**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 main process used for vinylchloride production is the balanced process. This is the only process for which emissionfactors have been found sofar..

## 2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of vinylchloride plants contribute in 1990 according to Corinair 90 on average 0.02% to the total NMVOC emission in the reporting countries.

**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 | $CO_2$ | $N_2O$ | $NH_3$ |
| 1,2 Dichloroeth. + Vinylchl. (balanced process) | 040505 | - | - | 0.02 | - | - | - | - | - |

- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).[1]

## 3 GENERAL

### 3.1 Description

The balanced process is described in great detail on the sites of USEPA and some companies.A short description is given below..

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: $CH_2{=}CH_2 + Cl_2$ ® $CH_2ClCH_2Cl$

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

oxychlorination: $CH_2{=}CH_2 + 2\ HCl + \tfrac{1}{2}\ O_2$ ® $CH_2ClCH_2Cl + H_2O$
1,2-dichloroethane: $2\ CH_2ClCH_2Cl$ ® $2\ CH_2{=}CHCl + 2\ HCl$

overall: $2\ CH_2{=}CH_2 + Cl_2 + \tfrac{1}{2}\ O_2$ ® $2\ CH_2{=}CHCl + H_2O$

- 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 catalyticly 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

Not relevant

### 3.3 Techniques

See section 3.1.

### 3.4 Emissions

The major emissions to air are: 1,2-dichloroethane, vinylchloride, and other chlorinated hydrocarbons. The sources are mainly fugitive sources..

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 fugitive sources leakage can be limited by use of for instance more sophisticated types of seals

## 4 SIMPLER METHODOLOGY

Use of an overall emission factor for the production emissions. The amount of emitted VOC is then directly related to the 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 the USA in 1990 :**

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

## 7 POINT SOURCE CRITERIA

These plants can be considered as point sources.

## 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

### Emission factors for 1.2 dichloroethane

In the criteria document for 1.2.dichloroethane (4) an emission factor of 10 kg/ton product is proposed based on data from 1981.

**Table 8.2: Emission factors for vinylchloride (balanced process)**

| Source | factor (kg/ton) | Quality Code |
|---|---|---|
| Information from vinylchloride plant TNO 1992 [1] | 0.76 | C |
| Information from vinylchloride plant TNO 1987 [2] | 2.2 | C |

The criteriadocument for vinylchloride ( 5) (1981) gives an emissionfactor of 4-5 kg/ton for uncontrolled emissions and 0.13 kg/ton for best available technology.
The Handbook of emissionfactors (6) gives 0.1-0.2 kg/ton for abated emissions.

The World Bank Handbook gives emission factors of 0.02- 2.5 kg VOC per metric ton product, depending on the applied abatement which are consistent with the factors for individual plants mentioned above..

## 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** | **ClHC'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 Emission inventory [1]** |
|---|---|
| Methane | 1.2% |
| Ethylene | 10.9% |
| 1,2-dichloroethane | 42.3% |
| Toluene | 0.2% |
| Other Chlorinated hydrocarbons | 43.8% |
| Other hydrocarbons | 1.6% |

The World Bank Handbook (3) gives the following profile: 45% ethylene dichloride, 20% vinyl chloride 15 % other halogenated hydrocarbons , and 20 % other hydrocarbons

## 10 UNCERTAINTY ESTIMATES

The uncertainty depends on the information available about the applied abatement methods

## 11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant.

## 12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

## 13 TEMPORAL DISAGGREGATION CRITERIA

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

## 14 ADDITIONAL COMMENTS

No additional comments

## 15 SUPPLEMENTARY DOCUMENTS

No 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 Communication to TNO from vinylchloride producing plant in The Netherlands (1992.)
2 Communication to TNO from vinylchloride producing plant in The Netherlands (1987).
3 World Bank group Pollution Prevention and Abatement Handbook Petrochemicals Manufacturing Page 371 and 372 (1998)
4 Criteria document 1.2. dichloroethane . Reported by RIVM Nr……. Year 1983
5. Criteria document vinylchloride Reported by RIVM Nr …..Year 1983
6 Handbook of Emissionfactors Part 2 Industrial Sources Ministry of Housing, Spatial Planning and the Environment M.E.Reinders (editor)(1983)

## 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).
- USEPA Locating and estimating air emissions from sources of ethylenedichloride plants.

Report EPA 450/4-84-007

- Siemens AG Gas Analysis in VCM (Vinylchloride monomer )Production Plants

http://www.processanalytics.com

## 19 RELEASE VERSION, DATE AND SOURCE

Version : 1.2

Date : September 2006

Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
TNO
The Netherlands

Update by:
P.F.J. van der Most

## 20. POINT OF ENQUIRY

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