SNAP CODE: **040501**

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

NOSE CODE: **105.09.50**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Ethylene is produced by thermal cracking of nafta fractions.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of ethylene plants according to Corinair 90 were 0.00 to 0.06% 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
Ethylene	040501	0	0	0.3	0	0	0.1	0.1	-

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 $PM_{2.5}$ (as of December 2006)).[1]

3 GENERAL

3.1 Description

The feed is preheated in heat exchangers and brought to the reaction temperature of 750 - 850° Celsius by adding hot products and steam to the reaction furnace. Additional steam isadded to dilute the reaction mixture. The residence time is kept short (about 0.1 sec.) to limit side reactions (coke formation).

After the reaction the gas mixture is quenched with cold oil, which in turn is used to produce steam. The oil gas steam mixture is separated in different fractions in a rectification section. In several steps the most important products of the mixture are separated. The low boiling products ethylene, propylene and the butylenes are separated after drying, compression and distillation.

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

For many applications ethylene must not contain acetylene. The acetylene is removed from the ethylene by selective hydrogenation.

After separation from the reaction mixture, ethane and propane are recycled to the reaction furnace feed, methane is used as fuel gas and hydrogen is used for hydrogenation (of acetylene).

The C-4 mixture is used as feed for the butadiene production.

The typical feed (ethane to heavy petroleum distillates) results in a production of about 36% ethylene, 13% propylene, 8% butylenes and 7% aromatics.

3.2 Definitions

Not relevant.

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are CO2, NOx, CO and hydrocarbons. The first three compounds are produced during the combustion of fuel gases in the reaction furnace, the hydrocarbons are mostly emitted by leakage and flaring of the residual gases.

For the Netherlands all cracking processes together produced in 1986 4000 tons of VOCs per year. Ethylene production is estimated by a proportional share, being 36% of the total VOC emission. This emission, 1440 ton, is related to a production capacity of about 2700 kton ethylene per year and a realized production of about 2400 kton ethylene per year.

Emissions can be subdivided as follows:

Emission source	**[1]**	**[2]**
leakage losses from appendages, pumps, etc.	72%	75%
flaring, disruptions	18%	5%
losses due to storage and handling	1%	13%
combustion emissions	5%	<1%
other process emissions	4%	7%

About 73% of the VOC emissions can be considered as production independent (leakage etc. plus losses due to storage etc), but process operation time dependant (i.e. production capacity dependant). The other 27% is production dependant.

In a Canadian report [3] a subdivision specific for the emission from ethylene plants is given:

Process	51%
Fugitive	46%
storage and loading	1%
Spills	1%

3.5 Controls

The losses due to leakage can be limited by use of better seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an default emission factor for ethylene production emissions where the amount of emitted VOC is directly related to the ethylene production. For the Netherlands, 4000 ton VOC emission related to the thermal cracking activity, 36% ethylene in the thermal cracking product, and 2400 kton ethylene produced this would give an overall emission factor of 0.6 ton VOC/kton ethylene produced.

5 DETAILED METHODOLOGY

A more detailed method would be using emission factors for each piece of equipment, such as valves, flanges, etc. This way a 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. Hence, 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 [3] the use of this methodology instead of the simpler one resulted in a considerably lower estimate of the process emissions.

6 RELEVANT ACTIVITY STATISTICS

Relevant statistics are the production capacity for ethylene and the realised ethylene production. Table 6.1 lists ethylene capacity and Table 6.2 production in several countries and regions (note that the countries statistics may not add up to the regional figures, since various sources of information have been compiled).

Table 6.1.: Ethylene capacities for some countries and regions for 1990

Country/Region	ktons/y	Source
China	1928	ChemWeek 12/2/92
Korea, South	1155	ChemWeek 12/2/92
Japan	5976	ChemWeek 12/2/92
Taiwan	845	ChemWeek 12/2/92
Thailand	315	ChemWeek 12/2/92
Africa + Middle East	3500	EurChemNews 23/3/92
Asia/Pacific	10900	EurChemNews 23/3/92
Eastern Europe	7900	EurChemNews 23/3/92
South America	3200	EurChemNews 23/3/92
USA + Canada	22000	EurChemNews 23/3/92
Western Europe	16500	EurChemNews 23/3/92

Table 6.2.: Ethylene production for some countries and regions for 1990

Country/Region	ktons/y	Source
Australia	1054	Chem&EngNews 29/6/92
Canada	2434	Chem&EngNews 29/6/92
China	1572	Chem&EngNews 29/6/92
Czechoslovakia	619	Chem&EngNews 29/6/92
France	2246	Chem&EngNews 29/6/92
Germany, West	3075	Chem&EngNews 29/6/92
Hungary	234	Chem&EngNews 29/6/92
Japan	5810	Chem&EngNews 29/6/92
Poland	308	Chem&EngNews 29/6/92
Romania	243	Chem&EngNews 29/6/92
Taiwan	776	Chem&EngNews 29/6/92
U.K.	1496	Chem&EngNews 29/6/92
U.S.A.	16556	Chem&EngNews 29/6/92
U.S.S.R.	3065	Chem&EngNews 13/4/92
Western Europe	14400	EurChemNews 27/4/92
Western Europe	12223	UN Statistics 1990

Table 6.3 Ethylene production in 2004 in kiloton/year (International Petrochemical Information Forum)

	Asia	Western Europe	North America	South America
Ethylene	18.406	21.408	31.772	3.723

7 POINT SOURCE CRITERIA

Ethylene production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

As stated in section 4, an overall VOC emission factor for the ethylene production in the Netherlands is 0.6 ton VOC per kton ethylene produced.
An example of a more detailed emission factor calculation is given below:

Based on the data presented in section 3.4 and an ethylene percentage of 36 of the product from the typical feed (sections 1, 3.1) the emission factor of VOC for the ethylene production (without taking notice of other products) can be estimated in more detail as follows:

1 0.389 ton VOC/kton ethylene production capacity (leakage and losses)

Namely, 0.36 * 0.73 * 4000 ton VOC per 2700 kton ethylene production capacity for leakages and losses during handling and storage (together 73% of emissions).

2 0.162 ton VOC/kton ethylene produced (combustion, flaring, other processes)

Namely, 0.36 * 0.27 * 4000 ton VOC per 2400 kton ethylene produced
Part of these emissions is already dealt with under other SNAP codes (combustion and flaring): 0.138 ton VOC/kton ethylene produced : 0.36 * (0.18 + 0.05) * 4000/2400.

In Table 8.1 emission factors used in different countries are presented.

Table 8.1.: Emission factors for ethylene

Source	Factor (kg/ton)	Quality Code
Information from ethylene plant 1987 [4]	2 (new plant)	C
Information from ethylene plant 1987 [4]	5 (old plant)	C
Handbook of emissionfactors (1983) (8)	2 -3.5	C
Internal report from US origin [5]	10[1]	C/D
Environment Canada [3]	0.9, 1.8, 5.1, 8.2	D
Borealis AB [2]	2 - 7	C

[1] with an estimated capacity of 200 kton/y

The World Bank Handbook (ref 7) gives as emissions from a naphtha cracker 0.6 to 10 kilograms per metric ton of ethylene produced, depending on the quality of the abatement methods applied. These figures are consistent with the figures from the Netherlands

9 SPECIES PROFILES

Table 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1: Composition of the VOC emissions for different sources [1]:

	methane	**ethylene**	**propylene**	**Benzene**	**others HC's**
leakage loss	70%	5%	3%	1%	21%
flaring and disruptions	10%	40%	25%	1%	24%
storage and handling loss	0%	0%	0%	1%	99%
Combustion	75%	10%	0%	1%	14%
other process emissions	70%	5%	3%	1%	21%

Table 9.2: Overall VOC emission profile for ethylene plants

	TNO ER [1]	**EPA [6]**
Methane	58.8%	12.5%
Ethane	-	37.8%
Ethylene	11.5%	-
Propane	-	23.9%
Propylene	6.8%	-
n-butane	-	15.0%
n-pentane	-	8.1%
Benzene	1.0%	2.1%
Toluene	-	0.5%
Methanol	-	0.3%
other HC's	22.0%	-

The World Bank Handbook (1998) gives 75% of alkanes, 20 % of unsaturates hydrocarbons (half of them ethylene) and 5 % aromatics.

10 UNCERTAINTY ESTIMATES

As the data on which the proposed emission factors are based are rather old they should only be used as default factors with the appropriate uncertainty.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

- The emission factors given are mainly based on internal information gathered by TNO during the emission inventory in the Netherlands. Comparison with data from other countries should improve the quality. The probably newer world bank data are consistent with these data.
- These data assume an average feed and an average composition of the production process in which a wide range of other commodities are produced in addition to ethylene.
- The leakage losses are estimated with emissions factors used for the chemical industry as a whole. No subdivision within the chemical industry is made.
- The flaring emission is based on an assumed combustion percentage. The measurement of the amount of gas flared is inaccurate and in most cases only roughly estimated.
- One factor is used for all countries. It would be more accurate to use a different factor for each country or each group of countries.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

13 TEMPORAL DISAGGREGATION CRITERIA

The ethylene 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

Detailed reports from USEPA and UNECE on refinery processes.

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 Communication from ethylene producing company in the Netherlands (1992).

2 Borealis AB, Sweden, personal communication 1995.
3 Environment Canada: Emissions of Volatile Organic Compounds from selected organic chemical plants, B.H. Levelton & Associates Ltd., 1990.
4 Communication from ethylene producing company in the Netherlands (1987).
5 Internal report of an ethylene producing company from American origin.
6 EPA, SPECIATE Program..
7. World Bank group. Pollution prevention and abatement Handbook. Petrochemicals manufacturing. Page 371 and 372 (1998)
8 Handbook of emissionfactors Part 2 Industrial sources Ministry of Housing, Physical Planning and Environment . M.E.Reinders (editor) (1983)

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- Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 14, 4th Edition (1995).
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20. POINT OF ENQUIRY

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