SNAP CODE: 040502

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

Propylene

NOSE CODE: 105.09.51

NFR CODE: 2 B 5

#### 1 ACTIVITIES INCLUDED

Propylene is produced by thermal cracking of petroleum fractions. These fractions can vary from ethane to heavy petroleum distillates.

#### 2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of propylene 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 [%]							
		$SO_2$	NO <sub>x</sub>	NMVOC	CH <sub>4</sub>	СО	CO <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>
Propylene	040502	-	-	0.2	-	-	-	-	-

 $<sup>0 = \</sup>text{emissions}$  are reported, but the exact value is below the rounding limit (0.1 per cent)

#### 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 is added to dilute the reaction mixture. The residence time is kept short (about 0.1 sec.) to limit side reactions (cokes 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.

<sup>- =</sup> no emissions are reported

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

# 3.3 Techniques

See section 3.1.

#### 3.4 Emissions

The major emissions to the 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 due to leakage and flaring of the residual gases.

For the Netherlands all cracking processes together produce 4000 ton of VOC's per year. Propylene is given a proportional share, being 13%, of the total VOC emission. This emission, 520 ton, is related to a production capacity of about 975 kton propylene per year and a realized production of about 870 kton propylene per year.

Emissions can be subdivided as follows [1]:

leakage losses from appendages, pumps, etc.	72%
flaring, disruptions	18%
losses due to storage and handling	1%
combustion emissions	5%
other process emissions	4%

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.

#### 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 propylene production emissions. The amount of emitted VOC is then directly related to the propylene production. For the Netherlands, 4000 ton VOC emission related to the thermal cracking activity, 13% propylene in the thermal cracking product, and 870 kton propylene produced this would mean an overall emission factor of 0.6 ton VOC/kton propylene produced.

## 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 [2] 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 propylene and the realized propylene production. Table 6.1 lists propylene capacity and Table 6.2 propylene production in several countries and regions.

Table 6.1: Propylene capacity in some regions for 1990 or 1991

Region	ktons/y	source	year	
Western Europe	9400	EurChemNews 27/4/92	1990	
World	36600	EurChemNews 27/4/92	1991	

Country/Region	ktons/y	source
Australia	608	Chem&EngNews 29/6/92
Canada	765	Chem&EngNews 29/6/92
France	1433	Chem&EngNews 29/6/92
Germany, West	1829	Chem&EngNews 29/6/92
Japan	4215	Chem&EngNews 29/6/92
Taiwan	398	Chem&EngNews 29/6/92
U.K.	750	Chem&EngNews 29/6/92
U.S.A.	9918	Chem&EngNews 29/6/92
U.S.S.R.	1366	Chem&EngNews 13/4/92
Western Europe	8800	EurChemNews 27/4/92
Western Europe	6880	UN Statistics 1990

Propylene production in some countries and regions for 1990

## 7 POINT SOURCE CRITERIA

**Table 6.2:** 

Propylene plants can be considered as point sources if plant specific data are available.

# 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

As stated in section 4, an overall VOC emission factor for the propylene production in the Netherlands is 0.6 ton VOC per kton propylene produced.

Based on the data presented in section 3.4 and an propylene percentage of 13 of the product from the average feed (sections 1, 3.1) the emission factor of VOC for the propylene production (without taking notice of the other products) can be estimated in more detail as follows:

- 0.389 ton VOC/kton propylene production capacity (leakage and losses). Namely, 0.13 \* 0.73 \* 4000 ton VOC per 975 kton propylene production capacity for leakages and losses during handling and storage (together 73% of emissions).
- 0.162 ton VOC/kton propylene produced (combustion, flaring, other processes).
  Namely, 0.13 \* 0.27 \* 4000 ton VOC per 870 kton propylene produced.
  Part of these emissions are already dealt with under other SNAP codes (combustion and flaring): 0.138 ton VOC/kton propylene produced.
  Namely, 0.13 \* (0.18 + 0.05) \* 4000/870.

For propylene the same emission factors are used as for ethylene (see ethylene for other factors) except in the 1985 NAPAP Emission Inventory (0.45 kg/ton for propylene and 0.40 for ethylene).

## 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	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.: The overall VOC emission profile for plants

	TNO ER [2]
methane	58.8%
ethylene	11.5%
propylene	6.8%
benzene	1.0%
other HC's	22.0%

## 10 UNCERTAINTY ESTIMATES

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

- These data so far assume an average feed and an average composition of the production process in which besides propylene also a wide range of other commodities are produced.
- 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.
- The emission factors used in Section 8 are derived from propylene plants in the Netherlands.
- 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

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

#### 13 TEMPORAL DISAGGREGATION CRITERIA

The propylene plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

#### 14 ADDITIONAL COMMENTS

## 15 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.

## 17 REFERENCES

- 1 TNO Emission Registration 1992.
- 2 Emissions of Volatile Organic Compounds from selected organic chemical plants, B.H. Levelton & Associates Ltd., 1990.

#### 18 BIBLIOGRAPHY

- Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 14, 4<sup>th</sup> Edition (1995).
- Winnacker-Küchler, Chemische Technologie, Organische Technologie I, Band 5, 4. Auflage (1982) (in German).

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**TNO** 

The Netherlands

# 20 POINT OF ENQUIRY

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