

SNAP CODE: 040509

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

NOSE CODE: 105.09.83

NFR CODE: 2 B 5

1 ACTIVITIES INCLUDED

Polypropylene is produced by polymerization of propylene. This can be done in several ways: all using a Ziegler-Natta catalyst. Most ways use a solvent, either propylene or hexane/heptane. In one process type the polymerization is operated in the gas-phase.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of polypropylene plants according to Corinair 90 were on average about 0.1% of the total NMVOC emission in a 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 ₂ O	NH ₃	PM*
Polypropylene	040509	-	-	0.1	-	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

* = PM (inclusive of TSP, PM₁₀ and PM_{2.5}) is <0.1% of total PM emissions

3 GENERAL

3.1 Description

All processes use a Ziegler-Natta catalyst. A commonly used Ziegler-Natta catalyst is Al(CH₂CH₃)₂Cl complexed with TiCl₄.

The different processes are:

- Gas-phase polymerization.
The propylene is led through a reactor with catalyst. Liquid propylene is used for cooling (interstage cooling). Unreacted propylene is recovered and recycled. Reactor operation temperatures are 70 - 90°C.
- Solvent polymerization.

- solvent is propylene.
Liquid propylene and catalyst are led into the reactor. After the reactor solid isotactic polypropylene is separated from the unreacted propylene, which contains dissolved atactic polypropylene and catalyst. The polypropylene is dried with nitrogen. The unreacted propylene is recovered and recycled. During the propylene recovery the atactic polypropylene is recovered as deposition.

Reactor operation conditions are: T: 50 - 70°C; p: 2500 - 4000 kPa.

- solvent is hexane or/and heptane.
Solvent, catalyst and propylene are added to the reactor. The reactor effluent is flashed to recover the unreacted propylene. Then the effluent is washed with alcohol to extract the catalyst and the alcohol phase and solvent phase are separated. The solid isotactic polypropylene is separated from the solvent in a centrifuge. The isotactic polypropylene is dried before storage. Reactor operation conditions are: T 50 - 90°C; p 500 - 1500 kPa.

The solvent is recovered, during which the atactic polypropylene forms a slimy mass at the bottom of the apparatus. The atactic polypropylene can be recovered.

- The newest process (the Montedison-Mitsui high yield process) differs from the process described above in that a better catalyst with a higher yield is used, so less catalyst is needed. This has as advantage that no separate catalyst phase exists. After the flashing the effluent is split using a centrifuge in two fractions: one with solid isotactic polypropylene and 'trapped' solvent, the other with solvent and dissolved atactic polypropylene. The solvent from both fractions is recovered and recycled; the isotactic polypropylene is dried with nitrogen; the atactic polypropylene is also recovered.

3.2 Definitions

Not relevant

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emission to air is: propylene.

For the Netherlands the VOC emission due to the polypropylene production was in 1992 304 ton/y. This emission can be related to a production of 353 kton/y and a capacity of 371 kton/y (data for 1992).

The VOC emission can be subdivided as follows:

Emission source	[1]
Leakage losses from appendages, pumps, etc.	94 %
Flaring, disruptions	0.2%
Losses due to storage and handling	6 %
Combustion emissions	0 %
other process emissions	0 %

3.5 Controls

The losses due to fugitives can be limited by use of modern abatement methods.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the polypropylene production to estimate total emissions. The amount of emitted VOC is then directly related to the polypropylene 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.: Polypropylene capacity in some countries

Country or Region	kton/y	source	year
Latin America	830	EurChemNews 13/4/92	1991
Indonesia	10	EurChemNews 1/6/92	1990?

Table 6.2.: Polypropylene production in some countries and regions for 1990

Country or Region	kton/y	source
France	779	Chem&EngNews 29/6/92
Germany, West	509	Chem&EngNews 29/6/92
U.K.	296	Chem&EngNews 29/6/92
U.S.A.	3773	Chem&EngNews 29/6/92
Japan	1942	Chem&EngNews 29/6/92
Korea, South	574	Chem&EngNews 29/6/92
Australia	19	Chem&EngNews 29/6/92
U.S.S.R.	127	Chem&EngNews 13/4/92

7 POINT SOURCE CRITERIA

Polypropylene production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for polypropylene

Source	factor (kg/ton)	Quality Code
Information from plant in the Netherlands 1987 [2]	8 (5 - 12)	C
Information from plant in the Netherlands 1992 [1]	0.86	C
EPA 1989? [3]	0.35	E

The Emission factors Handbook (4) gives the following emissionfactors:

Table 8.2 Emissionfactors for polypropylene (1983)

Substance	emissionfactor
saturated hydrocarbons	5-10 kg/ton
propylene	0.5-1.5 kg/ton
polypropylene	0.1-0.2 kg/ton
butanol 2	0.1-0.2 kg/ton

Table 8.3 AP 42 Particulate matter emission factor* for polypropylene (kg/Mg) [5]

Source	PM (kg/Mg)
Polypropylene (uncontrolled)	1.5

* = In the absence of more appropriate data use the AP 42 emission factor¹

9 SPECIES PROFILES

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

Table 9.1.: The composition of the VOC emissions for the different sources is [1]:

	propylene	isobutanol	other HC's
leakage loss	0%	4%	96%
flaring and disruptions	1%	0%	99%
storage and handling loss	0%	0%	100%
combustion	-	-	-
other process emissions	-	-	-

Table 9.2.: The overall VOC emission profile for polypropylene plants

	TNO ER [1]
methane	0%
ethylene	0%
isobutanol	3.8%
other hydrocarbons	96.2% ¹

¹ most likely all propylene.

10 UNCERTAINTY ESTIMATES

The uncertainty depends on the fit of the proposed default emission factors with the real process.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

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

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 16, 3rd edition (1981)
- 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 Communication to TNO from polypropylene producing plant 1992
- 2 Communication to TNO from polypropylene producing plant 1987
- 3 Environmental Protection Agency, AP-42
- 4 Handbook of Emissionfactors Part 2 Industrial Sources. Ministry of Housing, Spatial Planning and the Environment M.E.Reinders (editor) (1983)
- 5 US EPA (1996) Compilation of Air Pollutant Emission Factors Vol.1 Report AP-42 (5th ed.)

18 BIBLIOGRAPHY

The processes are extensively described on many sites for instance from the USEPA or the chemical industry.

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.3

Date : September 2006

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

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