

SNAP CODE: 040519

SOURCE ACTIVITY TITLE: PROCESSES IN ORGANIC CHEMICAL INDUSTRIES
(BULK PRODUCTION)
Phthalic Anhydride

NOSE CODE: 105.09.75

NFR CODE: 2 B 5

1 ACTIVITIES INCLUDED

Phthalic anhydride is manufactured from either *o*-xylene or naphthalene. Several types of oxidation are used to produce phthalic anhydride.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of phthalic anhydride plants contributes on average of about 0.1% to the total NMVOC emission in a country.

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 ₂ O	NH ₃
Phthalic Anhydride Production	040519	0	-	0.1	-	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

Using *o*-xylene as feed two processes are used:

- Fixed bed vapor-phase oxidation.

The feed is led into a multitubular reactor. This is operated at 380 - 400 °C and ambient pressure. The catalyst used is vanadium oxide with titanium dioxide on a non-porous carrier.

The *o*-xylene inlet concentration in the air feed is above the explosion limit of *o*-xylene. The yield is 1.09 kg phthalic anhydride per kg pure *o*-xylene.

- Liquid-phase oxidation.
As solvent acetic acid is used. The operation temperature is 150 - 245 °C and the catalyst is a mixture of cobalt, manganese and bromine salts. Under these conditions *o*-xylene is oxidated to phthalic acid. In the next step phthalic acid is dehydrated to phthalic anhydride.

This process has as advantage high yield, but as disadvantage high capital costs.

Using naphthalene as feed also two processes are used:

- Fixed bed vapor-phase oxidation.
Operation conditions are the same as for the *o*-xylene fixed bed oxidation, except for the catalyst. Vanadium oxide and alkali metal on silica support is used as catalyst.

The yield is 0.9 - 0.96 kg phthalic anhydride per kg naphthalene.

- Fluidized bed vapor-phase oxidation.
This is a process at lower temperature: 340 - 385 °C. A low activity catalyst of vanadium oxide on silica gel is used. The yield is lower as for the fixed bed process.

Phthalic anhydride recovery and purification from vapor-phase oxidations.

The reactor outlet is fed to a switch condenser. The tubes in the condensers first are cooled to solidify the phthalic anhydride on the outside of the tubes, then hot oil is circulated through the tubes. This causes the phthalic anhydride to melt and the liquid is collected in a tank.

The purification section consists of two columns. Both are operated under vacuum. The first column removes the low boiling by-products (maleic, benzoic, phthalic and citraconic acid) and the second the high boiling products.

Total by-product production is less than 1 wt.% of the phthalic anhydride production.

3.2 Definitions

3.3 Techniques

See section 3.1.

3.4 Emissions

The VOC emission can be subdivided as follows:

Cause of the emission
leakage losses from appendages, pumps, etc.
flaring, disruptions
losses due to storage and handling
combustion emissions
other process emissions

No data are available on relative distribution of emissions from these sources.

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 phthalic anhydride production emissions. The amount of emitted VOC is then directly related to the phthalic anhydride 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

Relevant statistics are published by the UN Statistical Office.

7 POINT SOURCE CRITERIA

SB plant can be considered as point source if individual plant data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 2: Emission factors for phthalic anhydride

Source	factor (kg/ton)	Quality Code
<i>o</i> -xylene oxidation factor, EPA [1]	1.3	C
naphthalene oxidation factor, EPA [1]	6.0	C

9 SPECIES PROFILES

The emitted products from the *o*-xylene oxidation process are: phthalic anhydride, maleic anhydride and benzoic acid.

The emitted products from the naphthalene oxidation process are: phthalic anhydride, maleic anhydride, naphthaquinone and products from the thermal incinerator (when present).

10 UNCERTAINTY ESTIMATES

At the time of publication there were not enough data to establish an uncertainty estimate.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Emission factors need to be confirmed or improved.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

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 17, 3rd Edition (1982).

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 US EPA, AP-42.

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.1

Date : October 1995

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

20 POINT OF ENQUIRY

Any comments on this chapter or enquiries should be directed to:

Pieter van der Most

HIMH-MI-Netherlands
Inspectorate for the Environment
Dept for Monitoring and Information Management
PO Box 30945
2500 GX Den Haag
The Netherlands

Tel: +31 70 339 4606

Fax: +31 70 339 1988

Email: pieter.vandermost@minvrom.nl