - 300 °C; p: 250 - 1500 kPa.

1,2-Dichloroethane selectivity is 93 - 96%.

The 1,2-dichloroethane is quenched with water or cooled with a heat exchanger, so the 1,2-dichloroethane and water in the effluent are condensed. The 1,2-dichloroethane and water are separated by a decantation. The remaining gas (containing 1 - 5% 1,2-dichloroethane) is further processed to recover all 1,2-dichloroethane.

1,2-Dichloroethane of both routes is sent to a purification section, where light and heavy impurities are removed.

The purified 1,2-dichloroethane is fed to a reactor where it is pyrolyzed to form vinylchloride. Operation conditions are: T: 500 - 550 °C; p: up to 2500 - 3000 kPa.

A 1,2-dichloroethane conversion of 50 - 60% per pass is used.

After cracking, rapid cooling is required to suppress by-product formation. This is done by contacting the effluent, with cold 1,2-dichloroethane. From the quench tower effluent first the hydrogen chloride and then the vinylchloride is removed. The hydrogen chloride is recycled to the oxychlorination reactor. The unreacted 1,2-dichloroethane is purified and recycled. All waste streams contain chlorinated compounds. From the fluid waste streams useful by-products can be recovered. The remaining waste streams can be vented or first incinerated or catalytically oxidated and then vented. The oxidation product stream containing hydrogen chloride can be recycled to the oxychlorination reactor (where the hydrogen chloride reacts with ethylene).

3.2 Definitions

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: 1,2-dichloroethane, other chlorinated hydrocarbons, methane. Methane is emitted due to combustion, 1,2-dichloroethane due to leakage and storage losses, the other chlorinated hydrocarbons due to leakage losses.

For the Netherlands, the VOC emission due to the acrylonitrile production is 320 ton/y. This emission is related to an acrylonitrile production of 420 kton/y and a capacity of 499 kton/y (data for 1992).

The VOC emission can be subdivided as follows:

Emission source	[1]
leakage losses from appendages, pumps, etc.	91%
flaring, disruptions	0%
losses due to storage and handling	4%
combustion emissions	2%
other process emissions	3%

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 vinylchloride production emissions. The amount of emitted VOC is then directly related to the vinylchloride 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: Vinylchloride production in some countries and regions for 1990 :

Country or Region	kton/y	source
U.S.A.	4826	Chem&EngNews 29/6/92

7 POINT SOURCE CRITERIA

These 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 vinylchloride (balanced process)

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [1]	0.76	C
TNO Emission Registration 1987 [2]	2.2	C

9 SPECIES PROFILES

Tables 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	1,2-dichloroethane	toluene	CIHC's	other HC's
leakage loss	0%	9%	42%	0%	48%	1%
flaring and disruptions	-	-	-		-	-
storage and handling loss	0%	0%	96%	0%	4%	0%
combustion	60%	10%	0%	1%	0%	29%
other process emissions	0%	82%	10%	6%	0%	2%

Table 9.2: The overall VOC emission profile for plants

	TNO ER [1]
Methane	1.2%
Ethylene	10.9%
1,2-dichloroethane	42.3%
Toluene	0.2%
CIHC's	43.8%
other HC's	1.6%

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****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.
See Verification Chapter for further details.

17 REFERENCES

- 1 TNO Emission Registration 1992.
- 2 TNO Emission Registration 1987.

18 BIBLIOGRAPHY

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 23 3rd edition (1983)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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