

**SNAP CODE:** 040518

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

**NOSE CODE:** 105.09.54

**NFR CODE:** 2 B 5

## 1 ACTIVITIES INCLUDED

Ethylbenzene can be produced both in liquid- and in vapour-phase. All processes use a catalyst with aluminium.

## 2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of ethylbenzene 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 <sub>2</sub>	NO <sub>x</sub>	NMVOC	CH <sub>4</sub>	CO	CO <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>
Ethylbenzene	040518	-	-	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<sub>2.5</sub> (as of December 2006).

## 3 GENERAL

### 3.1 Description

The liquid-phase ethylbenzene production can be operated in two ways:

- 1 The Union Carbide/Badger process.

Ethylene is sparged in the reactor containing a mixture of benzene, catalyst (AlCl<sub>3</sub>) and a promotor (monochloroethane or sometimes HCl). The reaction mixture is agitated to disperse the catalyst-complex and operated at low temperature and pressure. Almost complete conversion of ethylene is obtained. In the reactor polyethylbenzenes are transalkylated to ethylbenzene.

The reactor effluent is cooled and led into a settler. From the settler the catalyst-complex is recycled to the reactor and the organic phase is washed with water and a caustic

solution to remove any remaining catalyst. The waste aqueous phase (from the treatment of the organic phase) is neutralized and aluminum hydroxide is recovered and disposed as landfill or calcinated to recover aluminum oxide.

After the washing treatment the ethylbenzene is purified. Recovered benzene and polyethylbenzenes are recycled. The heavier compounds are used as fuel.

## 2 The Monsanto process.

Resembles the Union Carbide/Badger process. The reaction is operated at higher temperature, so less catalyst is needed. No catalyst complex phase is present, since all catalyst is dissolved, resulting in higher selectivity and higher overall yield.

Two reactors are used: one with only dry benzene, ethylene, catalyst and promotor; the second with the effluent from the first reactor plus (recycled) polyethylbenzenes.

The effluent of the second reactor is washed with water and a caustic solution to remove the catalyst complex. Further processing as above.

The vapour-phase operation of ethylbenzene can be operated in several ways:

- The simple process.  
A solid catalyst e.g. alumina on silica gel is used. Operation temperatures are  $>300$  °C; pressures  $>6000$  kPa. High benzene/ethylene ratios are used to minimize formation of higher alkylated ethylbenzenes. A small dealkylation unit, like the liquid phase process, is used to obtain higher overall yield.
- The Mobil/Badger process.  
Fresh ethylene, preheated benzene and recycled alkyl-aromatics are led to a single fixed bed reactor containing a ZSM-5 catalyst. In the reactor simultaneous transalkylations occur. Operation conditions are: high temperatures and moderate pressures.

Two reactors are used: one in use, the other being regenerated.

After the reactor a prefractionator is used to separate benzene, volatile components and ethylbenzene and high boilers. The top of the prefractionator is cooled; the condensate (mainly benzene) is recycled to the reactor, the uncondensable components are vented or used as fuel. The bottom product consists of crude ethylbenzene; this crude product is purified and recovered benzene and polyethylbenzenes are recycled to the reactor. The residue from the purification is used as fuel.

- The Alkar process.  
This process is used for feeds with low ethylene concentrations. The reactor contains a solid acid catalyst of activated alumina with some  $\text{BF}_3$ .

A separate transalkylation reactor is used to reform polyethylbenzenes.

Before the purification the non-reactive gasses are removed in a flash drum. During the purification of ethylbenzene, benzene and polyethylbenzenes are recovered and recycled.

### 3.2 Definitions

See section 3.1.

### 3.3 Techniques

See section 3.1.

### 3.4 Emissions

The major emissions to air are: methane, ethylene, benzene and toluene. Methane is released due to combustion, ethylene due to leakage loss and combustion, benzene due to leakage loss and toluene due to leakage and storage loss.

For the Netherlands, the VOC emission due to ethylbenzene production is 75.4 ton/y. This emission is related to a production of 989 kton/y and a capacity of 1429 kton/y (1992 data). The VOC emission can be subdivided as follows:

Emission source	[1]
leakage losses from appendages, pumps, etc.	92%
flaring, disruptions	0%
losses due to storage and handling	1%
combustion emissions	7%
other process emissions	0%

### 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 ethylbenzene production to estimate total emissions. The amount of emitted VOC is then directly related to the ethylbenzene 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: Ethylbenzene production in some countries and regions for 1990**

Country or Region	kton/y	Source
U.S.A.	3800	Chem&EngNews 29/6/92

## 7 POINT SOURCE CRITERIA

Ethylbenzene 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 ethylbenzene**

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [1]	0.1	C
TNO Emission Registration 1987 [2]	0.6	C
USA [3]	1 - 2	?

## 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	benzene	toluene	formal-dehyde	other HC's
leakage loss	0%	8%	48%	11%	0%	33 %
flaring and disruptions	-	-	-	-	-	-
storage and handling loss	0%	0%	0%	11%	0%	89%
combustion	37%	10%	0.1%	0.1%	0.3%	53%
other process emissions	-	-	-	-	-	-

**Table 9.2: The overall VOC emission profile for ethylbenzene plants**

	TNO ER [1]	EPA [4]
methane	2.6%	-
ethylene	8.1%	-
benzene	44.2%	-
toluene	10.2%	-
ethylbenzene	-	100%
other HC's	35.1%	-

**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 edition (19)
- 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 TNO Emission Registration, 1987
- 3 American Report
- 4 EPA, Air Chief, 1991

## 18 BIBLIOGRAPHY

## 19 RELEASE VERSION, DATE AND SOURCE

Version : 1.2

Date : October 1995

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

Updated with particulate matter details by:

Mike Woodfield  
AEA Technology  
UK  
December 2006

## 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