SNAP CODE: **040510**

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

NOSE CODE: **105.09.53**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Styrene can be made from ethylbenzene in two ways, either by the dehydrogenation process or the oxidation process. The first route is used in the majority of plants.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of styrene plants according to Corinair 90 were on average smaller then 0.01% to the total NMVOC emission in the reporting countries.

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

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
Styrene	040510	-	-	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

The hydrogenation process can be operated in two ways; in both processes steam is used for heat addition to the feed and for retarding coke deposition.

- The adiabatic process.
  Preheated ethylbenzene is mixed with superheated (800 - 950°C) steam (ratio 1:<14) and led over the catalyst. Operation conditions are: T: 610 - 660°C; p: <138 kPa.

  This process is the most common.

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

- The isothermal process.
  A tubular reactor with catalyst is used. Reaction heat is provided by indirect heat exchange. Operation conditions are: T: 580 - 610°C; p: <138 kPa. Ethylene/steam ratio is 1: 6 - 8.

The catalyst used in both processes is Fe_2O_3 with Cr_2O_3 as stabilizer and K_2CO_3 as coke formation retardant. After the reactor a settler separates vapor (vent gas; mostly hydrogen), water (saturated with aromatics) and liquid hydrocarbons (crude styrene).

In the purification section, which operates under vacuum, inhibitors are used to suppress polymerization of styrene. Benzene is recovered and recycled to the ethylbenzene plant; the residue is used as fuel. Ethylbenzene is recovered and recycled to the reactor feed.

The oxidation process is a three stage process.

In the first stage ethylbenzene is oxidized to form ethylbenzene hydroperoxide. Air is bubbled through liquid ethylbenzene, no catalyst is required. A series of reactors is used, each operating at a different temperature: in the first reactor the temperature is 135 - 160°C, in the last 125 - 155°C. The temperature is reduced to reduce formation of by-products (decomposition). The operating pressure is 800 - 1500 kPa.

In the second stage the hydroperoxide formed in the first stage reacts with propylene to form 1-phenylethanol and propylene oxide. The catalyst used are compounds of metal, e.g. Mo, W, V. Reaction temperature is 100 - 130°C.

In the third stage the 1-phenylethanol is dehydrated to form styrene.

3.2 Definitions

Not relevant

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: methane, styrene, toluene. Methane is emitted due to combustion, styrene and toluene due to leakage and storage loss.

For the Netherlands the VOC emission due to styrene production is 230.2 ton/y. This emission is related to acrylonitrile production of 928 kton/y and a capacity of kton/y (data for 1992).

The VOC emission can be subdivided as follows:

Cause of the emission	**[2]**
leakage losses from appendages, pumps, etc.	65.4%
flaring, disruptions	0.1%
losses due to storage and handling	19.0%
combustion emissions	15.5%
other process emissions	0 %

In a Canadian report [1] a subdivision specific for the emission from styrene plants is given:

Process	0.6%
Fugitive	89.1%
storage and loading	7.7%
Spills	2.6%

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 styrene production to estimate total emissions. The amount of emitted VOC is then directly related to the styrene 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. In a Canadian study [1] the use of this methodology instead of the simpler one resulted in a considerably lower estimate of the process emissions.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1.: Styrene production in some countries and regions for 1990

Country or Region	kton/y	Source
U.S.A.	3640	Chem&EngNews 29/6/92

7 POINT SOURCE CRITERIA

Styrene production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1.: Emission factors for styrene

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [2]	0.25	C
Canada [1]	0.7	?
USA [3]	18	?

The Worldbank Handbook (5) gives a range of 0.25 to 18 kg/ton product, depending on the quality of the abatement. The Handbook of emission factors (6) gives for the situation in the Netherlands a range of 0.05 to 0.5 kg/ton product, probably with good abatement.

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 [2]:

	methane	Ethylene	styrene	benzene	toluene	other HC’s
leakage loss	7%	0%	17%	4%	33%	39%
flaring and disruptions	0%	0%	0%	0%	0.2%	99.8%
storage and handling loss	0%	0%	39%	1%	22%	38%
Combustion	40%	10%	0%	0.2%	0.2%	50%
other process emissions	-	-	-	-	-	-

Table 9.2: The overall VOC emission profile for styrene plants

	TNO ER [2]	**Canadian [1]**	**EPA [4]**
Methane	10.8%	-	21.7%
Ethylene	1.6%	-	24.4%
Styrene	18.5%	7.6%	4.9%
Benzene	2.8%	0.3%	23.3%
Toluene	25.8%	0.0%	9.2%
Ethane	-	-	6.5%
ethylbenzene	-	-	9.9%
other hydrocarbons	40.5%	92.1%	-

10 UNCERTAINTY ESTIMATES

As the influence of the applied abatement is rather big the use of a default overall factor can result in a rather high uncertainty if the real abatement is not known.

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 expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 21, 3rd edition (1983).
- 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 Emissions of Volatile Organic Compounds from selected organic chemical plants, B.H. Levelton & Associates Ltd., 1990.
2 Communication with styrene producing plant by TNO during emission inventory 1992.
3 Internal report from styrene producing company.
4 US Environmental Protection Agency Airchief 1991.
5 World Bank Group Pollution prevention and abatement Handbook Petrochemicals Manufacturing (1998)
6 Handbook of emission factors Part 2 Industrial Sources Ministry of Housing ,Spatial Planning and the Environment M.E.Reinders (editor) (1983)

18 BIBLIOGRAPHY

Many detailed describtions of the process on internet.

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.3

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Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
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20. POINT OF ENQUIRY

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