Stuttgart University

Final report

UFOPLAN project

FKZ: 298 94 313/05

Resource-sparing production of polymer materials

UNIVERSITÄT
IKP
STUTTGART

Institute for Plastics Testing and Pastics Engineering (IKP)

on behalf of the Federal Environmental Agency

Umwelt
Bundes
Amt
für Mensch und Umwelt

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1 Introduction

The Federal Environmental Agency advertised the UFOPLAN project FKZ: 298 94 313 "Resource-sparing production of polymer materials taking polyolefine as an example" against the background of the importance of polymer materials in terms of value and quantity. New process technologies such as alternative synthesis processes and new catalyst concepts can be observed, above all though not least in the field of polyethylenes and polypropylenes. The globalization of markets and resulting cost pressure as well as statutory regulations and the self-obligation to treat the environment and its resources more responsibly, which can be summarised by keywords such as "responsible care" and "sustainable development", has meant that the chemicals industry is constantly having to further develop its processes.

Starting points for an improvement in terms of environmental protection could be:
- the more effective use of resources, initial products and process materials by reducing their specific input with the same production levels
- the reduction or more effective use of the process energy needed for synthesis, for example through new catalysts or energy recovery
- the use of by-products in other or combined plants and systems,
- the substitution of environmentally-relevant materials through less environmentally-relevant materials
- the avoidance or reduction of emissions through production-integrated or post-production emission reduction measures ("End-of-Pipe technologies")

Within the scope of this project the polymer synthesis processes used in Germany will be analysed and presented against the background of the work which has begun on drafting BAT reference documents on a European level.

To get a better impression of the range of polymer materials, we considered not only the polyolefines polyethylene, polypropylene, polystyrene and polyvinyl chloride but also the polymer materials acryl-butadiene-styrene and polyamide 6.6.

Within the scope of these investigations, industry was integrated in the flow of information at an early stage. This was regarded as being advantageous by both the Federal Environmental Agency and the IKP to enable an exchange of information.

2 Goals and investigation framework

The goal of this investigation is to present the possibilities of production-integrated environmental protection during the production of quantity and market-relevant polymer materials in Germany against the background of a future drafting of BAT reference documents. The achievement of this goal was split into the following partial areas:

- Description of the state of the art for the relevant polymer synthesis processes
- Characterization of environmentally-relevant material, energy and emission flows in the process in the form of mean annual figures to compensate operational and climatic fluctuations (e.g. energy demand to temper materials may be higher in Winter than in Summer)
- Presentation of technical and economic parameters for the respective syntheses to enable a classification of the processes and their environmental parameters in the context of technical and economic skeleton conditions
- Elaboration of ways to optimise the respective technology from an environmental point of view
- Presentation of the potential of existing and new technologies.

The investigation framework are the polymer syntheses with their specific input of energies and initial products as well as their process-specific products, by-products, emissions and wastes. In other words, the production of initial products and the provision of energy carriers will not be investigated within the scope of this work.

The investigation should analyse the individual methods and present possible starting points for their optimization. The goal of this study is to compare the different ways of producing identical or similar polymers. The different methods have often become established due to various other factors. These could be on the one hand location-specific marginal conditions of raw material supplies, a special legislative situation or process-specific requirements on a product quality or feature which cannot be achieved with a certain method. Thus, no general recommendation for one of these methods can be made on account of these varying marginal conditions.

Moreover, we would at this point like to point out that interdependencies may exist between the quoted figures in the Input-Output tables for a characterization of the environmentally-relevant material, energy and emission flows for the methods. This means it would be wrong to conclude that a plant may only be evaluated as BAT if it complies with the minimum limits for all quoted values. This will be explained in more detail in the corresponding chapters.

3 Structure of the plastics industry

This chapter will briefly explain the plastics-producing industry. A summary overview is sensible so that the relevance of this topic can be seen in an overall economic context. The number of companies involved, their turnover and number of employees are indicators of the productivity of a line of business and its contribution to the value chain. The question of the environmental-compatibility of a production process also has to be included in this connection to assess or avoid a possible expensive optimization of irrelevant partial areas. However, we will only present an overview here.

The following summary of data on the plastics industry is taken from publications of the Association of the Plastics Producing Industry e.V. (VKE). These publications use both official statistics and results of the association's own market surveys. The data represent a snapshot and enable the aforementioned classification in the overall economic picture for a limited period of time.

3.1 Overall economic significance

The German plastics industry has an important place on the world market. In 1998 7.9% of the world's plastic production came from Germany. This makes Germany the world's third biggest producer of plastics after the USA (27.2%) and Japan (8.9%).

The importance of the plastics industry in Germany for the national economy in 1998 is also significant. The plastics industry accounted for 6.4% of total industrial production. The chemicals industry 8.1%. The plastics industry comprises production,. processing and mechanical engineering for plastics. However, only the plastics producing industry can be seen as part of the chemicals industry. The share of industrial production (chemicals industry including plastics) is thus 14.5%. The chemicals industry takes third place behind mechanical engineering (19.6%) and automobile construction (17%).

3.2 Branch structure

The overall branch can be split into three parts; plastics production, plastics processing and mechanical engineering for plastics. The structure of these three partial sectors differs greatly. Whereas plastics production is dominated by only a few firms with high turnovers, plastics processing and mechanical engineering for plastics are characterised by a large number of smaller and very small firms (see Table 3.1).

Table 3.1: Structure of the plastic industry ´98 /13/

	Number of companies	**Employees**	**Turnover [billion DM]**
Production	55	60,600	31.7
Processing	6000	280,000	71.5
Mech. engineering	180	27,500	11.1

Since this report is concerned with processes for the production and synthesis of plastics, only this sector will be dealt with in the following. Table 3.2 provides a more precise description of the plastics producing industry.

Table 3.2: Statistical data on the plastics producing industry ´98 /13/

		1996	**1997**	**1998**
Production	[million t]	10.87	11,86	12.53
Import trade	[million t]	5.03	5,5	6.28
Export trade	[million t]	6.67	7.46	7.31
Turnover	[billion DM]	28.8	32.49	32
Employed persons	[-]	68,200	64,600	60,600
No. of companies	[-]	no figures	no figures	55

The plastics producing industry is export oriented, like the majority of the German economy. A foreign-trade surplus of DM 6.61 billion was made in 1998, which is around 20% of total turnover in the branch. The EU is the biggest trading partner in the plastics field, 72% of exports and 82% of imports are to or from EU countries.

Although a wide variety of products are manufactured in the plastics sector the majority of the market is accounted for by only a few "bulk plastics". The thermoplastics group is the biggest plastics group and the bulk plastics amongst thermoplastics are PE, PP, PVC and PS. These four materials alone account for 47% of total plastics production. In addition, the plastics PA and ABS are very important materials in industry, which is why they have also been included in this report.

Table 3.3: Statistical data on plastics production ´98 /13/

	Production [million t]	**Share of total production [%]**	**Price range [DM/kg]**
PVC	1.31	10.5	1.04 – 1.47
PE	2.07	16.5	1.21 – 1.72
PP	1.29	10.3	1.06 – 1.50
PS	1.24	9.9	1.50 – 1.74
PA	0.92	7.3	no figures
Total production	12.53		

The bulk plastics are only manufactured by a few producers in plants with a high product output. Table 3.4 showing the number of manufacturers per plastic is based on a VKE survey, though only 40% of the companies were included /14/.

Table 3.4: Producers of selected standard and industrial plastics in Germany /14/

	No. of producers
PE-LD	3
PE-HD	4
PP	5
PS / EPS	2
PVC	4
PA	9
ABS / SAN	2

4 Environmental legislation

This chapter will briefly summarise the relevant environmental legislation in connection with the production of polymers. It should enable the emission values named in later chapters to be classified within a legal context. The chapter by no way claims to present a complete picture.

4.1 Federal Republic of Germany

4.1.1 Principles of environmental legislation

Environmental legislation in Germany is classified according to the various media into which substances are emitted: emissions in air, water and waste materials.
The following laws are relevant for industrial plants such as plants which produce polymers in Germany in connection with the purpose of this study:

- Federal Immission Control Act BImschG
- Federal Water Act WHG
- Closed Substance Cycle Waste Management Act KrW-/AbfG

In addition, mention should be made of the Act on Environmental Impact Assessment (UVP) when a new plant is built.
Because of the basic federal structure of Germany the administrative implementation of the laws is the responsibility of the Länder, which can lead to specific differences between Länder. Table 4.1 lists the laws and their corresponding ordinances and administrative regulations.

Table 4.1: Laws and ordinances with respect to emissions from chemical plants

Law	**Ordinances and administrative regulations**
Federal Immission Control Act - BImschG	Federal Immission Control Ordinance
	Federal Immission Control Administrative Regulation
	TA Luft (Technical Instructions on Air Quality Control)
	TA Lärm (Technical Instructions on Noise Control)
Federal Water Act WHG Waste Water Charges Act AbwAG	Waste Water Ordinance
	Waste Water Acts of the Länder
	Charges Ordinance of the Länder
	Catalogue of substances harmful to water
	Sewage Sludge Ordinance
Waste Avoidance and Waste Management Act AbfG Closed Substance Cycle Waste Management Act KrW-/AbfG	Waste and Remaining Substance Monitoring Ordinance
	Waste Classification Ordinance
	Remaining Substance Classification Ordinance
	TA Abfall (Technical Instructions on Waste)
	TA Siedlungsabfall (Technical Instructions on Waste from Human Settlements)

4.1.2 Relevant ordinances and administrative regulations

4. BImSchV

- Ordinance on plants requiring approval 1985
- The ordinance relates to plants for the production of plastics or chemical fibres
- An approval is required for plant parts and process stages necessary for operation, ancillary equipment related to plant parts and process stages in a spatial and operational context and which may be important to prevent harmful environmental effects, the development of harmful environmental effects and other risks.
- The ordinance also applies for a number of plants of the same type which are spatially and operationally related (joint plant: same operation site, joint works equipment, comparable technical purpose)
- Research and development plants on a laboratory and technical centre scale do not require approval

TA Luft

- Technical Instructions on Air Quality Control / 1. BImSchVwV from 27.02.1986
- The goal is the limitation and determination of emissions from industrial processes.
- The TA Luft contains the following regulations:
  - Emission values which need not be exceeded according to the state-of-the-art
  - Emission-limiting requirements which are state-of-the-art
  - Other requirements to prevent harmful environmental effects through air pollution
  - Methods to determine emissions

The relevant substances are divided up into classes. Table 4.2 shows an overview of the limits for carcinogenic substances. Class III carcinogenic substances include for example acrylonitrile, 1,3-butadiene and vinyl chloride.

Table 4.2: Limits for carcinogenic substances /9/

	Mass flow [g/h]	**Value/Mass concentration [mg/m^3]**
Substance class I	0.5 or more	0.1
Substance class II	5.0 or more	1.0
Substance class III	25 or more	5.0

The listed mass concentrations may not be exceeded even if a number of substances from the same class are present. With a combination of Classes I and II the value 1 mg/m^3 and with a combination of Classes II and III the concentration 5 mg/m^3 may not be exceeded in the waste gas.

Table 4.3 shows the emission limits for overall dust. The overall dust represents the sum total of all particles emitted in the air.

Table 4.3: Limits for overall dust /9/

	Mass flow [kg/h]	**Value/Mass concentration [mg/m^3]**
Overall dust	>0.5	50
Overall dust	up to 0.5	150

Appendix E contains a list of relevant organic compounds and their classification. One organic substance which is relevant in this case is styrene (C_8H_8) in Class II

Table 4.4: Limits for organic substances /9/

	Mass flow [kg/h]	**Value/Mass concentration [mg/m^3]**
Substance class I	0.1 or more	20
Substance class II	2 or more	100
Substance class III	3 or more	150

The listed mass concentrations may not be exceeded even if a number of substances from the same class are present. If substances from a number of classes are present the mass concentration in the waste gas may not exceed a total of 150 mg/m^3 at a mass flow of 3 kg/h or more. Dustlike org. substances in Class II and III are to be treated as dusts.

Special regulations for certain types of plant: plants to produce polyvinyl chloride

The TA Luft also regulates in particular defined plants, e.g. plants to produce PVC. The remaining content of vinyl chloride (VC) in the polymer must be kept as low as possible at the transfer station from closed systems to make-up or drying in an open system. The limits listed in Table 4.5 may not be exceeded. Waste gas from dryers should be used as combustion air furnaces wherever possible.

Table 4.5: Maximum values for VC in polymers /9/

	max. values [mg VC per kg PVC]
Bulk PVC	10
Suspension homopolymer	100
Suspension copolymer	400
Micro-suspension PVC / Emulsion PVC	1500

AbwV Waste Water Ordinance

- Ordinance on the requirements on the discharge of waste water into bodies of water; as amended on 09.02.1999
- This ordinance contains regulations on the discharge of waste water (e.g. the use of water-saving washing and cleaning processes, indirect cooling, low-pollutant fuels and process materials)
- Compliance with requirements through shifting emission to the air or soil is not permissible
- Concentration limits may not be reached through dilution (e.g. blowing in fresh air or introducing fresh water)

- A mixing of waste waters for the purpose of joint treatment is on the other hand permissible. The requirements on the waste water are to be fulfilled at the place of origination before mixing.
- A mixed calculation for the respective parameters must be found for waste water flows which are discharged jointly but for which different requirements apply

AbwV Appendix 22

This appendix relates to the chemicals industry in general.
Field of application:

- Waste water produced during the production of substances by chemical, biochemical or physical methods (pre-, interim and post-treatment)
- This ordinance does not apply for introductions <10 m^3

General requirements:
The pollutant load should be kept as low as possible through suitable measures:

- the use of water-saving/waste water-free processes
- multiple use and cyclic management
- indirect cooling
- the use of low-pollutant fuels and process materials

The following requirements for the waste water apply for the place of discharge as regards the chemical oxygen demand (COD):

Table 4.6: Limits for the chemical oxygen demand COD /9/

COD concentration at place of origination of the waste water [mg/l]	Applicable COD concentration [mg/l]
> 50000	2500
> 750	Conc. corresponding to 90% reduction
750 and less	75
< 75	Actual concentration at place of origination

The following requirements on the waste water relating to the absorbable organically bonded halogens (AOX) apply before mixing and subsequent discharge:

- AOX for VC and PVC manufacturers' waste water: VC: 2 g/t; PVC: 5 g/t
- AOX requirements for existing discharges (plants legally operating before 1 January 1999): VC: 5 g/t; PVC: 1 mg/l or 20 g/t)

The figures relate to the place of discharge at the site.

4.2 European Union

4.2.1 Principles of environmental legislation

Environmental legislation in the European Union is also classified according to the various media into which substances are emitted: emissions in air, water and waste materials.

The following laws are relevant for industrial plants such as plants which produce polymers in the EU in connection with the purpose of this study:

- Combating of air pollution from industrial plants (Directive 84/360/EEC)
- Pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Directive 76/464/EWG)
- Integrated pollution prevention and control (Directive 96/61/EG)

In addition, the Act on Environmental Impact Assessment (UVP) (Directive 85/337/EWG) is to be taken into account when a new plant is built.

The individual member countries of the EU take the necessary measures to ensure that the Directives are implemented in the laws of the individual member countries. The individual countries are hereby free to decree stricter emission limits than those named in implementation guidelines for the Directives.

The emission limits specified in the Directives are determined on the basis of the Best Available Technology (BAT). **However, this should not prescribe a certain technique or technology.** The individual countries are obliged to exchange developments in the BAT with the other countries in the EU. **The emission limits should not cause disproportionately high costs.**

4.2.2 Relevant directives and implementation guidelines

Combating of air pollution from industrial plants (Directive 84/360/EEC)

- The operation and modification of plants are dependent on an approval. Emissions must be kept below all limits before an approval can be issued.
- The Directive also relates to plants producing polymers.
- The emissions of the following substance groups relevant for polymer production are limited:
  - Volatile organic compounds, in particular hydrocarbons
  - Dust
  - Chlorine and chlorine compounds

Pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Directive 76/464/EWG)

- A dilution of emissions is permissible, though the emission limit then has to divided by the dilution factor.
- Every discharge of the following substances into a body of water requires an approval, the goal is the complete avoidance of emissions in water:
  - Organic halogen compounds
  - Long-life plastics
- Emissions of the following substances into bodies of water must be completely avoided. Limits apply for surface water:
  - Stable and instable hydrocarbons
  - Substances which have a negative effect on the oxygen balance

Integrated pollution prevention and control (Directive 96/61/EG)

This Directive harmonises and extends the two aforementioned Directives. Emissions in soil for which no rulings yet exist, and waste management are included. This prevents a shift of environmental loads into other media. Reference is made to the pollutant groups and limits based on the BAT already specified in the aforementioned Directives.

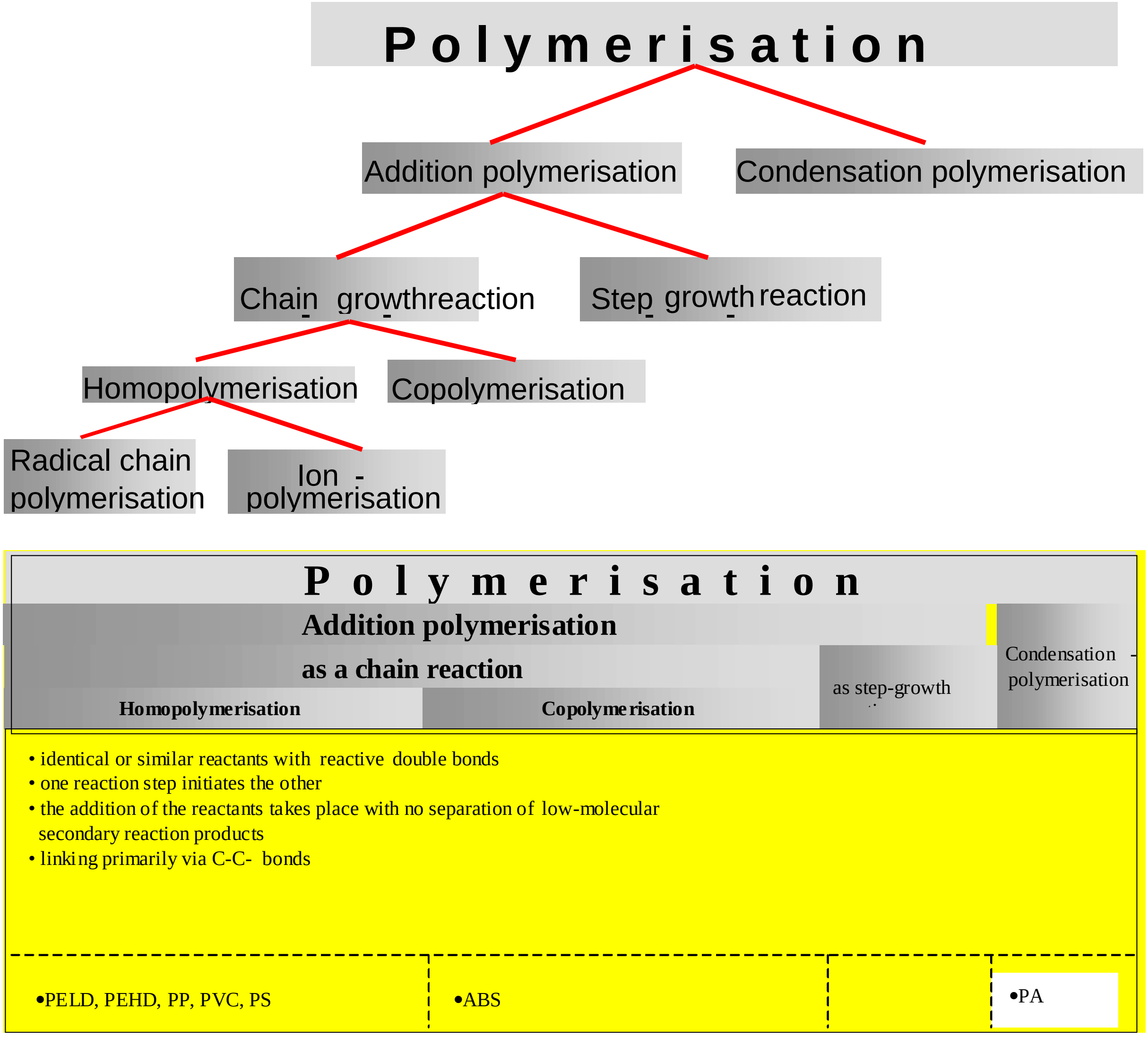
Directive 91/692/EWG (Harmonization and practical layout of reports on the implementation of certain environmental protection directives) provides a framework within which the member states must ensure that they report to the Commission every three years on the implementation of the directives in the individual states using a questionnaire.

The joint emission limits which have already been mentioned a number of times above are not explicitly listed in the directives. Rather, a framework is laid down within which the member states can specify such limits in implementation guidelines in co-operation with the Commission. However, such implementation guidelines as yet only exist for individual substances which are not relevant for this study such as quicksilver, cadmium, DDT and various halogenated hydrocarbons. The framework of the Directive has thus as yet only been inadequately filled out, no Europe-wide limits exist for the pollutants relevant for this report /15/.

As long as the implementation guidelines have not been elaborated, Directives 84/360/EEC and 76/464/EEC remain applicable, though only up until the year 2007 at most. Action thus needs to be taken /16/.

5 General information and product characterization

Thermoplastic polymers can be produced by three different reaction processes, polymerization, polycondensation and polyaddition (Figure 5.1). Bifunctional reactions have two functional groups per reactant (=monomer + polymer) /6/ and lead to linear polymers. The balanced reaction has to display a strict stochiometrics for the reacting functional groups in order to obtain high-molecule polymers and the absence of secondary reactions must be guaranteed.



- identical or similar reactants with reactive double bonds
- one reaction step initiates the other
- the addition of the reactants takes place with no separation of low-molecular secondary reaction products
- linking primarily via C-C- bonds

Figure 5.1: Overview of polymerization types /1/

Polymerization

Polymerization is the most important reaction process and produces amongst others the plastics polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS) listed in the present study. Polymerization is based on splitting the double bond between adjacent carbon atoms and using the released formation to form chains by stringing together identical monomers. Carbon (C) is tetravalent.

During the formation of a C-C chain tow bonds each can be used to hydrogen atoms (H) for (PE), CH_3 (PP), Cl (PVC) and benzene ring (PS) (Figure). The degree of polymerization (n) characterises the number of base units in a polymer molecule.

Depending on the activation (type of reaction initiation) a differentiation is made between radical and ionic polymerization. The course of the reaction process can be generally described as:

1. Start reaction - 2. Growth reaction - 3. Termination reaction

The following diagram sketches the energy curve over the reaction time of a homopolymerization from ethylene to polyethylene.

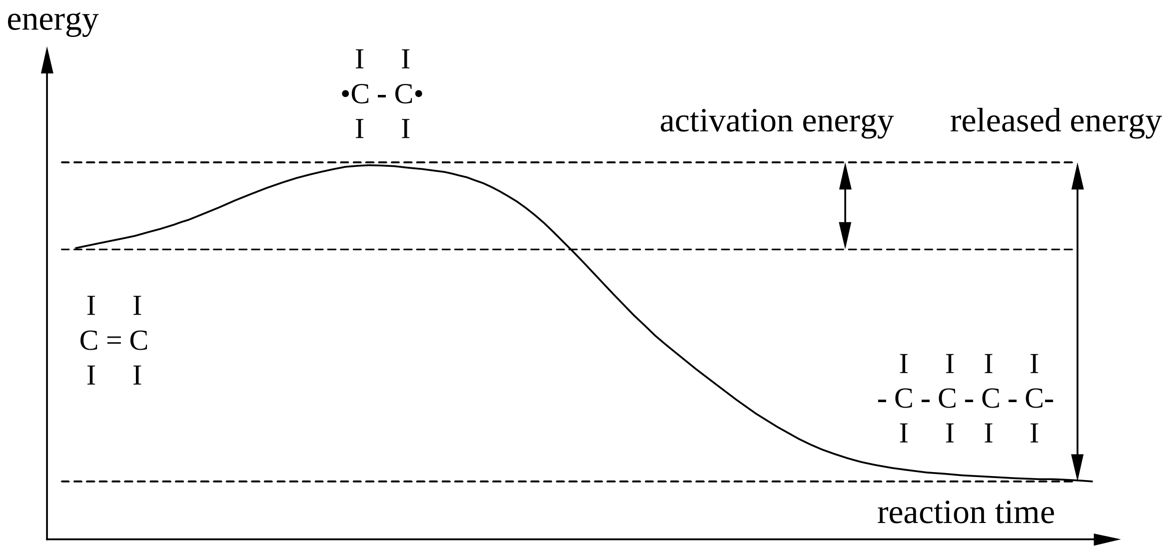


Figure 5.2: Energy curve of a polymerization from monomer via activated (radicalised) monomer to polymer.

You can see the energy needed for radicalization which makes the chain reaction possible, and the lower energy level of the polymer after the reaction.

Copolymerization

A copolymerization is a polymerization using different monomers or the linking of linear, trifunctional monomers (polymers or polycondensates with a reactive component) to a polymerisable (bifunctional) monomer. The graft copolymerization to produce the acrylonitrile-butadiene-styrene graft polymer (ABS) described in the study is an example of copolymerization.

Polycondensation

Polycondensation is a step reaction in which two identical or different reactive groups of compounds react with one another. This produces low-molecular by-products such as water and alcohol. Polyamide (PA) is a typical example of a polymer produced by polycondensation.

Polymeraddition

Polymeraddition is a reaction of at least two bifunctional compounds. An H-atom hereby migrates from one functional group in one compound to a double bond in the other compound. At the same time and new covalent bond is made between the two compounds. Polyaddition is irrelevant for this study.

5.1 Polyethylene

Polyethylenes (PE) display very different properties depending on the production conditions. Low-density polyethylenes (PE-LD) and high-density polyethylenes (PE-HD) will be described in more detail in the following. The extremely high-molecular (PE-UHMW) and the low-density linear polyethylene (PE-LLD) as well as copolymers, mixtures and reinforced and crosslinked PE materials (PE-X) will not be considered in this study despite their relevance. The common characteristics of the homopolymers PE-LD and PE-HD are the high tenacity, percentage elongation at break and resistance to chemicals and stress cracking, very low water absorption, v very good electric and dielectric properties as well as good processing properties. Polyethylene has the empirical formula $–(CH_2)_n$-.

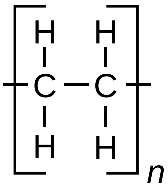


Figure 5.3: Structural formula for polyethylene

5.1.1 Low-density polyethylene (PE-LD)

A characteristic feature of PE-LD is a chain branching, i.e. PE molecules with side chains of different lengths (side-stable methyl groups with 20 to 40 CH_3 groups and 0.5 to 5 long-chain branches of 1000 C-atoms each). This results in the only average degree of crystallization of 40 to 50 %, low dimensional stability under heat and low material rigidity (modulus of elasticity).

The global production capacity for PE-LD in 1995 was around 17.3 million t/a. Germany produced around 1 million t of PE-LD (together with PE-LLD) in 1997, which is the second largest quantity after PVC production. /2; 11/.

The main producers of PE-LD/-LLD 1997: BASF, DOW/BSL, BP /14/.
The main producers of PE-LD/-LLD 2000: Elenac, DOW/BSL, EC Erdölchemie.

The most important field of application for PE-LD in Western Europe is films, accounting for 73%, which can be very different depending on their intended use. Coating and injection moulding as processing methods have retained their 7 % share for many years. The main field of use for PE-LD in Germany is the packaging industry with 64.2%. /10; 11/

5.1.2 High-density polyethylene (PE-HD)

PE-HD is only slightly branched with around 3 to 5 branches for every 1000 C-atoms. PE-HD thus displays a higher degree of crystallization (60 to 80 %), a higher dimensional stability under heat and material rigidity compared to PE-LD.

Because of its homopolar character, PE displays a very high chemical resistance to diluted acids, alkalines, saline solutions, solvents and alcohol, which is even higher for PE-HD than PE-LD. PE-HD only swells slightly in greases, oils and benzene. PE is not resistant to oxidising acids, aromatic and chlorinated hydrocarbons, ketones and detergents. Stress cracks can appear under such loads. PE is water-repellent, permeable for O2, CO2 as well as perfumes and aromatic substances, burns like a wax above 340°C and is only conditionally resistant to weathering. /10; 9/

The global production capacity for PE-HD in 1995 was around 16.9 million t/a. It is fourth in terms of global consumption (behind PE-LD, PVC and PP). Around 1 million tons were produced in Germany in 1997 and an analogous amount consumed /10; 11/

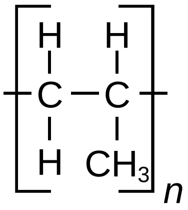
The main producers of this polymer in 1997 were: BASF, Borealis, DOW/BSL, DSM, Hostalen /14/.

PE-HD is the preferred material for injection moulding domestic goods as well as storage and transportation containers. The main consumers in Germany are the packaging (51%) and construction industries (22.2%). /10; 11/

5.2 Polypropylene

Polypropylene (PP) is one of the economically most important thermoplastics with a world-wide consumption of over 10 million t/a and an annual growth of approx. 8 %.

Polypropylene's properties are decisively determined by polymerization and the catalysts used. The base unit of PP consists 3 carbon and 6 hydrogen atoms.



$$\left[-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}- \right]_n$$

Figure 5.4: Structural formula of polypropylene

PP is a linear polymer and is classified as a polyolefine. The methyl (CH_3)-group is characteristic. Depending on the spatial arrangement of these groups to the main -C-C- chain, one differentiates between atactic PP (aPP) with an irregular CH_3-arrangement, isotactic PP (iPP) with CH_3-groups on one side of the carbon chain and syndiotactic PP (sPP) with an alternating CH_3-arrangement. Increasing the tacticity (regularity of the CH_3-arrangement) leads to an increase in the degree of crystallinity, fluxing temperature, tensile strength, rigidity and hardness.

Isotactic polypropylene is currently of great industrial interest (degree of crystallization 40 to 60 %). Non-crystalline atactic PP is used as elastomer components in PP copolymers. The production of syndiotactic PP has only recently become possible through the progress made in catalyst research. It is characterised by a high flexibility, though it crystallises slower and not as completely as iPP.

Polypropylene has a relatively high dimensional stability under heat up to around 135 °C and displays only a slight tendency to stress cracking. Impact resistance and rigidity can be varied within a wide range through copolymerization, fillers (talcum) and reinforcing agents (glass fibres). The slightly lower resistance to oxidation is a disadvantage.

Suspension and gas phase processes are important production methods. Apart from stereospecific Ziegler/Natta catalysts, used to obtain isotactic polypropylene Metallocen catalysts are also increasingly being used, which allow a better adjustment of the material properties.

PP displays hardly any stress cracking, is brittle as a homopolymer, though it is impact resistant as polymer blends, has a higher dimensional stability under heat than PE and is not as a resistant to oxidation. Parameters such as degree of crystallization, melting range, tensile strength, rigidity and hardness rise with an increasing isotactic share. PP has a complex structure, four different superstructures can be determined. Oxygen input and high-energy radiation lead to brittleness and the decomposition of PP. Natural PP is quite translucent (PP films for example are very transparent), is not resistant to UV without stabilization, water-repellent, chemically resistant to acids (apart from oxidising acids), lyes, saline solutions, solvent, alcohol, water, fruit juices, milk as well as oils, greases and detergents. PP is not resistant to aromatic and chlorinated hydrocarbons, benzene, benzine and strong oxidants. On the whole, the mechanical properties in particular are very temperature-dependent /10/.

World-wide consumption of PP at over 10 million t/a us directly behind that of PE-LD and PVC. PP production in Germany in 1997 was slightly above 1 million t, consumption 1.25 million t /10; 11/.

The main producers of polypropylene in 1997 were: BASF, Montell, Borealis, Targor /14/.

Polypropylene can be easily deformed, for example through injection moulding, extrusion and compression moulding and has a wide range of properties. It is thus used for a wide variety of purposes. The main uses are as injection-moulded parts (household goods, fittings, packaging, etc.), hollow bodies/containers and as extruded semi-finished products (pipes, films, foams, etc.) in Germany for example in the packaging industry (42.6%), automobile construction (14.2%) and in electrical engineering (7%) /10; 11/.

5.3 Polyvinyl chloride

Polyvinyl chloride (PVC) is classified as a vinyl polymer and is currently one of the most important plastics with a consumption of around 9 million t/a. The base unit consists of 2 carbon, 3 hydrogen and 1 chlorine atom(s).

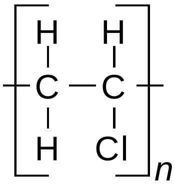


Figure 5.5: Structural formula for polyvinyl chloride

The Cl-group is generally arranged irregularly to the main chain (atactic) and leads to a largely amorphous polymer structure.

PVC has been produced for decades according to process patents dating from 1912 and 1913. Current processes are based on radical polymerization whereby the molecular weight is largely determined by the reaction temperature. In principle the PVC polymers are classified as soft PVC (PVC-P, p-plasticised, contains plasticizer) and hard PVC (PVC-U, u-unplasticised, without plasticizer). PVC polymers differ through the arrangement of the CHCl-groups, particle size and shape, grain structure and grain distribution.

PVC-P is soft, brittle when cold and characterised by plasticizer migration. Flexibility, tenacity, transparency and chemical resistance can be modified within a wide range. PVC-U has a high mechanical strength and rigidity, hardness and chemical resistance. Good electrical properties in the low voltage and low frequency range are characteristic of PVC.

Additives such as functional substances (e.g. stabilizers), fillers (e.g. chalk) and reinforcing agents (e.g. glass fibres) permit a wide range of properties and uses. PVC-P is used amongst others for cable sheathes, seals, electric plugs, protective clothing, shoe soles, coated textiles, floor coverings and films. Application examples for PVC-U are piping, accoutrements, fittings, eaves gutters, window frames, housing parts and foams.

The world-wide capacity for PVC is 20 million t and around 9 million t/a is consumed /10/. Thus, PVC takes third place amongst polymers after PE-LD and PP in terms of volume.
In 1997 Germany produced around 1.5 million t, corresponding to 21.2 %, making it the plastic with the highest production /11/.

The main producers of polyvinyl chloride in 1997 were: BASF, DOW/BSL, EVC, Solvay, Vinnolit, Vestolit /14/.

Main fields of use for PVC are the building sector (60.5%), packaging industry (9.8%), electrical/electronic industry (4.3%), vehicle industry (3.9%) /11/.

5.4 Polystyrene

Normal polystyrene (PS) is a atactic and thus non-crystalline linear polymer. It is characterised by a high rigidity and hardness, transparency, very good electric and dielectric properties, low water absorption and a very good processability. The product surfaces are glossy and have a very low roughness. The permanent working temperature is –10 °C (minimum) and 70 °C (maximum).

PS has a low impact strength. Improvements can be achieved through the addition of elastomers. Various types of rubber such as butadiene rubber or nitrile rubber are used to produce styrene-butadiene-rubber (SBR) or acrylonitrile/polybutadiene/ styrene-graft polymer (ABS).

Special catalysts can be used to produce isotactic PS materials (iPS) with a degree of crystallinity of around 50 % and a fluxing temperature for the crystallites of 230 °C. However, the industrial significance of i-PS is still low.

Polystyrenes with the empirical formula $–CH_2\text{-}CHC_6H_6\text{-}$ have two carbon atoms bonded to hydrogen and a phenyl ring in the base unit.

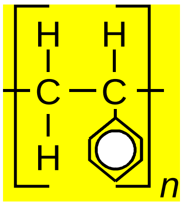


Figure 5.6: Structural formula of polystyrene

Polystyrene is used in numerous fields of application: the packaging industry (including foams), household, sanitary sector, toys, electric, electronic and photo industry.

World-wide consumption of PS in 1990 was 6.9 million t/a. PS thus takes fifth place in terms of volume of standard plastics behind PE-LD, PVC, PP and PE-HD. In Germany 0.785 million t of PS were produced and 0.18 million t consumed in 1997 /2; 11/.

The main producers of PS/EPS in 1997 were: BASF, DOW, Styrenix /14/.

PS is used in very different fields such as household and sanitary sector, in the building trade (36.6%) or in the electrical/electronics (18.5%) and packaging industry (23.8%) /9; 11/.

5.5 Acrylonitrile-butadiene-styrene

Acrylonitrile-butadiene-styrene graft polymer (ABS) is one of the industrially most important polystyrene modifications. ABS has a higher impact strength and higher resistance to stress cracking than polystyrene homopolymers. Further characteristics are a higher strength and rigidity, hardness, resistance to scratches and dimensional stability under heat.

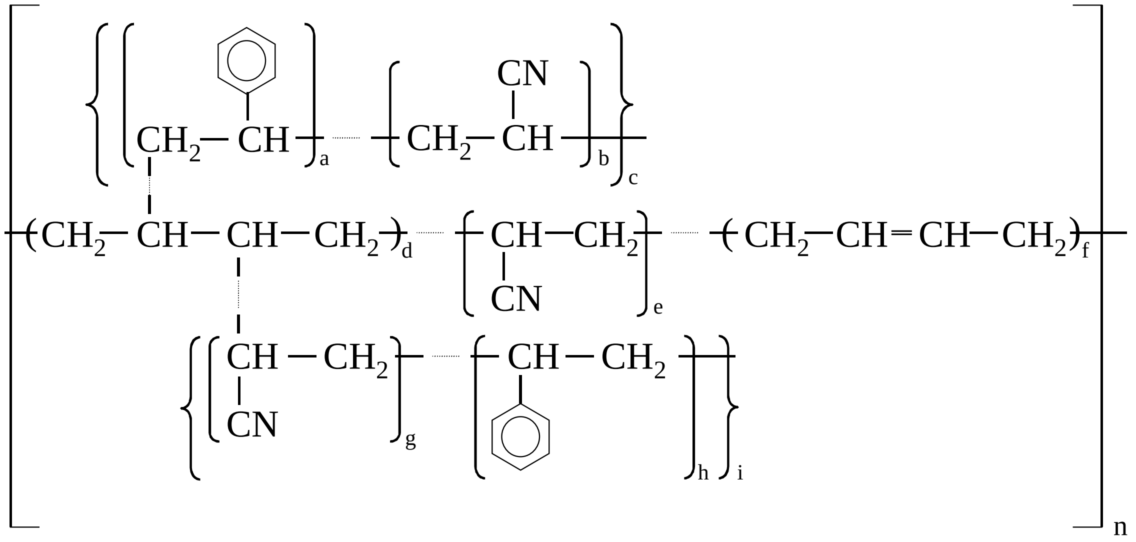


Figure 5.7: Structural formula for ABS

One of the two most important production processes for ABS is the graft polymerization of styrene and acrylonitrile onto a given polybutadiene latex.

Polymers produced by graft copolymerization are called graft polymers or graft copolymers. Their structure is characterised by longer sided chains on their main chains. Main and side chains can be chemically identical or different. Examples include ABS produced by the copolymerization of acrylonitrile and styrene in the presence of polybutadiene or by the polymerization of styrene in the presence of small quantities of an elastomer.

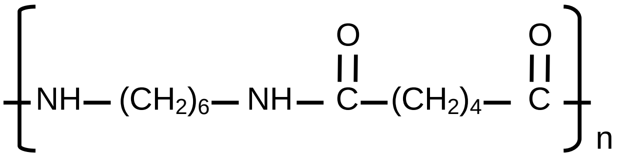
The graft polymer obtained is mixed with separately produced SAN and then dried. The second method is similar. Graft polymers and SAN are produced separately, dried separately and then granulated after mixing. The bond is made by pre-formed linking points consisting of C double bonds which are introduced during polymerization of the monomers, which also contain C double bond. ABS plastics cannot be made transparent due to the butadiene content and are not resistant to weathering. This is why ABS are generally used in copolymer blends after mixing with other plastics /10; 9/.

The main producers of ABS are: Bayer, BASF, DSM.

Injection moulded ABS is used for transport containers, housings for televisions and radios and safety helmets. Expandable ABS moulding compounds are processed to wall panels, shoe selvages, drawers, etc. /10/.

5.6 Polyamide

Polyamides (PA) are amongst the most familiar and most important polycondensates. The properties are essentially determined by the carbonamide group CO-NH. PA 6 (base unit: $-[NH\ (CH_2)_5CO]-$) and PA 6.6 ($-[NH\ (CH_2)_6NH-CO(CH_2)_4CO]-$) are PA types developed decades ago as moulding materials for injection moulding and extrusion.



$$\left[-NH-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}- \right]_n$$

Figure 5.8: Structural formula for PA 6.6

PA 6 is tough and hard, PA 6.6 is additionally characterised by a high wear resistance and dimensional stability under heat. With the same empirical formula $(C_6H_{11}ON)_n$ and same ratio of the number of CH_2 groups to CO-NH groups (one to five) PA 66 has a higher fluxing temperature (255 to 230 °C) and lower water absorption (8.5 to 9.5 %) than PA 6. The reason is the arrangement of the carbonamide groups of neighbouring polymer chains to one another. In PA 6.6 these carbonamide groups are always opposed so that each functional group can form a hydrogen bridge with no deformation of the molecules. In comparison, only every second carbonamide group can form a hydrogen bridge in PA 6.

Both polyamides, the structurally very similar PA 6.6 and PA 6, are the most familiar representatives of the PA family and are very important in injection moulding. They have been produced industrially since 1937 (PA 6.6) and 1938 (PA 6). PA 6.6 is the PA with the highest hardness, rigidity, wear resistance and dimensional stability under heat though at the same time has the high water absorption capacity characteristic of PA.

A disadvantage of the polyamides is the great dependence of the mechanical properties and dimensional stability on the moisture content. This led to the development of polymers such as PA 6.9, 6.10, 6.12, 11 and 12 with a lower water absorption capacity. PA 11 ($-[NH\ (CH_2)_{10}CO]-$) and PA 12 $-[NH\ (CH_2)_{11}CO]-$) in particular display a very low water absorption (e.g. 1.8 % for PA 12). This can be explained structurally by the relatively great distance between neighbouring carbonamide groups and the concomitant significant reduction in the cohesive forces. The lower intermolecular forces however also lead to a lower fluxing temperature (175 °C) and an increase in the material softness compared to PA 6.6.

The properties of polyamides can be significantly changed through chemical modifications such as cocondensation and copolymerization. Furthermore, the product properties of polyamides can be greatly affected by the production of blends, admixing of plasticizers, nucleators and stabiliser as well as reinforcement through powder and fibrous additives.

Polyamide production in Germany in 1997 amounted to 0.29 million t and consumption was around 0.22 million t /11/.

Polyamides are used in mechanical engineering and vehicle construction (39.5 %), the packaging industry (16.8 %) and in electronics (19.5 %) /11/.

The main producers of polyamides in 1997 were: BASF, Bayer /14/

5.7 Important properties of polymers

Table 5.1 summarises the most important properties of polymers.

Table 5.1: Important properties of polymers /6,11,17/

Code (DIN 7728)	Density (DIN 53479) ρ (g/cm^3)	Molecular weight/17b/ M_n (kg/mol)	Modulus in tension (DIN 53457) E (GPa)	Tensile strength (DIN 53455) σ_{Br} (MPa)	Elongation at break (DIN 53455) ε_{Br} (%)	Glass temp./17a/ T_g (°C)	Fluxing temp. T_m (°C)
PE-LD	0.914-0.928	200	0.2-0.5	8-23	300-1000	-130, -21	< 130/6/
PE-HD	0.94-96	13-42	0.7-1.4	18-35	100-1000	-130, -21	< 140/6/
i-PP	0.90-0.907	15-300	1.1-1.3	21-37	20-800	-13	176/6/
a-PS	1.05	92-210	3.2-3.25	45-65	3-4	100	-
PVC-P	1.16-1.35	28	-	10-25	170-400	81	-
PVC-U	1.38-1.55		1.0-3.5	50-75	10-50		-
ABS	1.04-1.06		1.9-2.7	32-45	15-30	85-100	
PA 6	1.13	16-25	1.4	70-85	200-300	40	230
PA 66	1.14	30	2.0	77-84	150-300	50/6/	255
PA 12	1.02		1.6	56-65	300	46	175

6 Process for the synthesis of low density polyethylene

One can in principle differentiate between two methods of polyethylene synthesis. Low density polyethylene (PE-LD) is traditionally produced by a high-pressure process and high density polyethylene (PE-HD) by a low-pressure process. Later methods use the gas phase process and control the morphology of the PE by using suitable catalyst systems. The high-pressure process is developing strongly towards PE-LD production.

The polymers differ in their degree of branching and thus density and degree of crystallinity (see Chapter 5.1 and 5.1.2).

Table 6.1 shows an overview of the production costs.

PE-LD	**HP autoclave**	**Tube reactor**
Capacity, 10^3 t/a	117	200
Capital costs, 10^6 \$	85	116
Monomer costs, \$/t	447	443
Catalyst, chemicals costs, \$/t	20	18
Electricity costs, \$/t	31	33
Other fuels and process materials, \$/t	5	2
Personnel costs, \$/t	10	6
Maintenance \$/t	15	13
Overhead, \$/t	35	29
Production costs, \$/t	565	544
Depreciation \$/t	71	59
Overall costs, \$/t	**636**	**603**

Table 6.1: Comparison of costs for PE-LD synthesis /3/

Methods with different capacities can only be compared on the basis of the production costs due to the different capital costs and depreciation possibilities (plant size).

6.1 High-pressure process PE-LD

6.1.1 Process description

A polymerization reactor can have two different forms. It can either be a high-pressure autoclave or a tube reactor with jacket cooling. Otherwise, the processes are very similar. Only the tube reactor is important in Germany. The reaction pressure is normally between 150 - 200 MPa (1500-2000 bar) for the autoclave process and 200 - 350 MPa (2000-3500 bar) for the tube reactor. This extremely high pressure calls for specialist technology and many key features and details are treated as internal information. The design of these thick-walled tubes differs largely from that of the low-pressure vessels. The wearing properties of components such as pumps and compressors must be given special attention on account of the high pressure. Figure 6.1 shows a secondary compressor for high-pressure synthesis.

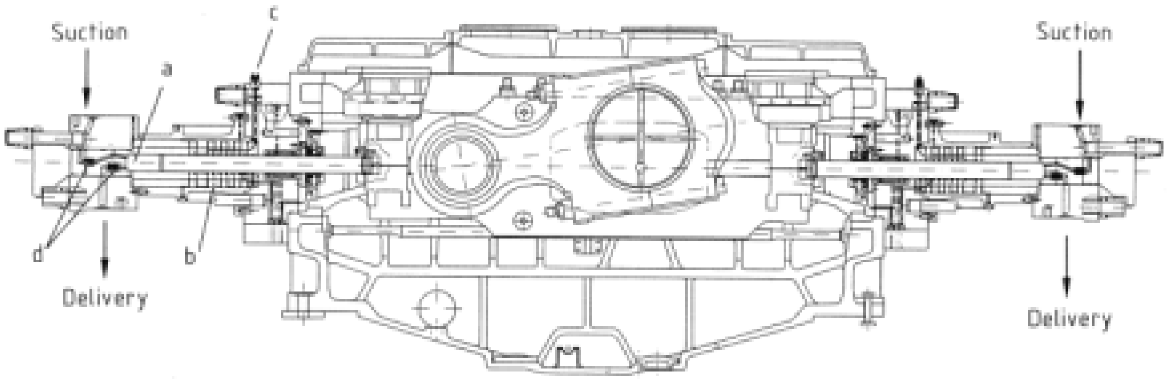


Figure 6.1: Secondary compressor for PE-LD synthesis /2/.

The figure demonstrates the compact design of high-pressure compressors. Naturally, more instruments are needed than for low-pressure synthesis. The seals are matched to the requirements of the higher pressure.

Ethylene is introduced from the pipeline at approx. 5 MPa and compressed to 25 MPa. After the primary compressor stage and input of the recycled ethylene the pressure is increased to 150 - 350 MPa in the secondary compressor stage.

The reaction pressure in the reactor is automatically controlled by a pressure control valve at the reactor output. The polymerised reactant mixture is then passed through a heat exchanger and cooled. The polymer temperature drops and the product can be forwarded to the pellet extruder. The polymer is now freed from the main share of the unreacted monomer. This takes place in an interim separator at 25-30 MPa. This pressure stage should be seen as a compromise between separation efficiency and compression energy savings. The separated monomer passes through a number of coolers and separators and recycled. The monomer still in the product is separated in a low-pressure separator and returned to the primary compressor. The polymer is then forwarded to an extruder. The pellets are subsequently dried, stored temporarily to remove volatile remaining monomers and their quality checked. They are then conveyed to a silo, mixed, stored and packed in tanks or bags.

The stirring autoclave (see Figure 6.2) is an adiabatic reactor (CSTR, continuous stirred tank reactor) and has a volume of approx. 1m^3 in larger plants. The necessary dwell time is approx. 30-60s. Newer plants have internal stirring motors. The elongated form of the reactor is due on the one hand to the manufacturing requirements (it is a thick-walled forging) and on the other to the process conditions (multiple zones). Multiple zones have different pressure-temperature ratios inside the reactor /2/.

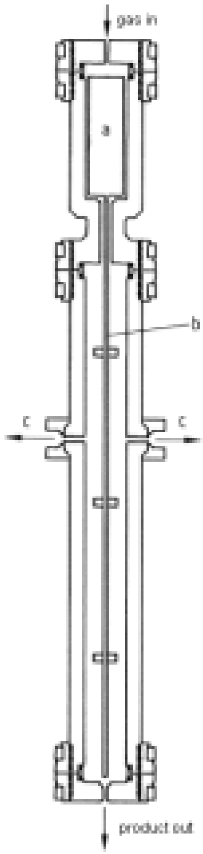


Figure 6.2: Autoclave reactor for PE-LD high-pressure synthesis /2/.

The reactor has cross holes for thermocouples, the initiator-input and monomer-input. Bursting nozzles and outlets are integrated directly in the reactor walls. This should guarantee a discharge during thermal decomposition with a great rise in pressure. The heat of reaction is transferred to the fresh ethane to achieve a cooling. The conversion share in % can be roughly calculated with the equation $0.075*\Delta T$ (ΔT = ethylene input temperature – reaction temperature).

Modern reactors have two or more zones with increasing temperatures (multiple zone reactors). The reaction temperature is kept constant by controlling the initiator amount in each zone. The first zone often displays temperatures around 180°C, and one can reckon with temperatures of around 290°C in the last zone. A good reaction calls for half-times, i.e. decomposition times for the initiator, of around 1s. Organic peroxides can be used as initiators.

The tube reactor has a number of 100 m jacketed tubes. These are straight tubes with 180° bends, with internal diameters of n D_i = 25 to 75 mm. A typical modern reactor has an internal diameter of around 60 mm (200 kt per annum). Because of the necessary compressive strength the ratio D_a/D_i is limited to 2.5. Thermocouples follow the course of the reaction. Initiator inlets, gas inlets and overpressure safety devices are installed along the reactor. Unlike the autoclave reactor, no aftercooler is needed for the 2nd compressor stage. The first section of the reactor services as a pre-heater. The ethylene temperature must be high enough to start the reaction. The necessary temperature depends on the initiator. The temperature interval ranges from 140°C for peroxide carbonates to 190°C for oxygen initiators. Turbulent grafting flows with a good axial mixing is the goal. Although the heat can transmit through the reactor wall, isothermal conditions should not be reached. Temperature peaks are unavoidable. If O_2 is used as an initiator – alone or generally in combination with peroxides – the oxygen supply acts as a control parameter for the temperature. This takes place in the low-pressure area of the reactor. If peroxide initiators are used the speed of the high-pressure pumps is the control parameter. Injecting initiator at various points in the reactor leads to a number of temperature peaks and better conversions than in the autoclave. Conversions of up to 35% are achieved with higher energy costs for compression (autoclave approx. 20%). However, the conversions to be achieved are a function of the product quality. In other words, the conversion rates cannot be increased at indefinitely since this would otherwise lead to a lower quality product /2/.

6.1.2 Process flow chart for high-pressure synthesis

These flow charts show the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

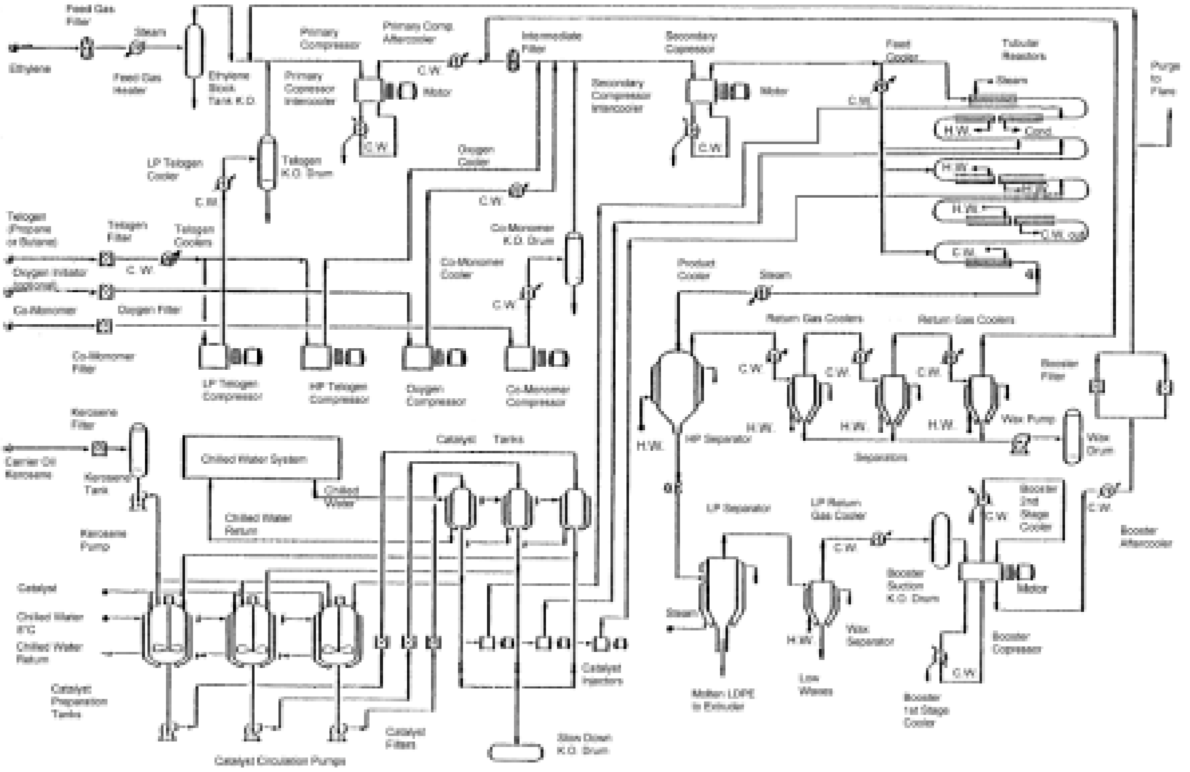


Figure 6.3: Flow chart for PE-LD preparation and reaction in a tube reactor /3/

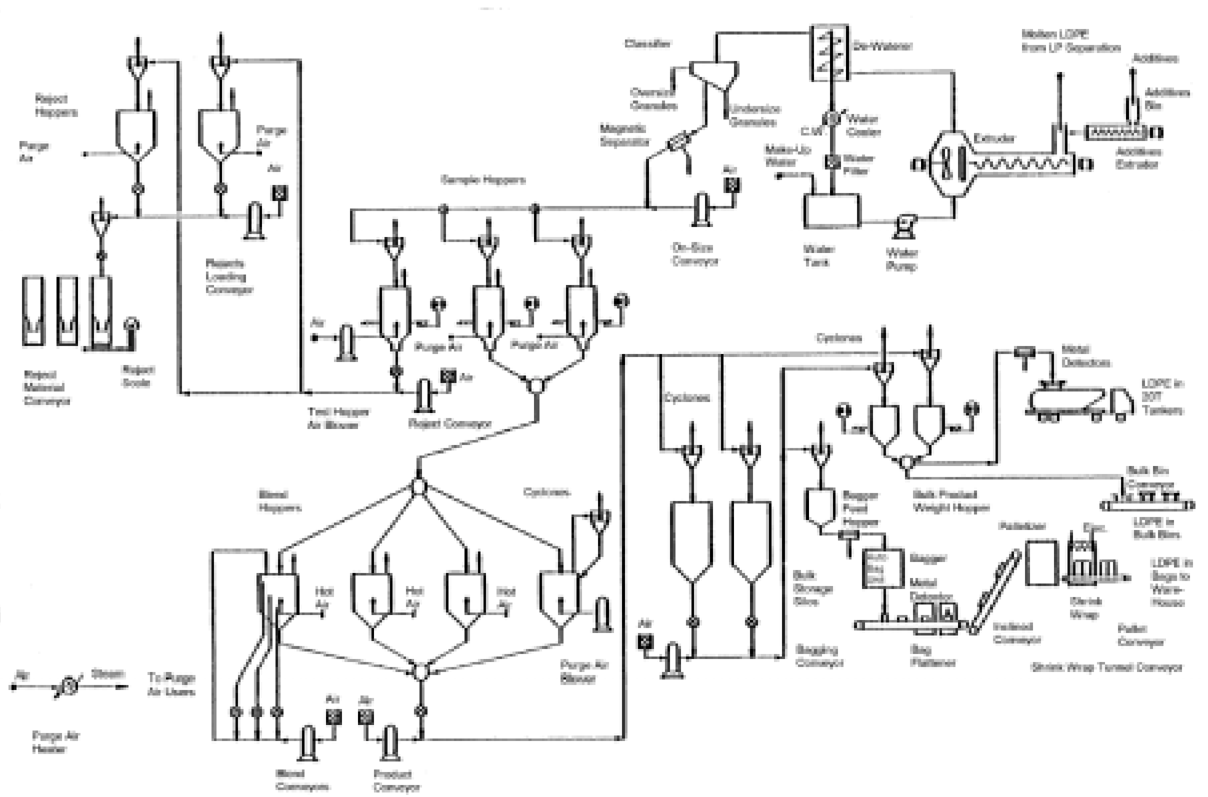


Figure 6.4: Flow chart for PE-LD extrusion and packaging /3/

6.1.3 Input-Output table

General comments (refer to all Input-Output tables)

The materials and energies used, products and by-products as well as emissions and wastes produced are important parameters to characterise the processes. This is why Input-Output tables have been drafted for the processes under consideration. The values represent a range of materials and energies which are seen as representative for the processes employed today in Germany.

The data records were compiled from published information. If reference quantities other than 1 kg polymer were used the figures have been converted accordingly. Since published information was not available or made available for all relevant materials and energies, estimates were made by the IKP to fill these gaps following research into the relevant input and output parameters. The data has not been taken from actual plants, though they do relate to actual technologies since they are based on experience gathered by the IKP in connection with the respective technology (on the basis of system comparisons, analogy conclusions from life-cycle investigations, etc.).

We would like to point out that interdependencies may exist between the quoted figures. This means it would be wrong to conclude that a plant may only be evaluated as BAT if it complies with the minimum limits for all quoted values. As becomes clear taking energy carriers (electricity, steam, fuels) as an example, the power requirements can be reduced if natural gas burners are used to supply energy to the dryer. This naturally leads to a certain demand for natural gas, which has to be gathered and provided.

The source of the data is shown in the comments column. Data marked "Industry" are mean annual figures validated by industry within the scope of the project. Data

with a source number are based on publications. Figures marked with 1) are mean annual estimates of the IKP. The data must be understood as calculated since although measured data exists for certain plants, no special measurements could be carried on plants during the project. Thus, the figures are not data from a reference plant but data intervals for a typical plant.
The system limits were described by the respective process flow charts. On the input side these are the requisite input products and energies, on the output side the emissions after emission reduction measures and wastes from production. These comments apply for all polymer processes discussed in this report.

PE-LD Input-Output table

Main product	Amount	Unit	Comment
PE-LD	1	kg	
By-product			
Ethylene (impure)	0.025 - 0.035	kg	1)
Steam (low-pressure)	0.8 - 1.0	kg	industry
Steam (medium-pressure)	0.1 - 0.2	kg	/3/
Energy carrier			
Electricity	0.825 - 1.05	kWh	/3/, /4/, 1)
Steam (very low pressure)	0 - 0.18	kg	/4/, industry
Kerosene	no data (not always used).	kg	(industry)
Substances			
Ethylene	1.01 - 1.05	kg	/3/, /4/, 1)
Cooling water	100 - 200	kg	/3/, /4/, 1)
Inert gas (nitrogen)	0.001 - 0.003	Nm3	/4/, 1)
Initiator	5E-5 - 0.002 (0.0002 - 0.001)	kg	/3/, industry
Process water	0.4 - 1.2	kg	1), industry
Compressed air	0.02 - 0.04	Nm3	1)
Emissions to air			
VOC	0.004 - 0.006	kg	1)
Particle	1.5E-6 - 7.5E-6	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	1.5E-5 - 8E-5	kg	1)
Biological oxygen demand (BOD)	1E-5 -1.5E-5	kg	1)
Solids (suspended)	<1E-4. 3E-4 - 4E-4 (not recorded)	kg	1) 2), (industry)
Nitrate	2E-5 - 3E-5 (not recorded)	kg	1), (industry)
Hydrocarbons	<7E-6 (not recorded)	kg	1), (industry)
Waste water	0.01 - 0.02	kg	1)
Cooling water	154 - 200 (not recorded)	kg	/3/, /4/, (industry)
Wastes			
Total waste	0.001 - 0.002	kg	industry
Near-domestic industrial waste	0.001 - 0.003	kg	1)

1) Figures based on IKP estimates
2) Figures from /5/ estimated by IKP

Ethylene is drawn off as a by-product to avoid a concentration of inert gases. This material flow can either be burned to recover energy, the ethylene can be cleaned with activated carbon or forwarded to an ethylene producer.

The steam demand was calculated in consideration, i.e. use of the by-product steam. Losses in efficiency may occur due to differences in pressure stages. The by-products low-pressure and medium-pressure steam should be regarded as optional.

The amount of cooling water depends largely on the amount of recirculated cooling water. However, it can be assumed that the majority of cooling water is recirculated in the system and thus the lower value range is more probable.

Nitrogen (N_2) is used as an inert gas to expel remaining ethylene from the pellets and possibly to supply the catalyst.

The value for the process water contains the necessary amount of make-up water extrusion.

The compressed-air is largely used to convey the pellets. The material input of compressed-air is not an environmentally relevant parameter as such but simply documents the plant concept. The current used to convey the compressed-air is included in the power consumption figure.

The VOC value relates to emissions of telogene and ethylene since no solvent is used. Because of the high pressure (up to 3000bar) the emissions are estimated with the relation VOC = 0.5% * quantity of organic input. This figure was compared with the figure from a life-cycle calculation by the Swiss Federal Office for the Environment, Forestry and Agriculture /27/.

The particle emissions for processes after extrusion such as conveying and filling are estimated to be comparable to those for PE-HD synthesis. The IKP estimate corresponds to a share of 0.5% to 2.5% for polymerization in the life-cycle emissions.

If one calculates the quantities of dissolved solids caused by the defined input of electricity in water (2E-5 to 4E-5 kg) and ethylene (0.0002 kg) from the figures quoted by APME /5/ and BUWAL /27/ out of the life cycle of 0.0005 kg, the IKP estimate would be too high at 3 to 4 E-4 kg, which is why the IKP estimate is < 1E-4.

The waste category should be understood as redundant and thus not additive. The industrial figures correspond to the sum total of all waste produced, the data for near-domestic industrial waste and hazardous waste only for these special wastes (values are this included in the sum for total wastes).

Figures marked "(not recorded)" are not recorded in industry since they are not classified as being relevant.

6.1.4 Parameter tube reactor

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

6.1.4.1 General parameters

Location	West Germany
Reference year	1988-1993
Production rate	100%

6.1.4.2 Technical parameters

Polymerization pressure	2000 - 3500 bar
Polymerization temperature	140 - 190 °C (also 250 - 330°C)
Catalyst efficiency	50 - 1200 g_{PE} / $g_{Initiator}$ (also 1000 –5000)
Polymerization time	65 s (also 120 s)
Conversion rate	20 - 35%

Apart from the information on the exemplary plants /**3**/, the figures in brackets represent information obtained directly from industry.

6.1.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process. The plant size cannot be seen as representative for all existing plants.

Annual capacity	150,000 t
Investment costs	approx. 135 million euro
Raw materials costs	approx. 443 - 500 euro / t_{PE}
Initiator / Initiator costs	approx. 13 - 18 euro / t_{PE}
Energy costs	approx. 35 - 40 euro / t_{PE}
Personnel costs	approx. 6 - 9 euro / t_{PE}
Maintenance costs	approx. 13 - 27 euro / t_{PE}

The personnel costs have been calculated on the basis of 25 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

6.1.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Under normal operating conditions the effect of a polyethylene plant on the environment is very slight. Some hydrocarbon emissions occur if telogenes or kerosene is used, though these are of no significant environmental relevance. Peroxide initiators place special demands on their storage, handling and preparation due to their toxicity. Emissions must always be minimised or avoided, not least for reasons of the protection of labour.

Reaction preparation

The considerable excess heat from the compressors can be used to pre-heat the monomer before the reaction.

The dissipation of the heat of the reaction in the autoclave is critical. Peroxides are thus used as initiators since these are reactive enough to start the reaction even at lower reaction temperatures. However, the storage and input of these peroxides into the reaction as a mixture with a carrier oil entails a lot of work (cooled storage due to risk of explosion). The normal initiator quantities which are used are between 0.5 and 2 kg per ton of polymer. The amount of initiator used depends on the desired molecular weight of the product (product type). Since the initiator amounts are a cost factor and the desired molecular weight is functionally related to the initiator amount, the minimum necessary amount of initiator is normally.

Air or O_2 can be used as an initiator in tube reactors. The higher reaction temperatures required by these initiators compared to peroxide initiators can be safely controlled by the tube reactor with its very large heat exchanger surface area.

Reaction

Tube reactor

Different temperature zones are set in the reactor, the heat of reaction drawn off at one point can thus be used in a different zone.

The conversion rate of the monomer per passage through the reactor is between 20 and 35%. Since the recovered monomer has to be compressed and heated before the next passage through the reactor the highest possible conversion rate (>30%) should be aimed at. The aforementioned division of the reactor into temperature zones with quenching through the input of cold monomer contributes to higher conversion rates.

The division of the reactor into temperature zones also enables an adjustment of the product quality over a wide range, thus increasing the plant's flexibility.

Autoclave reactor

Autoclave reactors are protected against overpressure by burst valves. When a critical pressure limit is reached there is a controlled, explosive release of the reactor contents into the environment. Plants with an autoclave reactor should thus not be situated in the direct vicinity of residential areas due to the possibility of an explosive pressure compensation, even though the environmental effects can be regarded as low during normal operation.

The conversion rate for an autoclave reactor is generally lower than that of a tube reactor at around 20%. More monomers thus have to be separated and re-compressed than in a tube reactor.

In order to obtain an even distribution of the molecular weight a stirrer in the reactor must ensure a uniform remixing.

This type of reactor should also be divided into temperature zones by means of quenching with cold monomers, thus increasing the conversion rate and offering the possibility of adjusting the product quality.

Polymer separation and monomer recycling

The majority of the monomer has to be separated from the mixture after the reactor in the high-pressure separator and recycled. The high pressure level of this monomer flow means that it only has to pass through one compression stage before re-entering the reactor. The monomer quantities separated in the low-pressure separator have to pass through both pressure stages. It is thus sensible to keep the share of monomer which is separated in the high-pressure separator as high as possible. A separation of >90% in the high-pressure stage appears possible. PTFE-coated cyclones can be used for this purpose.

Oligomers are produced in both monomer separation stages and these can be used for further industrial applications. Should this prove impossible, the oligomers should be burnt and the heat generated used as process heat, for example.

Part of the monomer recycling flow is normally transferred outward to avoid an enrichment of impurities in the material cycle. This discharged share should best be returned to ethylene producers where it can be recycled and used as a raw material for other purposes. Primary ethylene can be replaced in this manner, which in turn takes a load off the environment.

Processing

Following underwater granulation the water should be separated from the granulate as fully as possible in a centrifuge to enable a closed water cycle with water treatment (filter). The water demand is minimised through a closed water cycle.

The granulate is generally stored in small silos which are rinsed with nitrogen to prevent an enrichment of explosive monomers which still escape from the granulate as gas. A closed nitrogen cycle with treatment of the polluted nitrogen is sensible to minimise the use of primary nitrogen and avoid the disposal of polluted nitrogen.

6.1.6 Assessment

The by-product ethylene (impure) should be used for other purposes, wherever this is allowed by consumer structures, or put to material use on site. If this is not possible, thermal utlilization with energy recovery should be carried out.

Since this is a high-pressure process, the use of high-quality seals (e.g. of PTFE compounds) on flanges and accoutrements is commendable since this can prevent diffuse emissions of VOC.

If exhaust air flows are checked for organic constituents and possibly used for thermal afterburning with energy recovery this can be assessed as being positive for the environment. However, care should be taken to ensure that this is only carried out with relevant concentrations since otherwise the environmental improvements from emission reduction will be cancelled out through the higher energy input.

The input of ethylene as a raw material is a further important parameter. A two-stage monomer separation after the reactor is a suitable measure to achieve high conversion rates of monomers to polymers. The separation in the first pressure stage should be maximised to avoid pressure losses.

Plants which use fresh ethylene as quench in the tube reactor to control the reaction temperature have two advantages: the amount of cooling water is reduced and the fresh ethylene is pre-heated without having to use an additional energy carrier since it absorbs the heat of the reaction.

The compressors used in high-pressure synthesis make a substantial contribution to the energy demand. Pressure losses should be avoided wherever possible. There is a pressure loss during monomer separation so that the monomer can be removed from the polymer though the amount of monomer separated in the lower pressure stage can be shifted towards the high-pressure monomer separation.

The use of Metallocen catalysts leads to further increases in efficiency and greater flexibility in the product output.

7 Process for the synthesis of high-density polyethylene

High-density polyethylene is produced in a low-pressure process which can be split according to the phase in which the reaction occurs into:

- solution process
- suspension process
- gas phase process

The solution process is only used to produce certain low viscosity polymers on account of the high energy needed to remove the solvent and problems in the operation of plants /3/. This process will thus not be described in more detail in the following.

Apart from a classification of the process according to the reaction phase, one can also differentiate between the type of reactor and the solvent used. The most commonly used process variants are /2/:

- Suspension process in a stirred tank reactor (autoclave) with Ziegler catalyst and hexane as a solvent
- Suspension process in a loop reactor with chromium oxide catalyst ("Phillips process") and isobutane as a solvent
- Gas phase process in a fluidized bed reactor

A comparison of the production costs for these three processes is shown in Table 7.1.

Table 7.1: Comparison of costs of PE-HD synthesis after Ullmann /2/

PE-HD	Suspension process in an autoclave	Suspension- process in a loop reactor	Gas phase process
Capacity, 10^3 t/a	200	200	200
Capital costs, 10^6 $	135	105	90
Monomer costs, $/t	456	445	449
Catalyst, chemicals costs, $/t	22	20	26
Electricity costs, $/t	16	16	15
Other fuels and process materials, $/t	10	11	5
Personnel costs, $/t	6	6	6
Maintenance, $/t	15	13	9
General overheads, $/t	26	29	22
Production costs, $/t	553	539	553
Depreciation, $/t	68	53	45
Overall costs, $/t	620	592	577

7.1 Suspension process in an autoclave

7.1.1 Process description

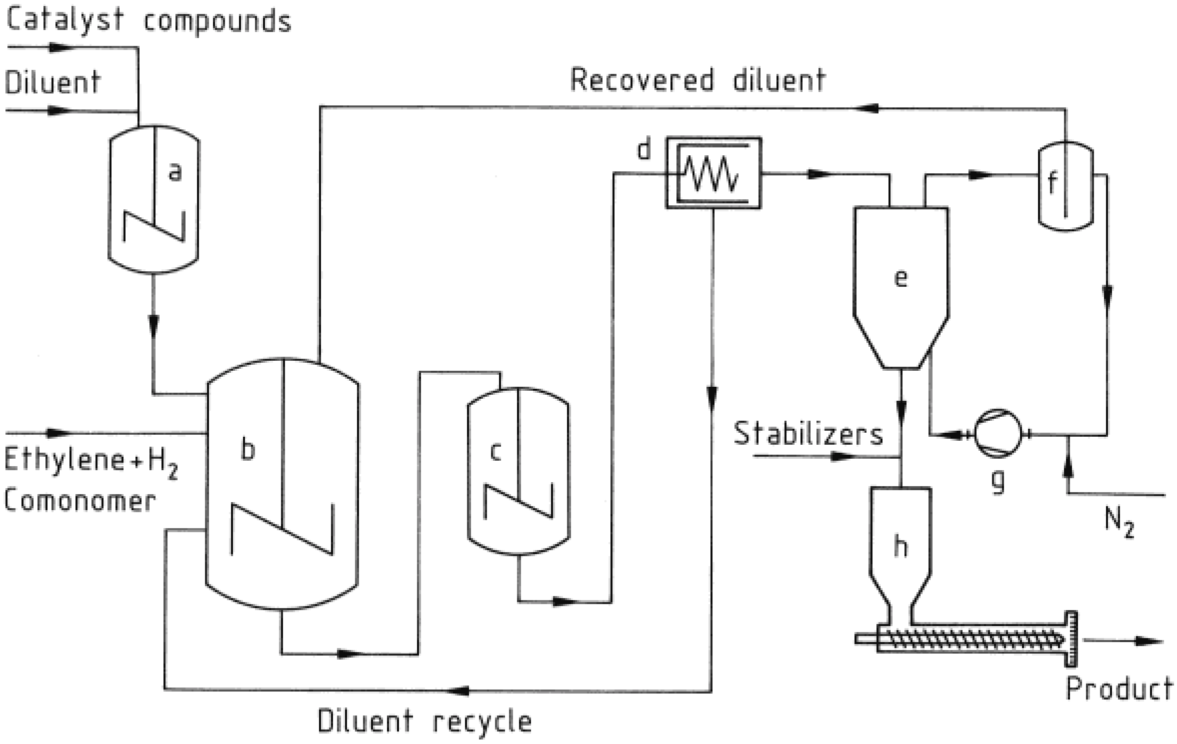
Since Ziegler catalysts have been patented, the synthesis of PE-HD as a suspension in hydrocarbon solvents has been a comfortable production possibility. Since only the catalyst technology was licensed a number of process variants were developed. A cleaning stage for solvent residues was needed in earlier plants, though these have now become superfluous due to the increased activity of the catalysts. Further variations relate to the choice of the organic suspending agent. High-boiling suspending agents require more energy for removal from the polymer, cleaning often takes place by steam stripping. Because of the low flash point, the use of energetically more favourable low-boiling suspending agents such as hexane requires greater care during operation of the plant. Modern plants nevertheless prefer low-boiling suspending agents.

Figure 7.1 shows a process flow chart for the common Hoechst process. The pressure in the plant is between 0.5 MPa and 1 MPa, enabling the construction of larger reactors with around $100m^3$. The reaction temperature is between 80°C and 90°C. A low-boiling hydrocarbon, normally hexane or cyclohexane, is used as a suspending agent.

The constituents of the catalyst and co-catalyst trialkylaluminium are mixed with solvent in ruin-down tank and fed into the reactor depending on the desired rate of reaction. The flow chart shows one reactor, a number of reactors can also be connected in series. In the subsequent "run-down" reactor the dissolved ethylene is almost completely consumed, so that no cleaning stage for ethylene is needed.

The concentration of the polymer suspension is an important process parameter. A high concentration allows a high rate of production with the given reactor volume, but the transfer of heat from the reactor's cooling jacket and the operation of the stirrer in the reactor become more difficult. The maximum concentration of the polymer suspension depends on a number of factors, e.g. the type of solvent, grain size and shape, though basically on the swarm density of the polymer particles. The polymer suspension concentration can vary between 15 % by weight and 45 % by weight, though is normally between 30 - 35 % by weight.

The polymer suspension enters a centrifuge after leaving the "run-down" reactor which removes the main share of the suspending agent. The separated suspending agent is returned directly to the reactor. The suspending agent still contains residual catalyst and trialkylaluminium, so that metering of the fresh catalyst and trialkylaluminium has to be adjusted accordingly. The polymer is dried in a flow of hot nitrogen in a fluidized bed reactor and freed from any remaining suspending agent. The suspending agent can be condensed out of exhaust gas from the fluidized bed reactor for recycling. Additives and stabilisers are added to the polymer before granulation and any catalyst residues neutralised. A further separation of the catalyst is not necessary. The polymer powder leaves the plant as a product or fused during its passage through an extruder and then granulated /2, 3/.



a) Catalyst preparation vessel; b) Polymerization reactor; c) Run-down reactor; d) Centrifuge; e) Fluidized-bed drier; f) Diluent condenser; g) Nitrogen circulator; h) Powder-fed extruder

Figure 7.1: Suspension process in an autoclave to produce PE-HD /2/

7.1.2 Process flow chart

This flow chart shows the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

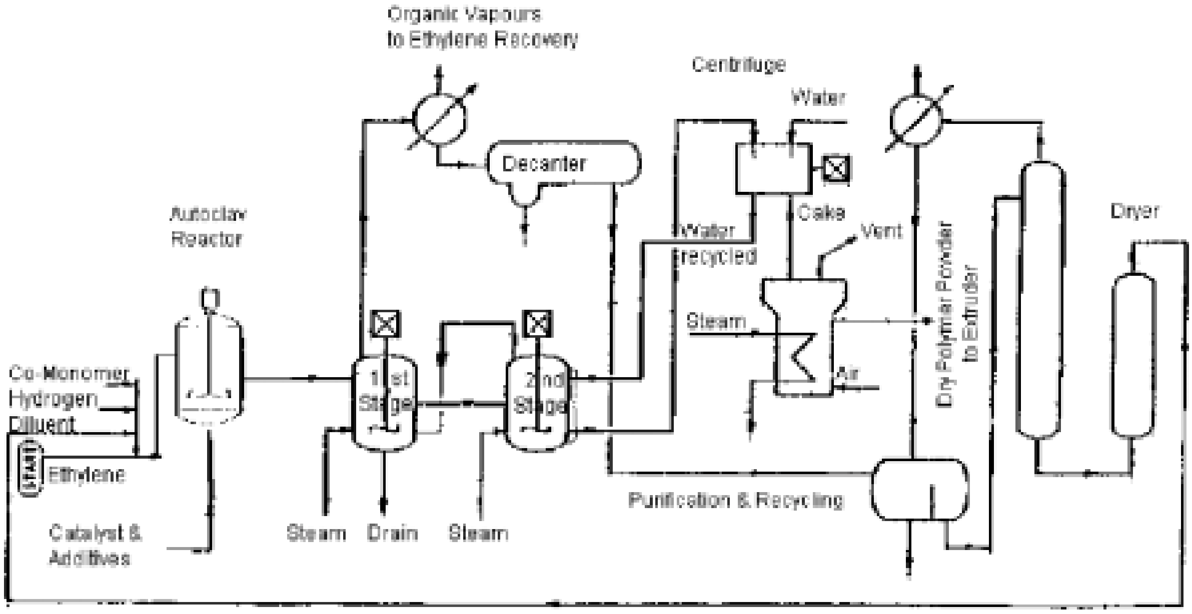


Figure 7.2: Suspension process in an autoclave to produce PE-HD /3/, with integrated stirring vessel.

7.1.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
PE-HD	1	kg	
By-product			
Ethylene	0.002 - 0.02	kg	1)
Energy carrier			
Electricity	0.3 - 0.45 (0.35)	kWh	/3/, /12/, 1)
Steam (total, no pressure data)	0.3 - 1	kg	/12/, 1)
Materials			
Ethene	1.01 - 1.06 (1.02)	kg	/3/, /12/, 1)
Inert gas (nitrogen)	0.030 - 0.11	Nm3	/12/, 1)
Cooling water	20 - 250	kg	/3/, 1)
Process water	0.5 - 4	kg	1)
Compressed-air	0.02 - 0.04	Nm3	1)
Hexane	0.004 - 0.015	kg	1)
NaOH 50%	0.01 - 0.015	kg	1)
Hydrogen	0.0001 - 0.0005	kg	/3/, 1)
Catalyst	8.33E-5 - 3E-4	kg	/6/, 1)
Emissions to air			
Waste air	0.04 - 0.06	kg	1)
VOC	0.0025 - 0.0035	kg	1)
Particle	1.5E-6 - 6.5E-6	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	6E-7 - 2.5E-5	kg	1)
Biological oxygen demand (BOD)	1.2E-6 - 8E-6	kg	1)
Solids (suspended)	< 2.5E-5	kg	1)
Nitrate	5E-10 - 9E-5	kg	1)
Hydrocarbons	1E-5 - 1.5E-5	kg	1) 2)
Heavy metals	6E-10 - 1E9	kg	1)
Wastes			
Near-domestic industrial waste	0.001 - 0.0035	kg	1)
Hazardous waste	0.00006 - 0.00075	kg	1)

1) Figures based on IKP estimates
2) Figures from /5/ estimated by IKP

The ethylene listed as a by-product can be returned to the production process or separated before the decanter for use in other applications. If it is returned the input quantities of ethylene are within the range shown in brackets.

The amount of cooling water depends largely on the amount of recirculated cooling water. However, it can be assumed that the majority of cooling water is recirculated in the system and thus the lower value range is more probable. The compressed-air is largely used to convey the polymer. The material input of compressed-air is not an environmentally relevant parameter as such but simply documents the plant concept. The current used to convey the compressed-air is included in the power consumption figure.

The demand for hydrogen to check the molecular weight was estimated higher by IKP for certain plants than quoted in /3/.

The amount of catalyst used is a reference value and depends to a large extent on individual parameters of the respective plant. Starting points are provided by /6/ and /28/. Common transition metal catalysts have values up to 12 kg PE/g catalyst. More recent developments in transition metal catalysts achieve values of up to 70 kg PE /g catalyst.

The VOC life cycle emissions of PE-HD are approx. 0.01710 kg per kg of PE-HD. Ethane and steam generation alone account for approx. 80% of emissions. The rule of thumb estimate (0.5% or the organic input material as emission) is also regarded as too high on account of the relatively low pressure level in the plant t.

The COD life cycle emissions are approx. 0.0012 kg. Ethane and electricity generation have the highest amounts (>90%). Further processes which play a subordinate role in the formation of COD include the production of NaOH and nitrogen. Estimates are thus based on 0.5 - 2% of the emissions from polymerization.

If one calculates the quantities of dissolved solids in water caused by the defined input of initial products and energy (>93%) defined in the table from the figures quoted by APME /5/ out of the life cycle (0.00015 kg), one arrives at the lower value (polymerization <7%) of 1E-5 kg.

The value for heavy metals depends largely on the type of catalyst used.

7.1.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

7.1.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

7.1.4.2 Technical parameters

Polymerization pressure	5- 10 bar
Polymerization temperature	80- 90°C
Catalyst efficiency	no data
Polymerization time	2 h
Conversion rate	>98%

7.1.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	80,000 t
Investment costs	approx. 50 million euro
Raw materials costs	500 - 550 euro / t_{PE}
Initiator / Initiator costs	approx. 30 euro / t_{PE}
Energy costs	approx. 38 euro / t_{PE}
Personnel costs	approx. 15 euro / t_{PE}
Maintenance costs	approx. 20 euro / t_{PE}

The personnel costs have been calculated on the basis of 20 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

7.1.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Reaction preparation

The use of low-boiling solvents calls for a lower energy demand in the subsequent stages than if high-boiling solvent were to be used though it entails higher expenses for safety technology on account of the higher explosion risk. The energy to remove the solvent from the polymer is lower, cleaning is often by means of steam stripping.

The reduction of diffuse hexane emissions is important sine the effects of hexane vapours can be detrimental to health /29/.

Reaction

The reaction takes place in a cascade of stirring vessels. Only approx. 50% of the monomer is converted in the first stage. If a suitable dwell time in the reactors is selected the quantity of unreacted monomer is so low that no monomer recycling is needed. Any remains are removed from the polymer with the solvent (hexane) and recycled.

New types of Ziegler catalysts are so effective that amounts of < 0.0002kg catalyst/ kg of polymer can be used. This means that the amount of catalyst remaining in the polymer is so low that no energy-intensive separation of the catalyst from the polymer is needed.

A good mixing in the reactors should be ensured suitable stirrers so as to avoid caking on the reactor walls.

Polymer separation and monomer recycling

Organic vapours are extracted from the 1st reactor for purification. High and low-molecular impurities are separated in a multi-stage process. These impurities should be burnt and the waste heat used. The recovered solvent which contains ethylene residues can be recycled.

The product is freed from solvent residues in a centrifuge and dryer. Remaining contents 0.1 % by weight of solvent can be achieved. The solvent removed in the dryer by a hot air flow should be condensed and recycled.

7.1.6 Assessment

The increased activity of the catalysts e.g. on the basis of titanium chloride and Co catalysts with trialkylaluminium compounds makes a separation of the catalyst from the polymer superfluous. This saves one process stage and can be assessed as being positive for the environment.

The use of low-boiling solvents such as hexane or cyclohexane leads to a lower energy consumption during separation of the catalyst from the polymer and can also be assessed as a positive factor. Measures to ensure a safe operation must be guaranteed on account of the higher explosion risk.

If exhaust air flows are checked for organic constituents and possibly used for thermal afterburning with energy recovery this can be assessed as being positive for the environment. However, care should be taken to ensure that this is only carried out with relevant concentrations since otherwise the environmental improvements from emission reduction will be cancelled out through the higher energy input.

The installation of a "run-down" reactor to avoid an ethylene cleaning stage is advantageous. This leads to savings in energy and possibly material resources.

A higher concentration of solids in the polymer sludge when this leaves the reactor is advantageous to guarantee a more efficient production with respect to the energy and materials. This leads namely to a lower energy demand during separation of the solvent from the polymer. The goal should be solid concentrations of > 30%.

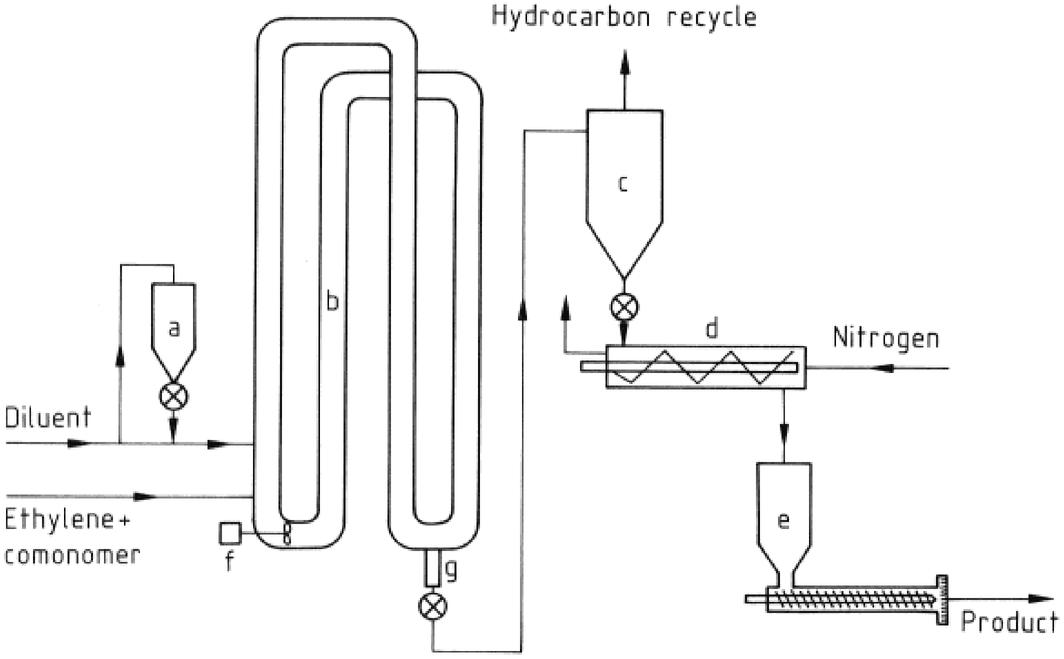
The connection of a number of reactors in series may prove advantageous. This allows a flexible adjustment of the capacity, inefficiencies and excess production can be avoided, input and process materials can be adapted to the respective situation.

Catalysts of transient metals display advantages in terms of the response of the hydrogen, leading to a lower demand for hydrogen. High catalyst activities can also be expected to that the necessary amount of catalyst is low.

7.2 Suspension process in a loop reactor

7.2.1 Process description

A simplified process flow chart is shown in Figure 7.3. The loop reactor built of wide-mouthed tubes was developed to avoid deposits, which interfered in the autoclave. The reactor has a high ratio of surface area to volume, facilitating heat exchange and enabling short dwell times. A pump wheel moves the reaction mixture in a turbulent flow at a speed of 5 – 10 m/s through the reactor. The reaction conditions include temperature, pressure, speed, catalyst, solvent. They are not a consequence of the catalyst but the catalyst is an integral part of the conditions. All of these parameters affect the speed of reaction. The reaction conditions here are 100°C, 3 – 4 Mpa and chromium oxide catalyst are aimed at the required production rate. The suspending agent used is isobutane, which facilitates separation through evaporation and allows higher working temperatures than a long-chain organic suspending agent. The catalyst is rinsed out of the flash tank in the reactor by the suspending agent. The polymer is removed from the reactor in a sedimentation zone, this permits a polymer suspension concentration of 55 – 65 %, which is input into the evaporation reactor. The concentration of the polymer suspension circulating in the reactor is 30 – 35 %. The suspending agent escapes in an evaporator, is condensed and returned to the system after the process. Since the fluid content of the polymer cake when this leaves the flash tank is lower (10-15 % by weight) than in an autoclave reactor (approx. 30-35 % by weight) less energy (air, steam, inert gas) is needed for stripping. The remaining suspending agent is removed in a conveyor which is rinsed with nitrogen. Granulation is carried out analogous to the process in the autoclave with an extruder. /2/



a) Catalyst hopper and feed valve; b) Double loop reactor; c) Flash tank; d) Purge drier; e) Powder-fed extruder; f) Impeller; g) Sedimentation leg

Figure 7.3: Suspension process in a loop reactor to produce PE-HD /2/

7.2.2 Process flow chart

This flow chart shows the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

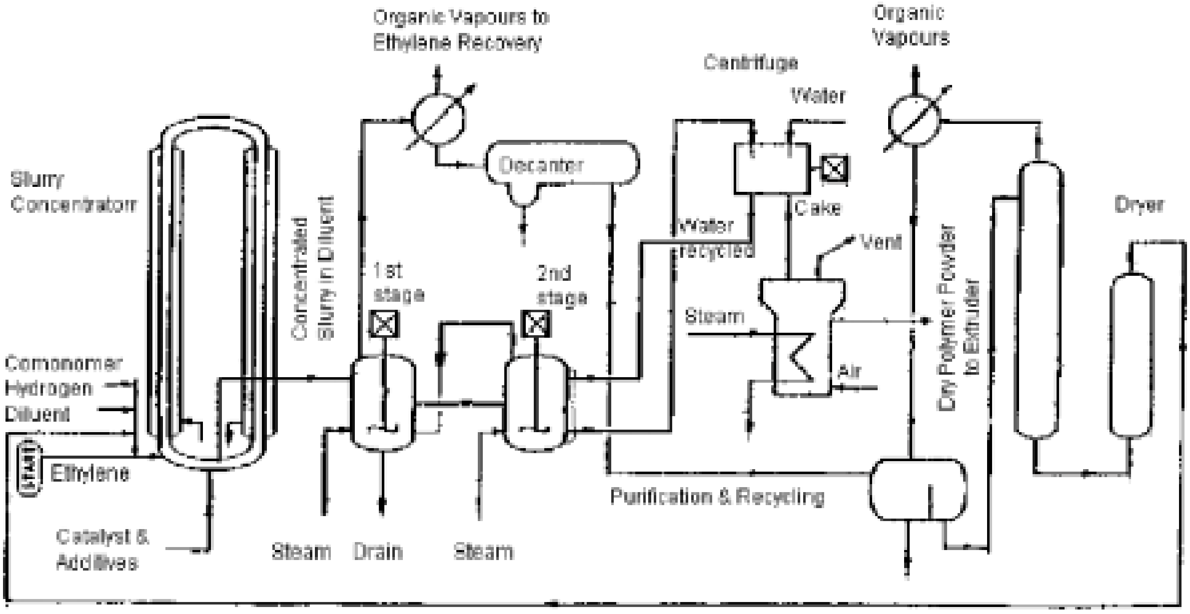


Figure 7.4: Suspension process in a loop reactor to produce PE-HD /3/

7.2.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
PE-HD	1	kg	
Energy carrier			
Electricity	0.3 - 0.5	kWh	1), industry
Steam (total, no pressure data)	0.16 - 0.25	kg	1), industry
Materials			1)
Ethene	1.01 - 1.03	kg	1)
Inert gas (nitrogen)	0.030 - 0.05	Nm3	1)
Cooling water	20 - 150 (100 - 200)	kg	1), (industry)
Process water	0.5 - 4	kg	1)
Compressed-air	0.02 - 0.04	Nm3	1)
Isobutane	0.004 - 0.006	kg	1)
Catalyst	0.0001 - 0.0002	kg	1)
Emissions to air			1)
Waste air	0.04 - 0.05	kg	1)
VOC	0.005 - 0.0075	kg	1)
of which isobutane	0.002 - 0.003	kg	1)
Particles	1.5E-6 - 6.5E-5	kg	1)
Emissions to water			1)
Chemical oxygen demand (COD)	6E-7 - 2.5E-5	kg	1)
Biological oxygen demand (BOD)	1.2E-6 - 8E-6	kg	1)
Solids (suspended)	< 2.5E-5 (not recorded)	kg	1), (industry)
Nitrate	5E-10 - 9E-5 (not recorded)	kg	1), (industry)
Waste water	3 - 4	kg	1)
Hydrocarbons	7E-6 - 1.5E-5 (not recorded)	kg	1), (industry)
Heavy metals	8E10 - 1.2 E9 (not recorded)	kg	1), (industry)
Wastes			1)
Overall waste	0.001 - 0.0035	kg	industry
Near-domestic industrial waste	0.001 - 0.0035 (not recorded)	kg	1), (industry)
Hazardous waste (solvent)	0.00004 - 0.0005 (not recorded)	kg	1), (industry)

1) Figures based on IKP estimates

The energy demand of the impeller (relative to the product quantity) has been estimated with a 20% higher electrical energy demand than that of the autoclave.

The cooling water amount is lower than that for an autoclave reactor since a better transfer of heat to the reactor walls is possible. The amount of cooling water depends largely on the amount of recirculated cooling water. However, it can be assumed that the majority of cooling water is recirculated in the system and thus the lower value range is more probable.

Isobutane is used as a diluent for the slurry.

Since isobutane is more volatile than hexane and higher temperatures and pressures are prevalent, a higher interval for VOC emissions has been estimated.

The particle emissions are comparable to those of the autoclave reactor technology since these relate mainly to the those parts of the plant after the reaction. The further emissions and wastes are estimated as being comparable to those for the autoclave reactor.

The waste category should be understood as redundant and thus not additive. The industrial figures correspond to the sum total of all waste produced, the data for near-domestic industrial waste and hazardous waste only for these special wastes (values are this included in the sum for total wastes).

Figures marked "(not recorded)" are not recorded in industry since they are not classified as being relevant.

7.2.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

7.2.4.1 General parameters

Location	West-Germany
Reference year	1990-1993
Production rate	100%

7.2.4.2 Technical parameters

Polymerization pressure	30-40 bar
Polymerization temperature	100 -150°C (100 – 110°C)
Catalyst efficiency	3000 - 10000 g_{PE}/g_{Kat}.
Polymerization time	1.5 h.
Conversion rate	no data

Apart from the information on the exemplary plants /**3**/, the figures in brackets represent information obtained directly from industry.

7.2.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	70,000 t
Investment costs	approx. 50 million euro
Raw materials costs	approx. 525 euro / t_{PE}
Initiator / Initiator costs	approx. 30 euro / t_{PE}
Energy costs	approx. 25 euro / t_{PE}
Personnel costs	approx. 30 euro / t_{PE}
Maintenance costs	approx. 10 euro / t_{PE}

The personnel costs have been calculated on the basis of 20 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

7.2.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Reaction preparation

A solvent with a low boiling point is used so that it can be easily separated from the polymer.

The low boiling point of the solvent entails the risk of higher diffuse emissions. Since isobutane is not toxic, care should be taken to ensure that the measures are economically justifiable. A reduction of the isobutane emissions reduces the formation of photooxidants and at the same time the resource requirements if the solvent is recycled.

Reaction

High peripheral speeds should be prevalent in the reactor to prevent materials caking to the reactor walls (fouling).

The polymer concentration in the reactor is around 30-35%. To avoid an unnecessarily high separation of solvent from the polymer the polymer should first be allowed to settle in a side arm of the reactor before being extracted. In this way the mixture can be concentrated to an approx. 65% polymer share.

Polymer separation and monomer recycling

The solvent is separated in a flasher after it leaves the reactor. Since the solvent has a lower boiling point a single-stage separation is generally adequate. Any solvent remaining in the polymer can be removed by rinsing with nitrogen in a dryer. It is sensible to treat the nitrogen and use it in a closed cycle. The solvent produced during nitrogen treatment should be recycled.

7.2.6 Assessment

The Phillips process is rated as favourable in terms of raw materials and energy consumption.

An advantage of the loop reactor is that the high peripheral speeds prevent deposits on the reactor walls. This reduces the energy and materials inputs and losses in efficiency during cleaning of the plant.

The use of a low-boiling solvent should be seen as positive since the energy inputs for evaporation and separation of the solvent are lower.

The high polymer concentrations (>60%) in the slurry when this leaves this reactor are also a positive factor from an environmental aspect. This calls for a lower input of energy carriers and steam when stripping the suspension.

Single-stage separation of the solvent is advantageous in terms of the mechanical and technical input.

The molecular weight is controlled via the temperature, so that no hydrogen is needed. Since this is a high-energy substance (120 MJ/kg) this can be understood as an environmental advantage.

7.3 Gas phase process in a fluidized bed reactor

7.3.1 Process description

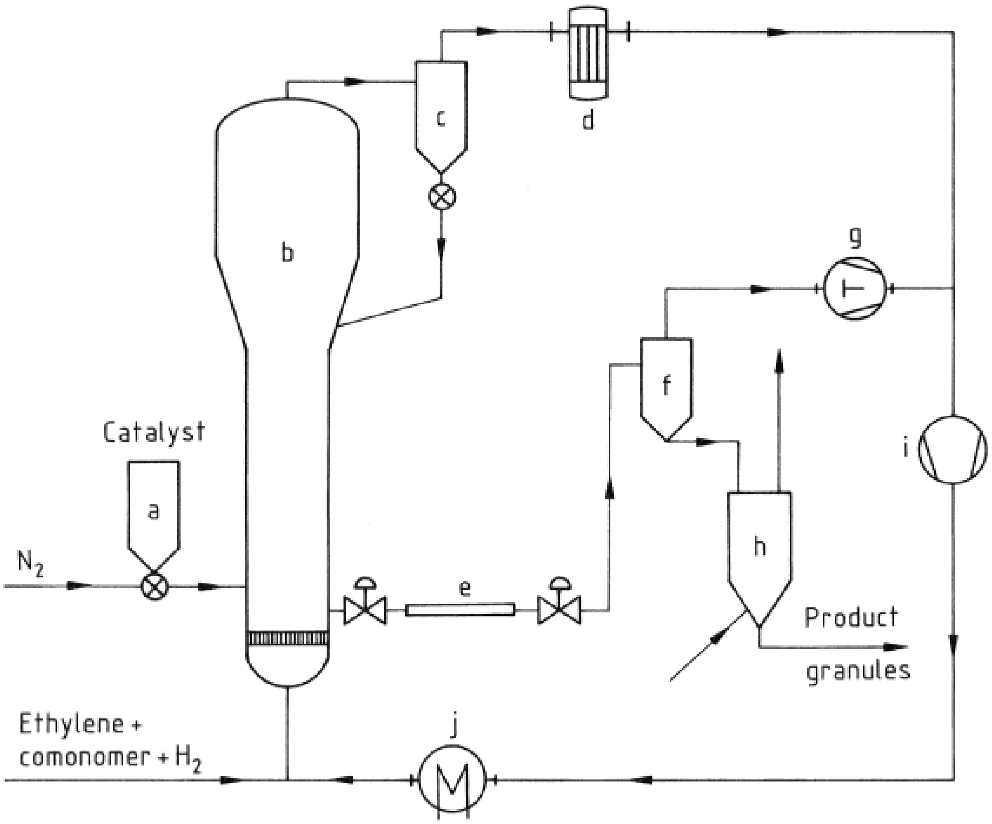
Fluidized bed processes for the production of PE-HD were developed in the late sixties by Union Carbide and Naftachemie. Despite new technologies, the process was initially unable to displace the established suspension process, which cost roughly the same. One advantage of the gas phase process is that the plant can be used to produce PE-HD or PE-LLD depending on the demand. Polymers with different melt-flow Indices (MFI) and different densities can be produced. The process thus does not have the same restrictions as the suspension and solution process, where the solubility and viscosity sets certain limits on the variety of polymers which can be produced.

Figure 7.5 shows a process flow chart for the Union Carbide fluidized bed technology. The principle of this process is comparable to the Unipol process to produce PP if propylene is used as a monomer instead of ethylene and possibly if a special catalyst is used (see Chap. 8.2).

The reactor has a characteristic shape with a cylindrical reaction zone and a zone in which the reactor widens to reduce the velocity of the flowing gas. This means that particles torn from the fluidized bed and entrained in the gas flow fall back into the bed. The fluidized bed is approx. 4m high, in an expanded state 10m. The overall reactor is 30 m high. Gas enters the reactor though a distributing plate which homogenizes the gas flow and supports the polymer particles in the reactor when the gas flow is switched off. In a fluidized state the fluidized bed reacts more or less like a autoclave (CSTR), the material flow of the bed material leads to a mixing of materials and heat in the reactor. The bed material primarily flows upwards inside the reactor and falls along the reactor walls. The reaction temperature is 80°- 105°C, depending on the density of the product being produced. The pressure is between 0.7 MPa and 2 MPa. Lower pressures were initially used for butene and hexene as comonomers to avoid a condensation in the cooler for recycling. Today, however, the condensation is utilised to increase the output since the evaporation of fluid olefine absorbs more heat from the polymerising particles. The conversion rate for HD-PE is approx. 2% per passage, and is higher if olefine comonomers are used in the condensation mode.

The correct position of feed and delivery points for the catalyst, cocatalyst and polymer powder is important to avoid a discharge of catalyst particles, which would lead to a lower conversion rate. A cyclone and/or filter prevents particles entering the recycling cooler and compressor. The polymer is drawn off with a valve and passed to a dust cyclone where the remaining monomers are separated and re-compressed. The main cycle compressor generates a gas flow with a high volume flow rate but small pressure rise. Since the process takes place at temperatures near the melting point of the polymer an exact temperature control is needed. The temperature can be controlled by the quantity of catalyst added. The reactor must be prevented from running away since there is then a risk that the entire reactor content would bake. To stop the reactor quickly, the catalyst activity is stopped by adding CO_2.

The choice of catalyst is decisive for the success of the process. The catalyst grain grows to 15-20 times its original size through a multiplication process. This affects not only the course of fluidization. The polymerization rate and heat transport also have to be controlled to prevent a fusion of particles or runaway of the reaction. Catalysts based on SiO_2 or $MgCl_2$ with a particle diameter of 50 µm have proven suitable here /2/.



a) Catalyst hopper and feed valve; b) Fluidized-bed reactor; c) Cyclone; d) Filter; e) Polymer take-off system; f) Product recovery cyclone; g) Monomer recovery compressor; h) Purge hopper; i) Recycle compressor; j) Recycle gas cooler

Figure 7.5: Gas phase process in a fluidized bed reactor to produce PE-HD /2/

7.3.2 Process flow chart

This flow chart shows the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

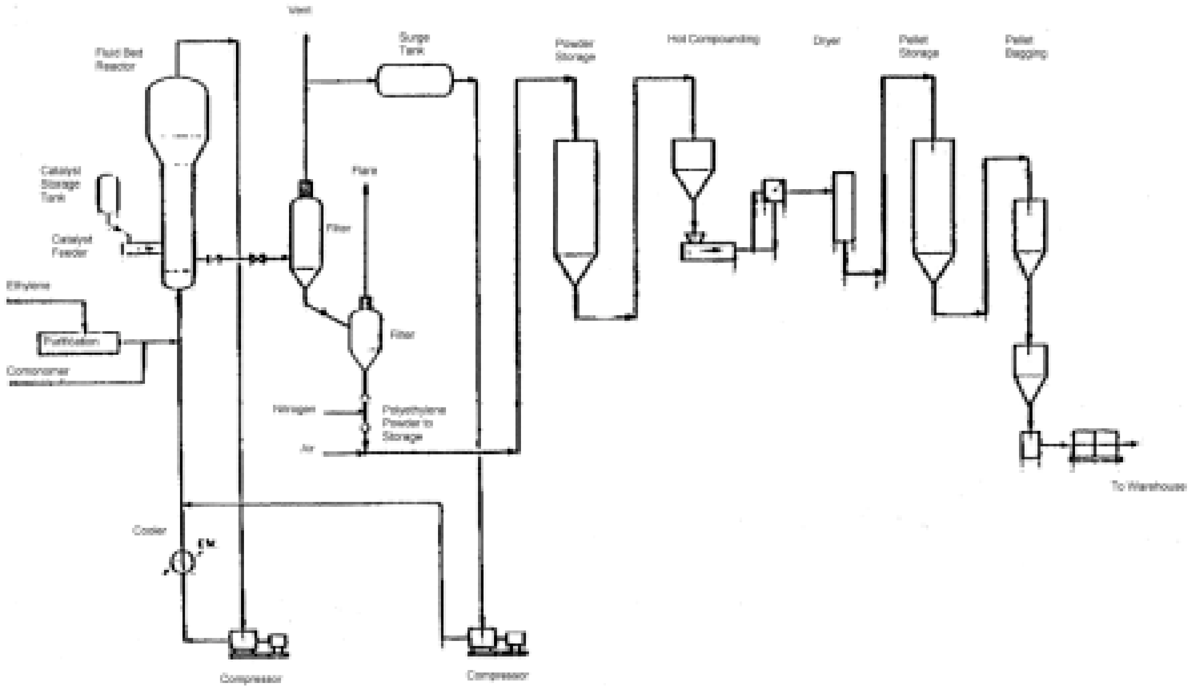


Figure 7.6: Gas phase process in a fluidized bed reactor to produce PE-HD /3/

7.3.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
PE-HD	1	kg	
Energy carrier			
Electricity	0.3 -0.45	kWh	/3/, /4/, 1)
Steam (total, no pressure data)	negligible	kg	1)
Fuel	8E-6- 1E-5	kg	/3/
Materials			
Ethene	01.01.02	kg	/3/, /4/, 1)
Inert gas (nitrogen)	0.03 - 0.08	Nm3	/3/, /4/, 1), (industry)
Cooling water	60 - 140 (100 - 200)	kg	/3/, 1), (industry)
Compressed-air	0.04 - 0.06	Nm3	1)
Hydrogen	1.5E-4 -1.7E-4	kg	/3/
Catalyst	1.5E-6 - 1.0E-4	kg	/4/, industry
Emissions to air			
Waste air	0.1 - 0.15	kg	1)
VOC	0.003 - 0.005 (> 0.01)	kg	1), (industry)
Particles	3E-6 - 8E-5 (> 4E-4)	kg	1), (industry)
CO	4.8E-6 -6E-6 (not recorded)	kg	1), (industry)
CO2	0.024 - 0.031 (not recorded)	kg	1), (industry)
Emissions to water			
Chemical oxygen demand (COD)	negligible (< 0.12)	kg	1), (industry)
Biological oxygen demand (BOD)	negligible (< 0.04)	kg	1), (industry)
Solids (suspended)	negligible (not recorded)	kg	1), (industry)
Nitrate	negligible (not recorded)	kg	1), (industry)
Wastes			
Total waste	< 1.0	kg	industry
Near-domestic industrial waste	0.001 - 0.0035 (not recorded)	kg	1)
Hazardous waste	negligible (not recorded)	kg	1)

1) Figures based on IKP estimates

The fuel demand is quoted at 0.1 gcal/t (= 0.4187 MJ/t). This corresponds for light heating oil with 42.7 MJ/kg to approx. 0.00001 kg/kg, for kerosene with 43 MJ/kg to approx. 0.000009 kg/kg.

The compressed-air demand is rated higher than with the slurry method since the air passes through more parts of the plant.

The amount of catalyst refers to a transient metal catalyst.

The diffuse VOC emissions are rated lower than in an autoclave reactor since monomer conversion is approx. 99% and no solvents are used. The pressure in the reactor is however twice as high at up to 2 MPa. The CO from the fuel conversion processes to generate process heat or electricity, which is not part of our considerations here, is dominant. If fuels is used for drying an emission of approx. 4.8E-6 kg to 6E-6 kg CO arises from this process-specific fuel conversion for stochiometric reasons. The same applies for CO_2, the process-specific emissions from drying are then approx. 0.024 kg to 0.031 kg CO_2 from fuel conversion.

The waste category should be understood as redundant and thus not additive. The industrial figures correspond to the sum total of all waste produced, the data for near-domestic industrial waste and hazardous waste only for these special wastes (values are this included in the sum for total wastes).

Figures marked "(not recorded)" are not recorded in industry since they are not classified as being relevant. Figures marked "negligible" are IKP estimates, figures in brackets have been provided by industry.

7.3.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

7.3.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

7.3.4.2 Technical parameters

Polymerization pressure	approx. 20 bar
Polymerization temperature	85°-105°C
Catalyst efficiency	9,000 g/g $_{\text{Kat}}$
Polymerization time	3-5 h
Conversion rate	2% per passage

7.3.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	75,000 t
Investment costs	approx. 40 million euro
Raw materials costs	approx. 470 euro / t_{PE}
Initiator / Initiator costs	approx. 35 euro / t_{PE}
Energy costs	approx. 25 euro / t_{PE}
Personnel costs	approx. 17 euro / t_{PE}
Maintenance costs	approx. 15 euro / t_{PE}

The personnel costs have been calculated on the basis of 25 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

7.3.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Compared to the two fluid phase processes a positive feature which should be stressed is that no solvent is used in the gas phase process. However, the process cannot be regarded as universal since not all PE types can be produced with this technology.

Reaction

No coolant is used in the reaction which has to be separated after the reaction.

The heat of reaction is dissipated by a heat exchanger in the gas return line. This excess heat can be used to pre-heat reaction components.

Conversion of the monomer per passage through the reactor is 2 – 3%. The monomer is left in the reactor cycle until the high conversions of 99% are reached. If the conversion per passage is as high as possible the amount off gas recovery drops.

The raw materials consumption is 1.01 $kg_{Monomer}$ / $kg_{Polymer}$ (> 99% conversion).

Polymer separation and monomer recycling

The polymer is drawn off from the base of the reactor and still contains monomer. The monomer is drawn off and approx. 90% of this can be re-compressed and returned to the process. The remaining 10 % has to be either processed and freed from impurities to prevent an enrichment of impurities in the reaction cycle, or burnt and the heat generated from this utilised. The waste monomer can also be used for other industrial applications.

In a 2nd stage of monomer separation the polymer is rinsed with nitrogen. The nitrogen flow is introduced into the rinsing tanks through a system of double valves. This prevents the nitrogen flow which contains monomers and is thus explosive from coming into contact with the transport air used in the further course of production. The nitrogen flow can be treated in a column and carried in a closed cycle. Otherwise, a least thermal afterburning with heat utilization should be carried out.

Processing

Following underwater granulation the water should be separated from the granulate as fully as possible in a centrifuge to enable a closed water cycle with water treatment (filter).

7.3.6 Assessment

The environmental improvements through the raw material utilization/conversion of >99% should be rated as positive. This reduces the input of initial products such as ethylene and is thus favourable from a resource-sparing and energy point of view.

A further advantage is the minimization of waste water amounts. The fluidized bed concept does away with any process water input, which leads to a treatment of waste water. The loads on water emissions are thus negligible.

If no coolant is input into the reactor this does not have to be removed later during polymer drying. This leads to not only material savings, no coolant used, but also energy advantages since no thermal process energy is used.

A closed water cycle for granulation can be seen as advantageous since the resource water is saved.

The possibility of doing away with a solvent has a number of advantages provided the specific process energy inputs do not rise significantly. No organic input material has to be provided, with corresponding consumptions of raw materials and energy, and there are no almost unavoidable diffuse emissions. Another positive aspect is that no work is needed to separate the solvent.

8 Process for the synthesis of polypropylene

The further development of the catalysts used polypropylene synthesis had far-reaching consequences. Due to the development of new processes based on the possibilities offered by the new catalysts and the changing range of properties of polymers, the development of catalysts for polypropylene synthesis will be briefly described in a few keywords:

1st generation catalysts:

Titanium catalysts; active centres an points of missing chlorine atoms in $TiCl_3$-crystals.

2nd generation catalysts:

Solvay catalysts; further development of 1st generation; at low temperatures below 100°C the active violet γ or δ form of the brown β-$TiCl_3$ are formed; smaller size of primary crystallite, the surface area and activity of the catalyst is increased.

The first and second generation catalysts (unsupported catalysts) were used in suspension processes with hexane as a solvent, in mass polymerization processes (Rexene, Phillips), in the BASF gas phase process (vertical agitation) and in the solution process (Eastman).

First catalysts on carrier material:

$TiCl_3$ still the catalyst; initially (Solvay) MgO and $Mg(OH)_2$ as carrier for the titanium components, then ground (active) $MgCl_2$, special random crystal structure; further improvement through Lewis bases (electron donors), isotacticity increased with no significant reduction in activity; problem: Ti has to be removed from the polymer (in practice around 1.7–2.5% Ti in the catalyst, compromise between activity and specificity)

3rd generation catalysts:

FT-1, ground catalyst components on carrier material (production: grind $MgCl_2$ with internal donor, titanise at high temperature with $TiCl_4$, wash with boiling heptane, dry, polymerize with $AlEt_3$), great increase in activity for 3rrd generation catalysts through separate titanisation, advantage: no removal of catalyst residues needed, disadvantage: atactic polymer still has to be removed; thus, production processes with 3rd generation catalysts hardly differ from older processes. Only the "simplified slurry" process of Montedison and Mitsui does away with a cleaning of the polymer from the catalyst and atactic PP.

4th generation catalysts:

Phthalate/hydrosilicon donors and spherical carrier which use fluid monomer in a homopolymer reactor. This generation of catalysts made a cleaning of the polymer from catalyst and atactic shares superfluous. A wealth of processes and process variants were developed. The processes described in this report were introduced in this development phase.

5th generation catalysts:

Metallocenes, very specific characteristics, co-catalysts (e. g. methylaluminiumoxane MAO) generally used for polymerization; possible combination with Ziegler-Natta catalysts, thus numerous new possibilities (possibly 6th generation). The processes developed for the 4th generation catalysts can also be employed for the later Metallocen catalysts. The advantages of the new catalysts are thus aimed more at improving the product quality and thus indirectly at the environmental performance of the process through higher yields and more flexible process variants with existing plants. 4th generation catalysts are probably the main ones being used at present.

8.1 Suspension process

8.1.1 Process description

A general suspension process is shown in the flow chart in Figure 8.1.

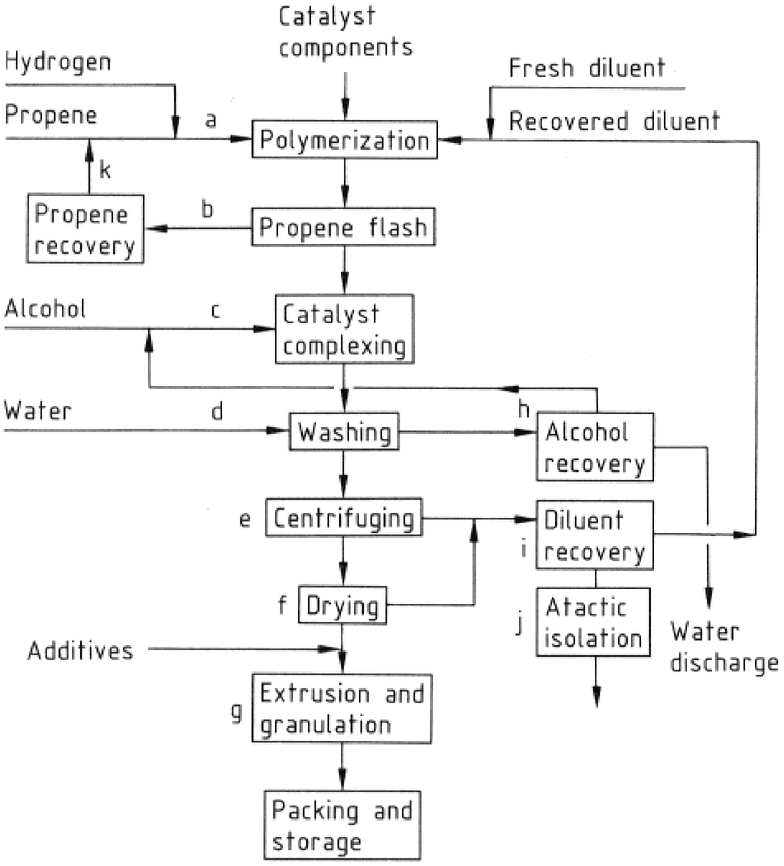


Figure 8.1: General flow chart for a suspension process to produce iPP /2/

The individual processes various manufacturers differ with respect to the process conditions employed and equipment. The flow chart shown here is, however, outdated inasmuch as modern processes no longer use solvents for suspension.

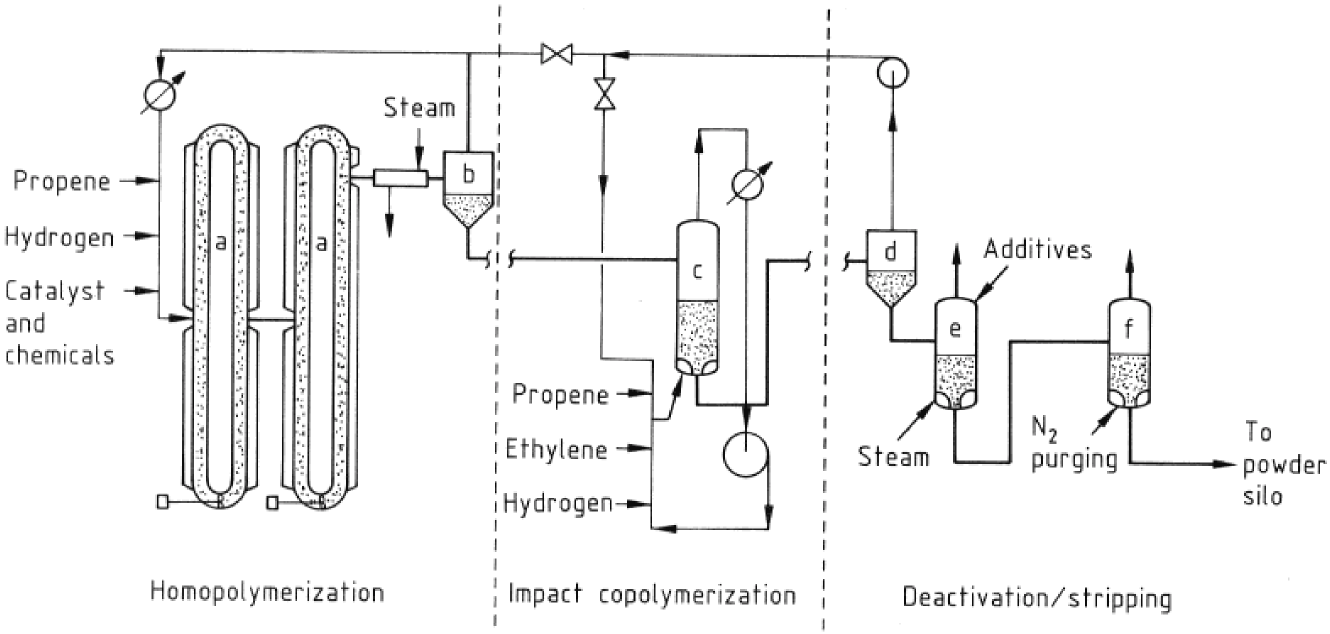
Liquid propylene with its worse solution properties is used in place of a solvent. Examples of modern processes without solvents are:

- Spheripol process
- Hypol process

Both processes will be described in more detail in the following.

Spheripol process with loop reactor and Himont catalyst

Figure 8.2 shows the process flow chart for a plant according to the Himont technology. It can be used to produce homopolymers and impact resistant copolymers depending on the catalyst. The catalysts are so active that they need not be removed from the polymer. The high stereospecifity of the catalyst means that hardly any atactic PP is produced and thus does not have to be removed from the polymer.



a) Loop reactors ; b) Primary cyclone ; c) Copolymer fluidized bed ; d) Secondary and copolymer cyclone ; e) Deactivation ; f) Purging

Figure 8.2: Process flow chart a suspension process to produce iPP according to the Spheripol process /2/

Polymerization takes place at temperatures around 70 °C and a pressure of around 4 MPa in liquid propylene which circulates in one or more loop reactors. A single axial agitator in each loop ensures high volume flow rates and thus a good exchange of heat to the water-cooled reactor walls. This also prevents particles from precipitating out of the suspension. The normal PP concentration is approx. 40 % by weight. The catalyst, co-catalyst and a stereoregulator on the basis of a Lewis base are continuously fed into the reactor. The first seconds of polymerization with the fresh, highly-active catalyst are decisive for the course of the reaction. This is why some plants have a pre-polymerization stage in which the catalyst components react at a lower temperature and monomer concentration. This can take place in a autoclave or loop reactor. The pre-polymerized material is then input into the loop reactor as normal. The mean dwell time for a single reactor is 1-2h. 2 loop reactors can be operated in series to even out the dwell time, modify the polymer and increase production.

A continuous flow of suspension flows through the heated zone into the cyclone (b). This cyclone is directly connected to the cyclone (d) during homopolymer production, the copolymerization stage is hereby bypassed. Any propylene which does not react evaporates in the first cyclone, is condensed with cooling water and returned to the reactor. A compressor is required for the second cyclone. The polymer is then conveyed into the tanks (e) and the catalyst deactivated with a small amount of steam. Residual moisture and volatile substances are removed to tank (f) with a flow of hot nitrogen before the polymer is conveyed to the storage tank and stabilised or extruded as granulate by normal methods.

Hypol process with a CSTR reactor and Mitsui catalyst

The firm of Mitsui developed an analogue suspension process using their own catalyst. The process differs from the Spheripol process inasmuch as a pre-polymerization takes place in an autoclave in connection with a washing. Two autoclave reactors are used in series, the heat is dissipated to the reactors by evaporating liquid propylene. The suspension is then forwarded to a heated and agitated evaporation reactor in which polypropylene is removed from the polymer and returned to the production process, similar to the Spheripol process. The two processes thus only differ with respect to the reactors and catalysts used, allowing a common consideration of the data for consumption and emission values.

8.1.2 Process flow chart

These flow charts show the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

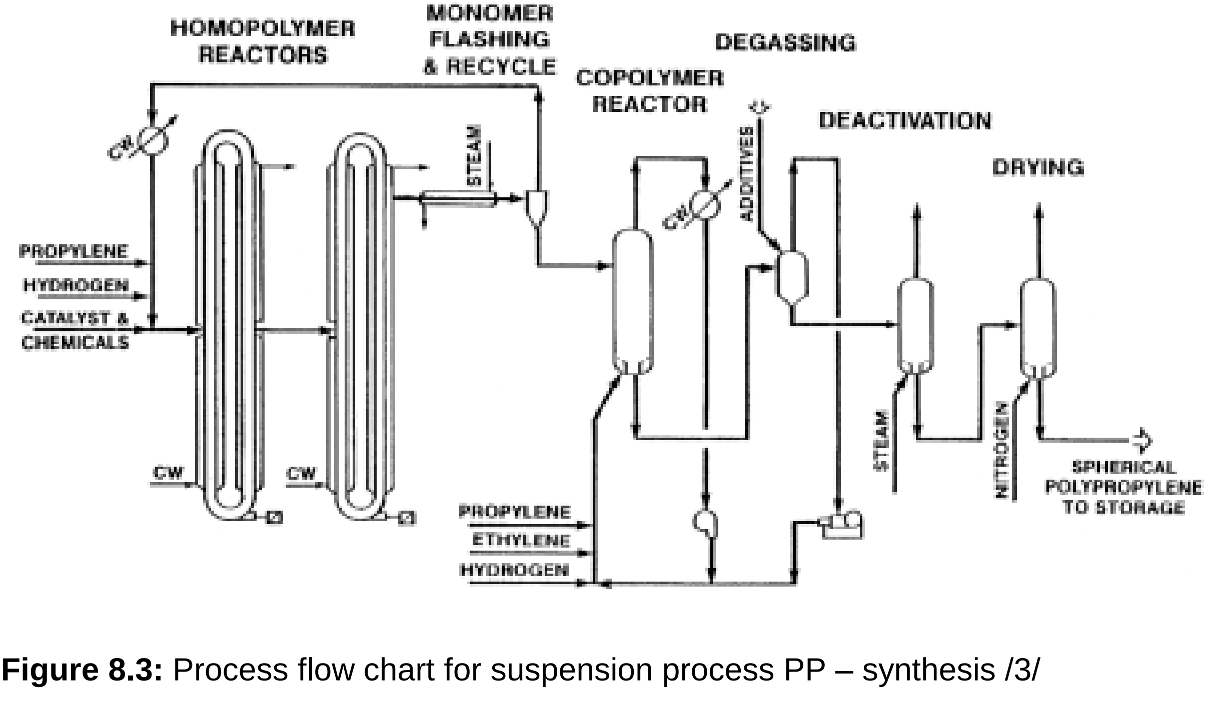


Figure 8.3: Process flow chart for suspension process PP – synthesis /3/

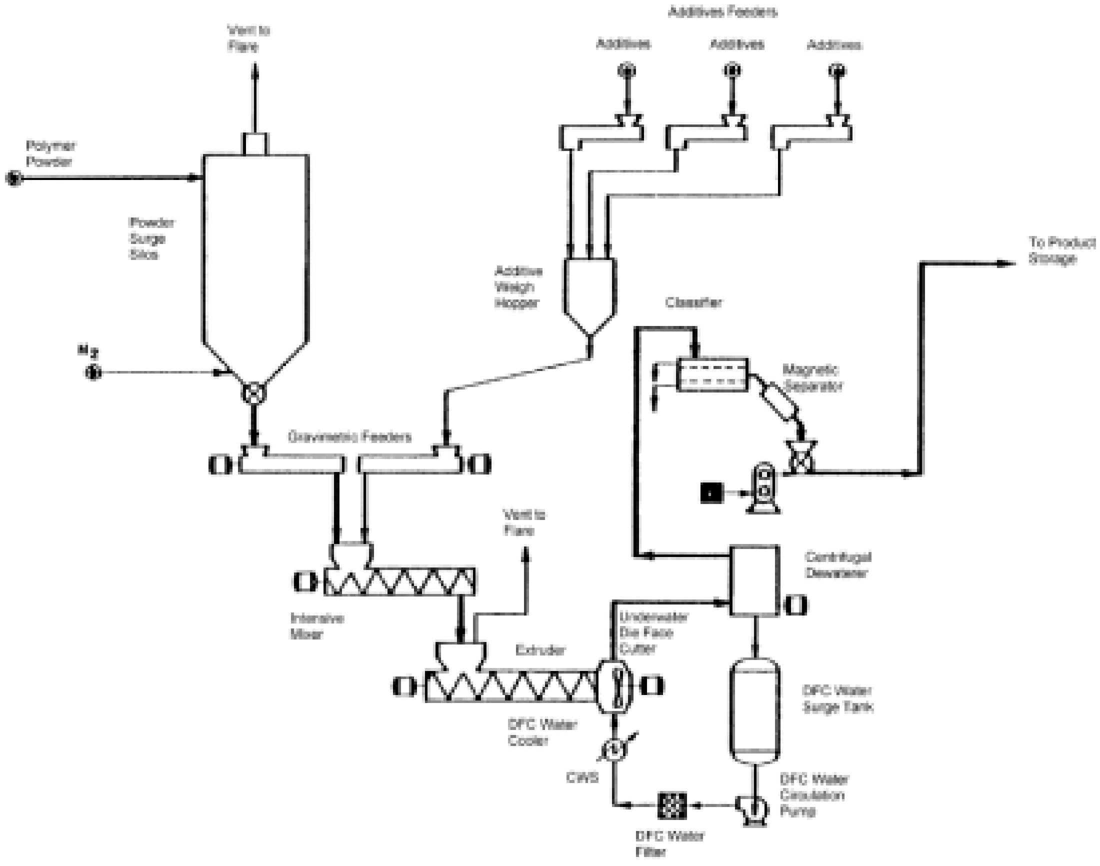


Figure 8.4: Process flow chart for a suspension process PP – granulation /3/

8.1.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

The values are representative for the following processes:

- Spheripol process with loop reactor, catalyst according to Himont, without solvent
- Hypol process with CSTR, catalyst according to Mitsui/Montedison, without solvent

Main product	Quantity	Unit	Remark
PP isotactic	1	kg	
Energy carrier			
Electricity	0.15 - 0.6	kWh	/3/, /12/, 1)
Steam (total,no pressure data)	0.15 - 0.5	kg	/3/, /12/, 1)
Heating gas	0.1 - 0.2	Nm3	1)
Materials			
Propylene	01.01.04	kg	/3/, /12/, 1)
Inert gas (nitrogen)	0.05 - 0.07	Nm3	1)
Cooling water	70 - 120	kg	/3/, /12/, 1)
Process water	2.5 - 3.5	kg	1)
Compressed-air	0.003 - 0.3	Nm3	1)
Hydrogen	3E-5 - 5E-3	kg	/3/, 1)
Catalyst	1.4E-5 - 1E-3	kg	/6/, 1)
Emissions to air			
Particles	1.5E-5 - 4E-5	kg	1)
NMVOC	1E-3 - 1.5E-3	kg	1)
CO	2E-6 - 1.5E-4	kg	1)
CO2	0.1 - 0.3	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	1.5E-4 - 2E-4	kg	1)
Biological oxygen demand (BOD)	2E-5 - 4E-5	kg	1)
Solids (suspended)	< 1.4E-5	kg	1)
Nitrate	1.8E-5 - 2.1E-4	kg	1)
Waste water	03.05.05	kg	1)
Hydrocarbons	1E-5 - 1.6E-5	kg	1)
Wastes			
Near-domestic industrial wastes	1.5E-3 - 1E-5	kg	1)
Hazardous waste	5.5 - 7.5E-4	kg	1)

1) Figures based on IKP estimates

The drying unit can be operated optionally with electricity or heating gas. The parameters power consumption and heating gas input thus affect each other directly.

The amount of cooling water depends largely on the amount of recirculated cooling water. However, it can be assumed that the majority of cooling water is recirculated in the system and thus the lower value range is more probable.

The compressed air is used primarily to convey the product.

A very fluctuating factor, depending on the special type, is the amount of catalyst used. 1st and 2nd generation catalysts have efficiencies of 1000$g_{Polmyer}$ /$kg_{Catalyst}$ to 70000 $g_{Polmyer}$ /$kg_{Catalyst}$/6/. The current use in plants according to the Himont/Sheriphol process are estimated at around 1E-4 - 5E-4 $kg_{Catalyst}$/$kg_{Polymer}$.

The life cycle emissions of NMVOC for PP are approx. 0.010 kg. The initial product propene accounts for approx. 78% and power generation approx. 12% as main contributors. The emissions released during polymerization are thus estimated at approx. 1E-3 to 1.5E-3 kg/kg.

The CO emissions from the optional gas firing for the drying unit can fluctuate depending on the burner control around a mean value of 6.6E-5 kg.

The CO_2 emissions from the optional gas firing for the drying unit are 0.26 kg for the combustion of 0.15 Nm^3 gas.

The life cycle emissions of COD for PP are approx. 1E-3 kg. The production of the initial products propene and nitrogen as well as the energy supply account for over 78%. The polymerization shares are estimated at approx.15%.
As for the values of hydrocarbons in water, APME /5/ quotes approx. 0.0001 kg/kg polymer for the life cycle. This corresponds with IKP estimates for German conditions. Initial product production and energy supply account for more than 90%. Polymerization thus lies between 1E-5 and 1.5E-5 kg.

8.1.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2,3/.

8.1.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

8.1.4.2 Technical parameters

Polymerization pressure	20-50 bar
Polymerization temperature	60°-80°C
Catalyst efficiency	no data
Polymerization time	2 h (Spheripol)
Conversion rate	no data

8.1.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	80,000 t
Investment costs	approx. 55 million euro
Raw materials costs	approx. 330 euro / t_{PP}
Initiator / Initiator costs	approx. 45 euro / t_{PP}
Energy costs	approx. 25 euro / t_{PP}
Personnel costs	approx. 15 euro / t_{PP}
Maintenance costs	approx. 20 euro / t_{PP}

The personnel costs have been calculated on the basis of 25 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

8.1.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Reaction preparation

The following are possible input materials:

- Propylene from the refinery with up to 20% propane (though normally far below this value). However, this input material necessitates a cleaning column to remove the propane from the residual monomer return line so as to prevent an enrichment of propane. This naturally entails environmentally-relevant energy inputs. If the propane is used for material or energy applications the extra input due to its removal can be classified as hardly or not environmentally relevant since a primary fuel is substituted.
- Propylene from the raw material recycling of PP. Propane no longer has to be cleaned in this case. Its industrial relevance is, however, slight. An assessment of the environmental advantages of such an alternative require a consideration of the entire life cycle since questions relating to the recycling and waste disposal or polypropylene have to be taken into account.

Reaction

Double design of the loop reactor to achieve a close particle size distribution. This facilitates further processing and removal of the residual monomer from the polymer.

The high-pressure pump to circulate the reaction mixture in the loop reactor must be adequately sealed to prevent emissions. To prevent a fouling of he reaction mixture on the reactor walls, the pump must be able to produce a high peripheral speed in the reactor.

A stereospecific catalyst must be used wherever possible to achieve a high yield of i-PP.

Polymer separation and monomer recycling

Residual monomers are recycled from the polymer in 3 stages:

- with a flasher
- with a high-pressure degasser, residual monomer contents of 0.03 $kg/kg_{Polymer}$ are possible after this stage
- a low-pressure flasher, residual monomer contents of 1000 – 2000 ppm are possible after this stage

Processing

The polymer is treated with steam in the fluidized bed reactor to deactivate the catalyst. This steam should be used for energy purposes. However, remember that the steam may be polluted with residual monomers and should be treated before being discharged into the environment (e.g. condensation of the steam and forwarding to waste water cleaning).

The waste air from the silos and extruder may also contain residual monomers. However, no relevant concentrations of gaseous residues normally occur. Recovery of these materials is thus sensible from both an environmental and energy point of view.

8.1.6 Assessment

The prevention of fouling (caking) through sufficiently high volume flow rates is should be assessed as positive in terms of the environment for two reasons. The use of coolant is reduced since the heat transmission would deteriorate though the fouling. Secondly, any openings in the system for cleaning purposes or the input of cleaning chemicals are minimised and thus emissions and the input of materials and energy (e.g. inert gas rinsing, steam rinsing) to avoid such emissions are reduced.

The double design of the loop reactors can be indirectly assessed as an environmental improvement since exact control over the range of products reduces faulty batches and thus the input raw materials can be better used with respect to the output quantity of product.

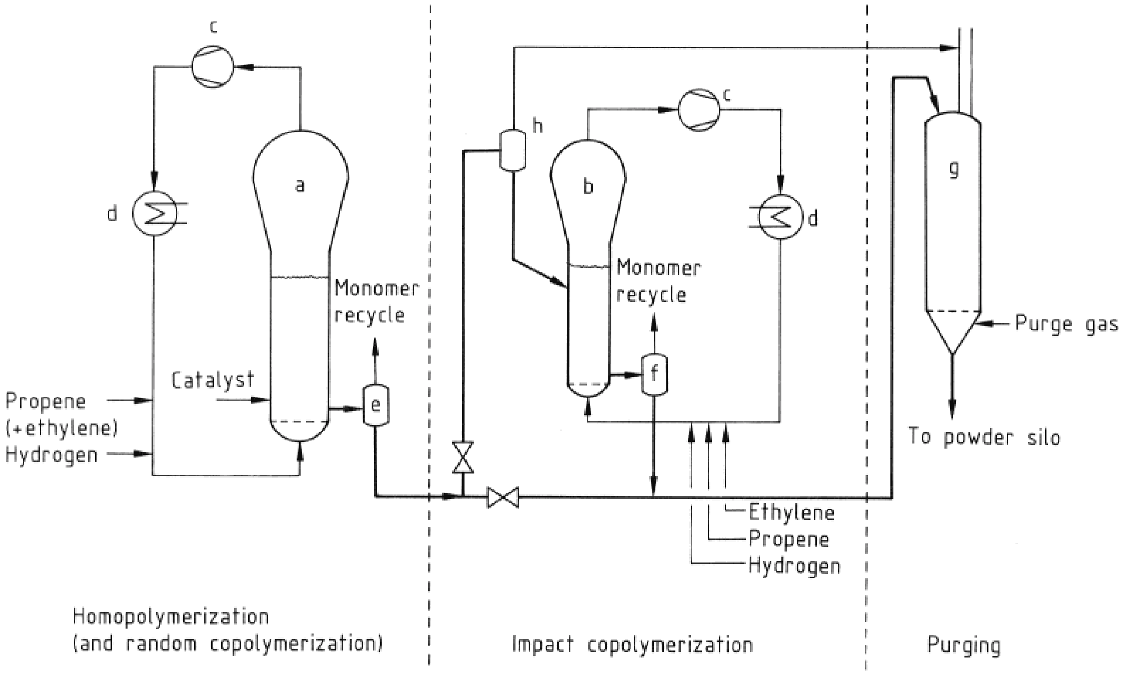
The use of stereospecific catalysts reduces not only the amount of catalyst required due to the higher activity but also leads to higher yields of the desired product quality with a concomitant optimised resource efficiency.

8.2 Gas phase process in a fluidized bed reactor

In gas phase processes, gaseous propylene is combined with a solid catalyst, whereby the catalyst is dispersed in dry polymer dust. Two different methods are common in industry, depending on the heat dissipation method selected. BASF and Amoco use autoclaves, with an alternating vertical and horizontal agitating motion, in connection with evaporation cooling. The Amoco process is irrelevant for Germany. Union Carbide / Shell use a fluidized bed reactor.

8.2.1 Process description

The striking feature of this process (see also Figure 8.5) is the fluidized bed reactor which widens at its top to reduce the gas velocity and entrainment of particles. Continuously fed flows of catalyst, monomer and hydrogen are mixed thoroughly in the fluidized bed. A large cooler in the loop for gas recovery draws off the complete heat of reaction from the considerable gas volume flows. In this system the fluidized bed reactor acts like a back-mixing autoclave reactor, there is no excessive separation of coarse particles. The reaction conditions are below 88°C and 4 MPa. The polymer and associated gas are bled from the reactor directly above the distributor plate with time-controlled valves passed through a cyclone (e) into a tank filled with nitrogen (g) to remove residual monomers from the polymer. With modern catalysts neither the catalysts nor atactic polymers have to be extracted.



a) Primary fluidized bed ; b) Copolymer fluidized bed ; c) Compressors ; d) Coolers ; e), f) Discharge cyclones ; g) Purge

Figure 8.5: Process flow chart for a gas phase process to produce iPP in a fluidized bed according to the Unipol process /2/

8.2.2 Process flow chart

See gas phase process for PE Chapter 7.3.2

8.2.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
PP isotactic	1	kg	
Propylene, impure	0.02 -0.04	kg	1)
Energy carriers			
Electricity	0.4 - 0.6	kWh	1)
Steam (total, no pressure data)	0.25 - 0.35	kg	1)
Materials			
Propylene	1.02 - 1.05	kg	1)
Inert gas (nitrogen)	0.04 - 0.05	Nm3	1)
Cooling water	40 - 60	kg	1)
Compressed-air	k.A.	Nm3	
Hydrogen	1E-4 - 2E-4	kg	1)
Catalyst	2.5E-5 - 3E-4	kg	/6/, /30/
Emissions to air			
Particles	3E-5 - 5E-5	kg	1)
NMVOC	3E-4 - 5E-4	kg	1)
Emissions to water			
Chemical oxyvgen demand (COD)	negligible	kg	1)
Biological oxygen demand (BOD)	negligible	kg	1)
Solids (suspended)	negligible	kg	1)
Nitrate	negligible	kg	1)
Wastes			
Near-domestic industrial waste	1.5E-3 - 1E-5	kg	1)
Hazardous waste	negligible	kg	1)

1) Figures based on IKP estimates

Impure propylene drawn from the head of the reactor is partly directly recycled or separated into fuel and purified propylene in a propylene cleaning stage with sump separation. This leads to a propylene conversion of approx. 99%).

The electricity demand for the gas phase process is due largely to the compressors used.

The nitrogen demand is relatively low since the gas phase process requires little drying work.

Since the process is controlled as a gas phase reaction in the fluidized bed, little cooling water is required.

The hydrogen input to control the molecular weight is estimated as being comparable to the Novolen process (see Chapter 8.3) /3/.

3rd generation catalysts have efficiencies of 4500 g_{PP}/g_{Kat}. 4th generation have 1200-1500 kg_{PP}/g_{Ti} with a 3% Ti share. This leads to a mean catalyst amount per kg PP of approx. 0.000025 kg

.

The particle distribution in the gas phase process is estimated as being finer, leading to higher particle emissions for the gas phase process than the slurry processes (estimated 25-50% higher).

The relatively low NMVOC emissions are due to a simple process control, high conversion/recovery rates for propylene and the possibility of dispensing with a solvent.

Emissions to water are negligible due to the gas phase reaction.

8.2.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

8.2.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

8.2.4.2 Technical parameters

Polymerization pressure	20-40 bar
Polymerization temperature	70°-90°C
Catalyst efficiency	no data
Polymerization time	no data
Conversion rate	97%

8.2.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	75,000 t
Investment costs	approx. 45 million euro
Raw materials costs	approx. 395 euro / t_{PP}
Initiator / Initiator costs	approx. 45 euro / t_{PP}
Energy costs	approx. 35 euro / t_{PP}
Personnel costs	approx. 30 euro / t_{PP}
Maintenance costs	approx. 5 euro / t_{PP}

The personnel costs have been calculated on the basis of 25 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

8.2.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

The Unipol process to produce PP can be regarded as being comparable to the PE-HD gas phase process except for the type of input monomer material (propylene instead of ethylene) and a special catalyst variant. The Unipol process can be used for both polymers, though this does not mean that comparable variants do not exist from other manufacturers of PE-HD which may be used in an in principle similar, though in certain partial areas different, process. The BAT options thus correspond to those mentioned in Chapter 7.3.5.

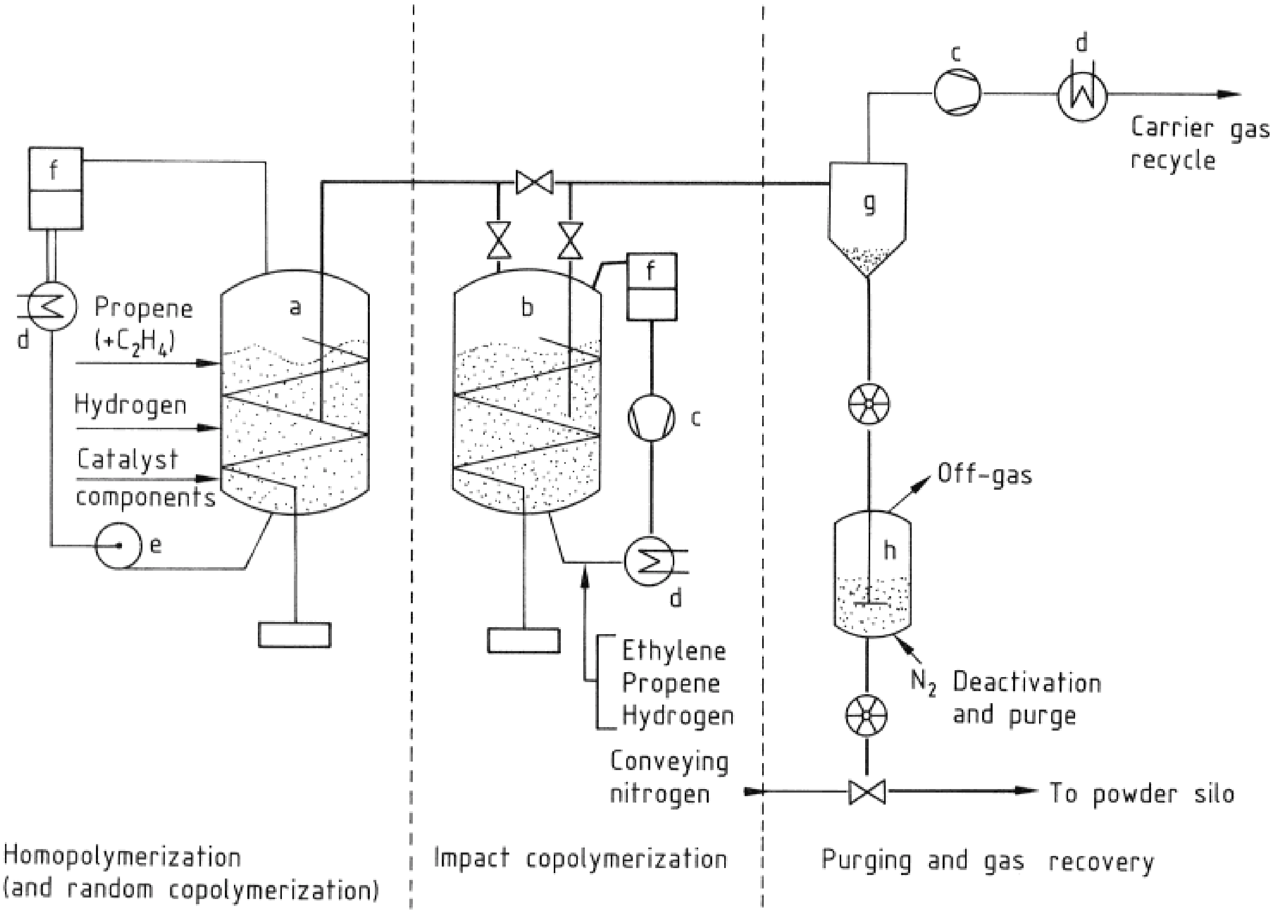
8.2.6 Assessment

On account of the aspects listed in Chapter 8.2.5 please refer to Chapter 7.3.6.

8.3 Gas phase process in a vertical reactor

8.3.1 Process description

Figure 8.6 shows the BASF process to produce homopolymer, impact resistant copolymer and PE-PP copolymer using highly-active and highly-stereospecific catalyst. The reactors with a capacity of 25-75m^3 are fitted with spiral agitators which ensure a good mixing. The homopolymerization only requires the first reactor in which the catalyst components are also dosed. These must be very well mixed with the polymer. The reaction conditions of 70-80°C and 3-4MPa ensure that the monomer is in a gaseous state in the reactor. Low hydrogen concentrations are used to be able to control the molecular weight over a wide range. The temperature is controlled by withdrawing gaseous propylene from the head of the reactor. The evaporation ensures the cooling, propylene is condensed and then returned to the reactor whereby the reactor content is mixed further by this input. 6 t of propylene are evaporated during cooling for every ton of PP produced.



a) Primary reactor ; b) Copolymerizer ; c) Compressors ; d) Condensers ; e) Liquid pump ; f) Filters ; g) Primary cyclone ; h) Deactivation/purge

Figure 8.6: Process flow chart for a gas phase process to produce iPP according to the BASF process /2/

Polymer and gas are constantly fed to the reactor in the low-pressure cyclone (g). The propylene is returned to the reactor from the cyclone after compression, liquefaction and possibly distillation. The polymer then passes through a rinsing tank in which a deactivator renders traces of the catalyst harmless and a flow of hot nitrogen removes propylene residues from the polymer. This is followed by stabilisation and extrusion to a granulate.

8.3.2 Process flow chart

These flow charts show the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

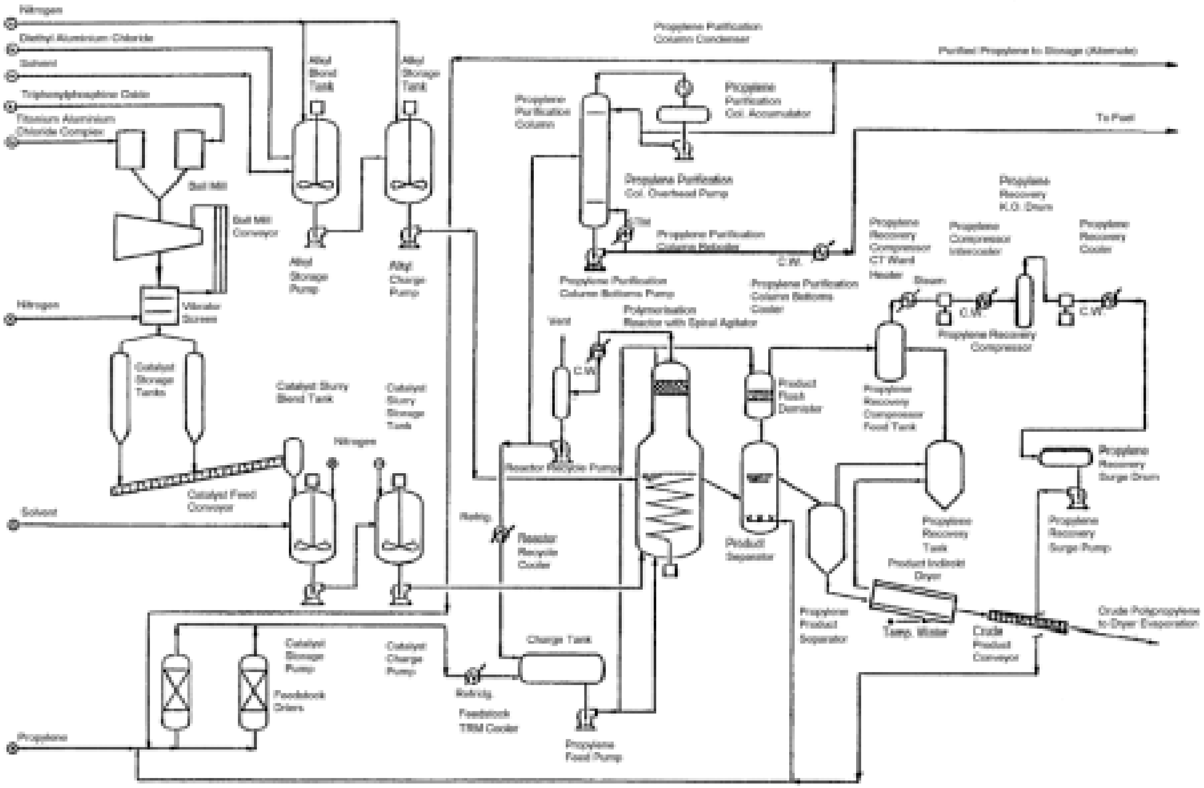


Figure 8.7: Gas phase process according to BASF – synthesis /3/

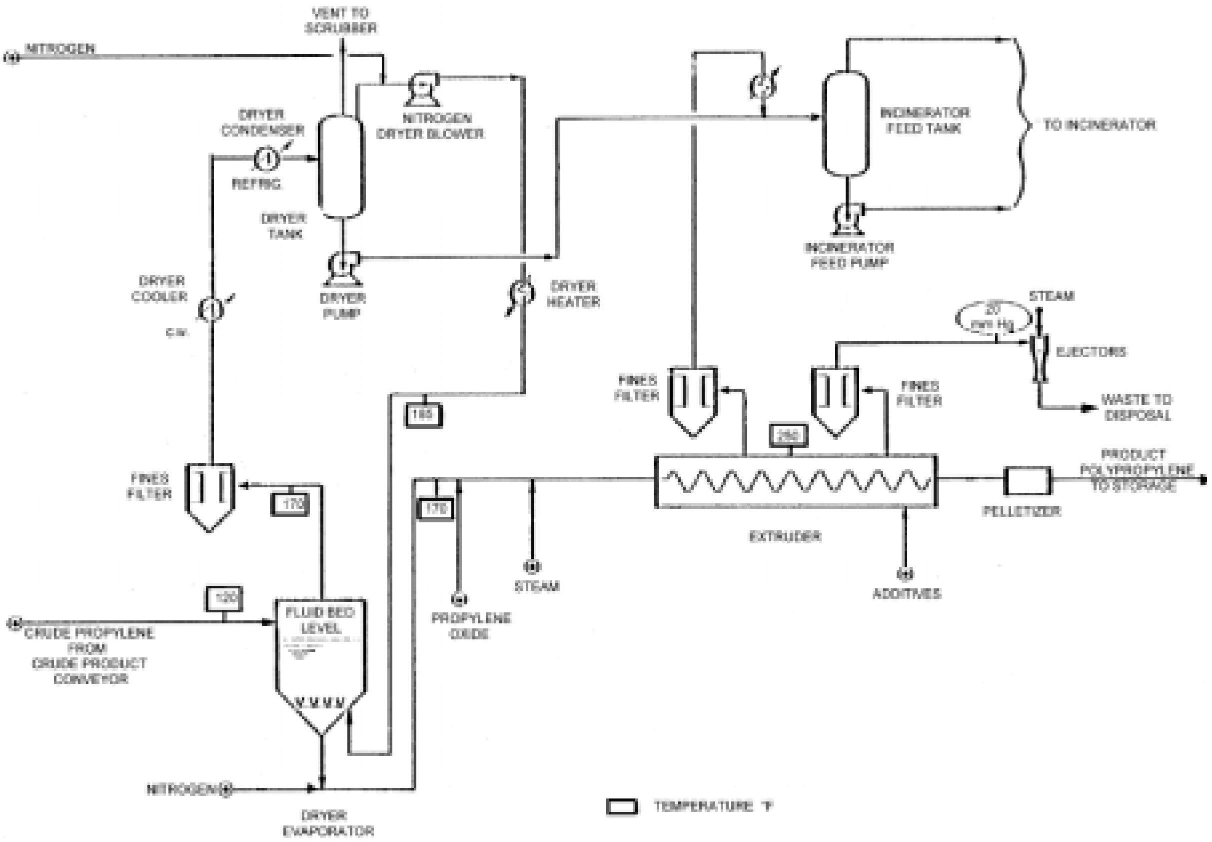


Figure 8.8: Gas phase process according to BASF – granulation /3/

8.3.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
PP isotactic	1	kg	
Propene, impure	0.02 -0.04	kg	1)
Energy carriers			
Electricity	0.35 - 0.5	kWh	/3/, 1)
Steam (total, no pressure data)	0.25 - 0.35	kg	1)
Materials			
Propene, impure	1.015 - 1.055	kg	/3/, 1)
Inert gas (nitrogen)	0.04 - 0.045	Nm3	/3/, 1)
Cooling water	40 - 85	kg	/3/, 1)
Process water	0.2 - 2	kg	1)
Compressed-air	k.A.	Nm3	1)
Wasserstoff	1E-4 - 2E-4	kg	/3/, 1)
Catalyst	2.5E-5 - 3E-4	kg	/6/, /30/
Emissions to air			
Particles	3E-5 - 5E-5	kg	1)
NMVOC	5E-4 - 8E-4	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	negligible	kg	1)
Biological oxygen demand (BOD)	negligible	kg	1)
Solids (suspended)	negligible	kg	1)
Nitrate	negligible	kg	1)
Wastes			
Near-domestic industrial waste	1.5E-3 - 1E-5	kg	1)
Hazardous waste	negligible	kg	1)

1) Figures based on IKP estimates

Impure propylene drawn from the head of the reactor is partly directly recycled or separated into fuel and purified propylene in a propylene cleaning stage with sump separation. This leads to a propylene conversion of approx. 99%).

The electricity demand for the gas phase process is due largely to the compressors used.

The nitrogen demand is relatively low since the gas phase process requires little drying work.

Since the process is controlled as a gas phase reaction in the fluidized bed, little cooling water is required.

The hydrogen input controls the molecular weight in the process /3/.

4th generation catalysts have efficiencies of 1200-1500 kg_{PP}/g_{Ti} at a 3% Ti-share. This leads to a mean catalyst amount per kg PP of approx. 0.000025 kg.

The particle distribution in the gas phase process is estimated as being finer, leading to higher particle emissions for the gas phase process than the slurry processes (estimated 25-50% higher).

The relatively low NMVOC emissions are due to a simple process control and high conversion/recovery rates for the monomer. The use of solvents in catalyst and cocatalyst conditioning leads to potentially slightly higher NMVOC emissions. Emissions to water are negligible due to the gas phase reaction.

8.3.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

8.3.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

8.3.4.2 Technical parameters

Polymerization pressure	25 bar
Polymerization temperature	70°C
Catalyst efficiency	no data
Polymerization time	no data
Conversion rate	97% isotactic

8.3.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	90,000 t
Investment costs	approx. 35 million euro
Raw materials costs	approx. 340 euro / t_{PP}
Initiator / Initiator costs	approx. 5 euro / t_{PP}
Energy costs	approx. 20 euro / t_{PP}
Personnel costs	approx. 15 euro / t_{PP}
Maintenance costs	approx. 12 euro / t_{PP}

The personnel costs have been calculated on the basis of 25 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

8.3.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

The gas phase process produces up to 5% a-PP or s-PP which have to be extracted from the product. This can be avoided with a stereospecific catalyst. The suspension process has advantages here since a higher share of i-PP is produced.

Reaction preparation

Processing the catalyst involves a number of stages in the gas phase process. The following should be take into account:

- Tanks and pumps should be well sealed to stop the solvent cyclohexane from escaping.
- After grinding the catalyst, any grains which are too large should be screened and returned to the grinder.

Reaction

The water has to be extracted from the monomer to avoid corrosion problems in the reactor.

Hydrogen, which can be used as a regulator for the molecular weight, is recycled with the monomer flow. The molecular weight can also be adjusted by controlling the temperature in the granulating extruder.

The reactor contains a filter to separate polymer from the gas phase (monomer). This filter should be regularly back-flushed with monomer so that the reactor does not have to be opened to clean the filter. This prevents monomer emissions.

Polymer separation and monomer recycling

The 3-stage cleaning of the polymer from residual monomer is carried out by flashing (degassing) the monomer, vacuum and an indirect dryer. A 3-stage cleaning is necessary since approx. 15% of the monomer leaves the reactor with the polymer flow.

Residual monomer should be recycled after the following process stages:

- After the reactor, partly with processing to remove traces of HCl and propane from the recycling flow. The waste product from the cleaning column should be burnt and the energy produced utilised (e.g. as process heat).
- After product separation. A 3-stage separation with dryer can be understood as a BAT option.

The heat from the monomer recycling flow can be used to control the reactor temperature.

A further cleaning of the polymer takes place in a fluidized bed reactor operated with nitrogen. This extracts solvents used for the catalyst from the polymer. The nitrogen can be freed from the solvents and entrained polymer particles with a stripping column and filter and the nitrogen can then be returned to the closed cycle. The separated rest is burnt and the heat produced can be utilised. It would not appear sensible to recycle the separated solvent similar to the suspension process since it is very polluted.

Processing

Nitrogen which is used to convey the polymer powder can be returned to the closed cycle after filtering.

The polymer powder is treated with steam in an extruder to deactivate the catalyst. The steam is removed from the extractor with two degassing stages (one of which in a vacuum). Since the steam now contains it should be cleaned in a column. Residues separated in the column can be burnt and the waste heat utilized.

8.3.6 Assessment

Material recycling of the separated and heavily polluted solvent is assessed as being of little environmental advantage since the energy and material inputs for processing could cancel out or be higher than the advantages of saving fresh solvent.

The use of stereospecific catalysts is on the other hand assessed as being environmentally advantageous since the desired product range selectively set (iPP). This leads to a higher efficiency of the input materials with respect to the desired products, which must be assessed as an advantage for reasons of both resource efficiency and energy savings.

The effective sealing of the pumps, tanks and fittings (see also Chapter **14**) to reduce the escape of cyclohexane is assessed as important and effective.

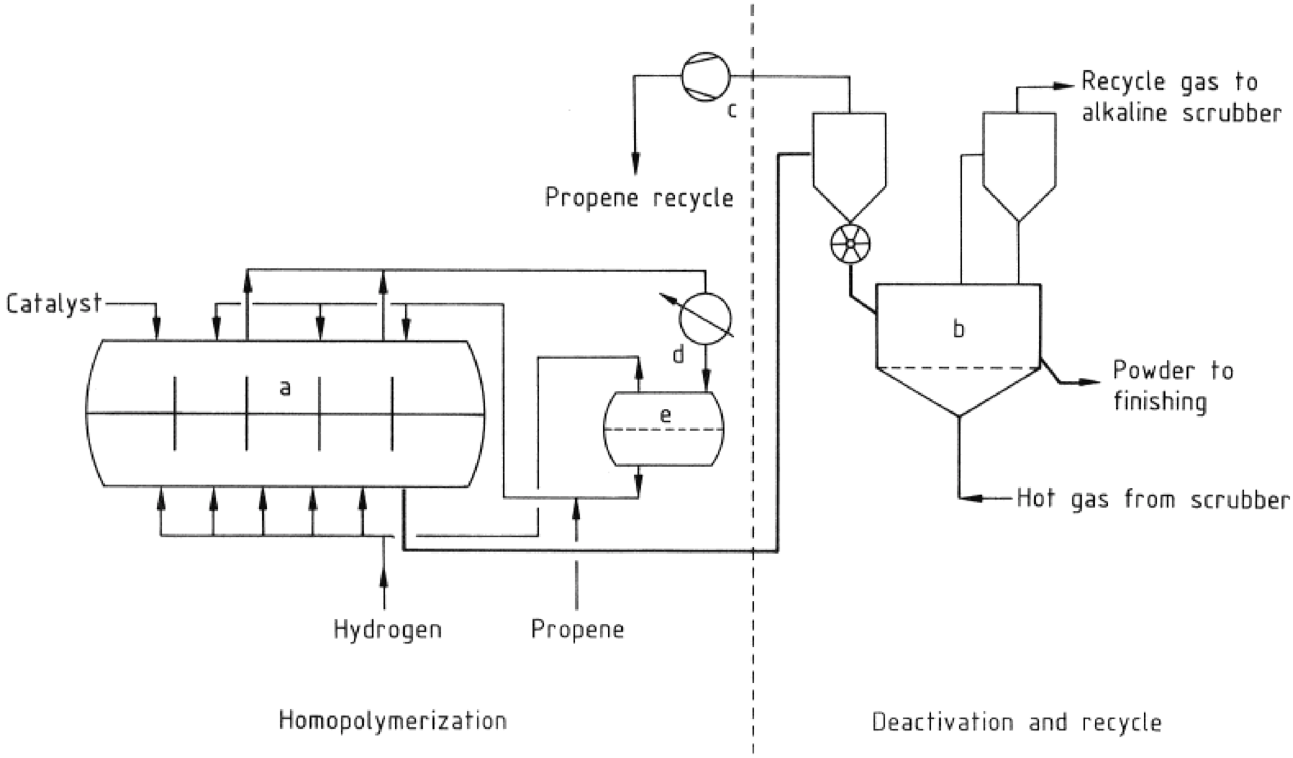
Environmentally positive effects can be expected from the 3-stage cleaning of the polymer from residual monomer since the monomer contents (up to 15% in the polymer flow) lead to improved conversion rates of monomer to polymer with effective separation. This can be estimated as a resource-sparing process, and the reduction of process emissions must also be seen as a positive aspect.

8.4 Gas phase process in a horizontal reactor

This process uses a horizontal instead of a vertical reactor like in the BASF process. Condensed recycled monomer sprayed into the head of the reactor is responsible for cooling. The reaction gas consists of gaseous propylene and hydrogen and is fed into the reactor in the sump. Figure 8.9 also shows a stage in which the catalyst is deactivated in a fluidized bed reactor. This was not necessary when 2nd generation catalysts high in chlorine were used.

The firm of Amoco claims that its reactor has an performance identical to that of 2-3 conventional autoclave reactors connected in series.

The Amoco process is irrelevant for German conditions. This, this process will not be dealt with in detail.



a) Horizontal reactor ; b) Fluidized-bed deactivation ; c) Compressor ; d) Condenser ; e) Hold/separator tank

Figure 8.9: Process flow chart for a gas phase process to produce iPP according to the Amoco process /2/

BP Amoco Chemicals has developed its own catalyst system (supported catalyst system) which is used in all plants. This is an optimised, 4th generation catalyst characterised by a high efficiency and high reactor throughput. The catalyst is supplied through a simple feed system characterised by low investment costs and a simple control /**31**/.

9 Process for the synthesis of polyvinyl chloride

This study concentrates on a description of the most common process: the suspension process. This process is used for over 80% of the quantities of PVC produced in Germany (emulsion PVC approx. 10-15%, PVC from mass polymerization approx. 5%). The processes differ with respect to their air emissions. The specific water amount in the emulsion process is lower, though the DOC contents are higher due to the emulsifiers used. Mass polymerization is a dry process and thus uses no process water.

Suspension PVC can be pre-dehydrated by mechanical drying, approx. 50% of the water to be removed can be mechanically removed. The residual water is removed thermally. With E-PVC, all water is removed thermally, leading to higher energy consumptions.

9.1 Suspension polymerization

9.1.1 Process description

Polyvinyl chloride (PVC) is produced on a commercial basis by radical polymerization. With this technology, vinyl chloride monomer (VCM) is finely dispersed by mixing in water. This takes place in autoclave reactors with jacket cooling or back-flow cooling at capacities between 25 and 200 m^3 (see Figure 9.1). Modern plants have cleaning possibilities in closed systems. This avoids emissions when the reactor is opened.

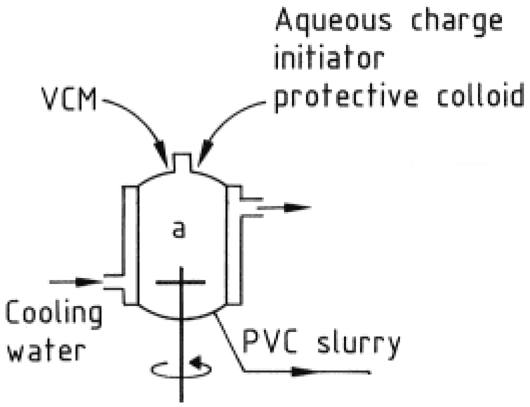


Figure 9.1: Autoclave reactor for PVC suspension polymerization /2/

An initiator which is soluble in the (organic peroxide e.g. diacetyl peroxide, diisopropyl peroxodicarbonate or alkyl peroxoester) is an important constituent and starts the polymerization. The suspension is provided with a stabiliser (protective colloid). These protective colloids affect the grain size and rheology of the PVC produced. The agitating concept also influences the grain size. The basic recipe (relative to 1 kg VCM) which can be used in the polymerization reactor can be quantified as follows:

- 1 kg VCM
- 0.9 – 1.3 kg deionised water

- 0.0005 – 0.0015 kg protective colloid
- 0.0003 – 0.0008 kg initiator /2, 3/

These figures vary depending on the PVC quality, reactor size and type of plant.

Other additives must be added as process materials to achieve the desired PVC quality. These are buffer substances, secondary and tertiary suspending agents and antioxidants. Different metering systems are needed depending on the initiator (solid or fluid activator). Figure 9.4 shows a design for solid activators.

The reactor is charged to approx. 95%, the maximum charge depends on the technology. The reactor is heated up to the reaction temperature during charging (45°-75°C). Depending on the marginal conditions in the plant it may be practical to pre-heat the monomer. The temperature causes the partial decomposition of the initiator into free radicals. The monomer drops begin to polymerize. The strongly exothermic reaction (1540 MJ/kg) is controlled by cooling (jacket cooling and/or condenser). Condensed monomer is returned to the reactor. The course of the parameters pressure (a), reactor temperature (b) and jacket temperature (c) is shown in Figure 9.2.

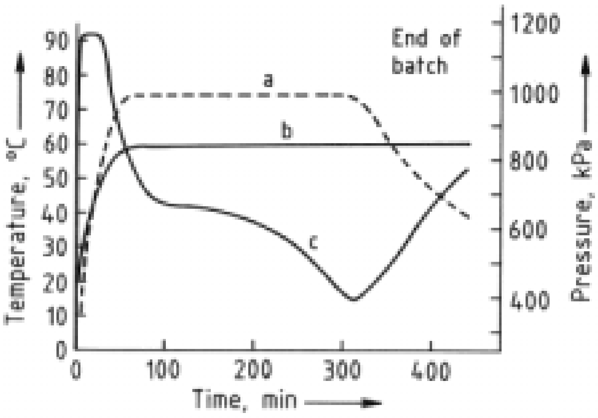


Figure 9.2: Reaction profile for a typical suspension polymerization /2/.

The reaction is stopped at a certain pressure. This is carried out either by introducing a deactivator or by drawing off unreacted monomer for recycling. After the extraction of unreacted components the residual monomer content may still be approx. 2-3%. This is removed by stripping. The reaction mixture is conveyed by a pump to an agitator tank and then to a stripping column (see Figure 9.3).

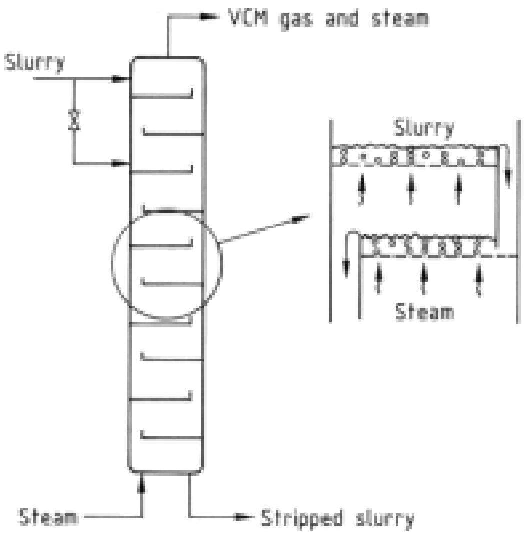


Figure 9.3: Stripping column /2/

The suspension is conveyed to a centrifuge via a heat exchanger and centrifuge tank (20%-30% moisture content after centrifuge). The remaining water is removed in a dryer (e.g. revolving dryer, fluidized bed dryer, cyclone or flash dryer). Fluidized bed dryers and cyclones can be regarded as modern technologies. They produce a dry powder with a residual monomer content of less than 1 ppm.

Unreacted monomer is recovered, liquefied and re-used. Water is extracted from the gaseous head product from the stripper first in a mist collector, then through condensation and separation. The VCM also condenses, is distilled for purification and returned to the polymerization reactor.

The waste gas remaining after the condensation of water and VCM still contains traces of VCM. There are 3 ways to avoid VCM emissions from the waste gas flow:

- Cleaning by absorption columns (shown in Figure 9.6). The VCM released by a regeneration of the columns can be recycled.
- Thermal afterburning
- Transfer to a chlorine producing plant where the chlorine contained in the VCM can be recovered.

9.1.2 Process flow charts

These flow charts show the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

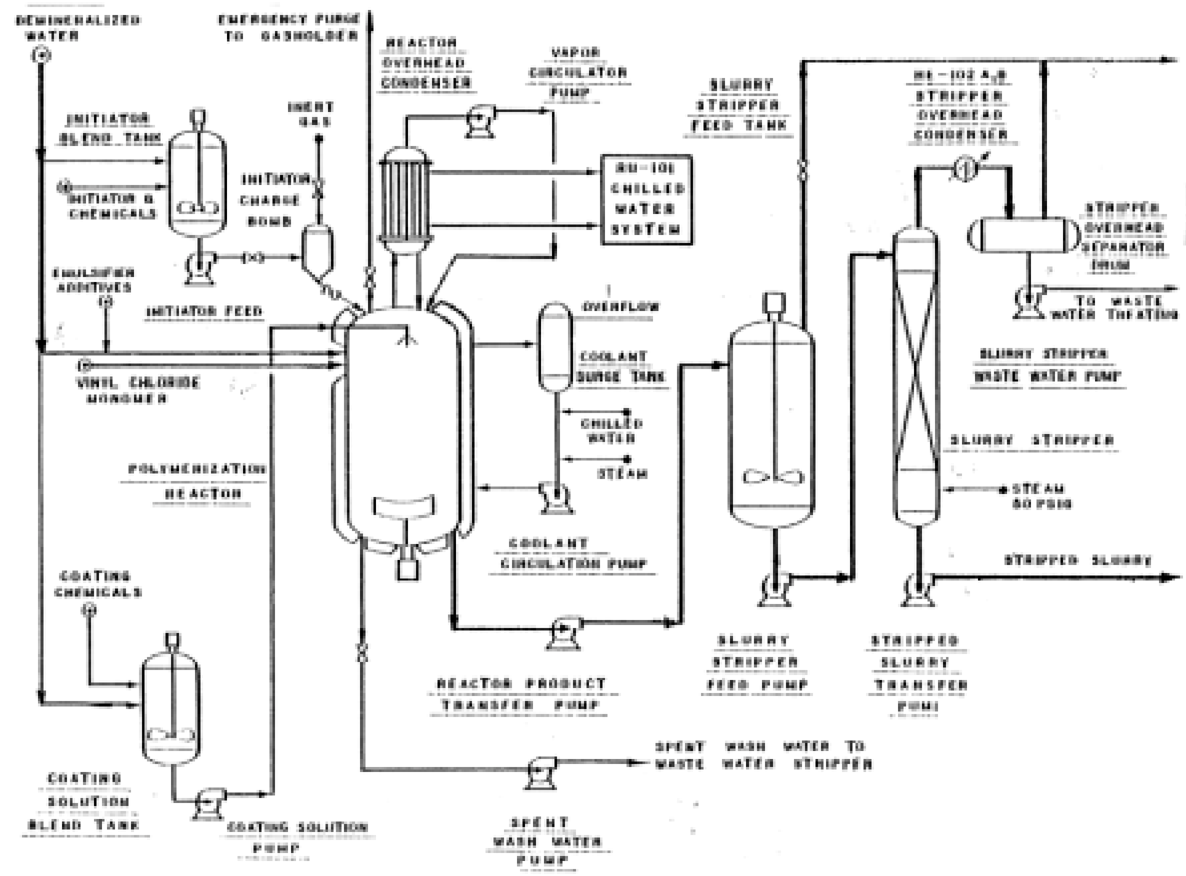


Figure 9.4: Process flow chart for S-PVC reaction and polymer separation /3/

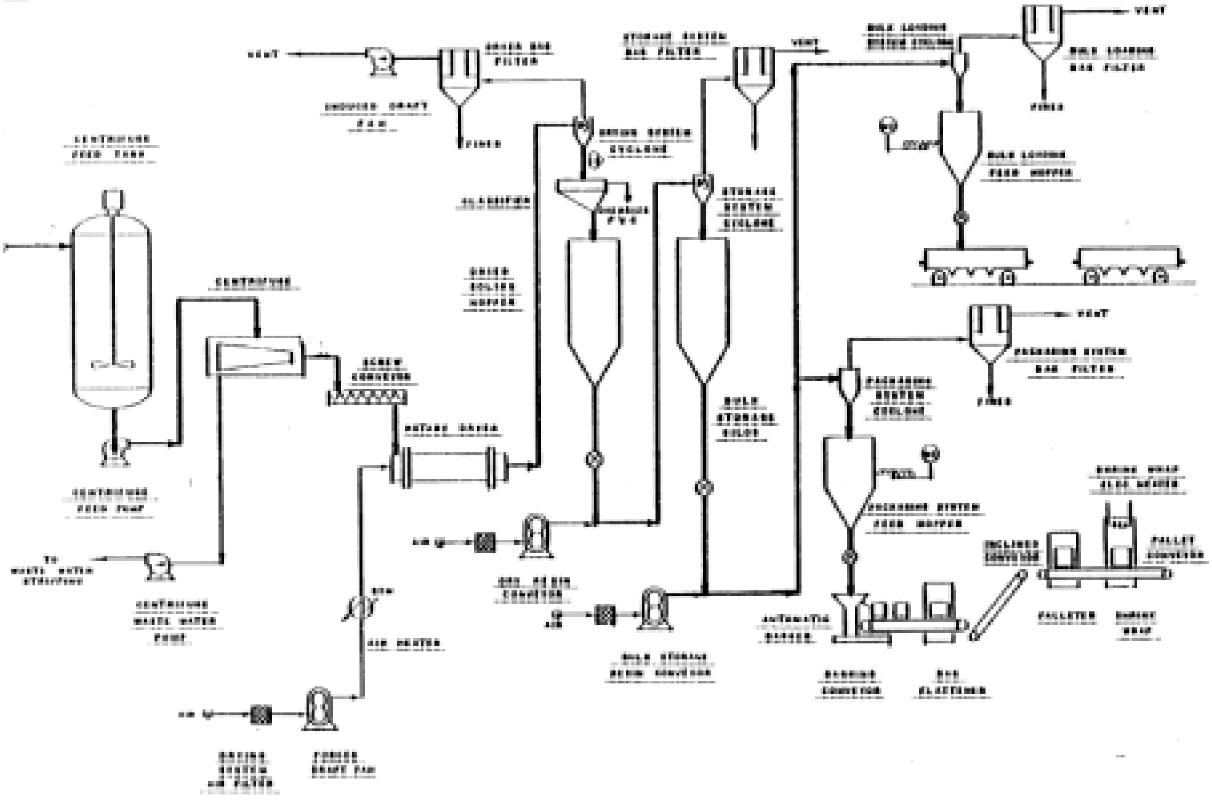


Figure 9.5: Process flow chart for drying and packaging /3/.

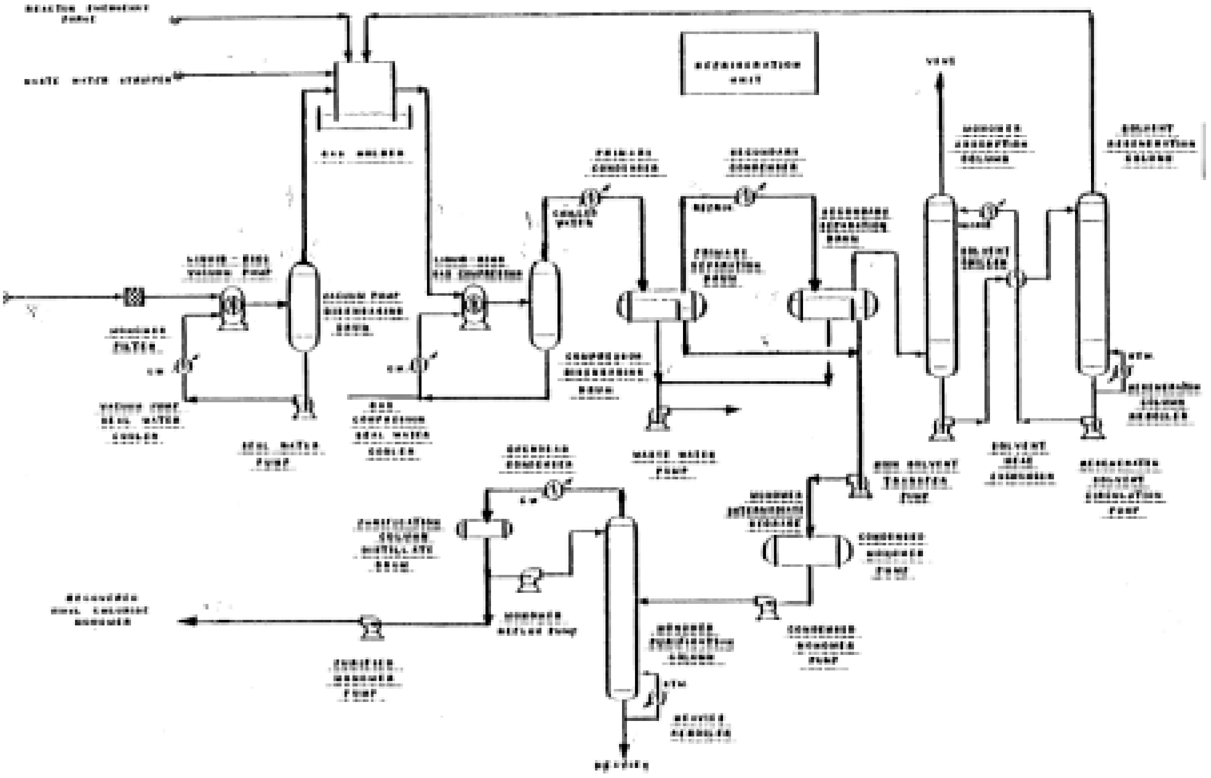


Figure 9.6: Process flow chart for monomer recycling /3/

9.1.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

On account of the above-average substance input in the PVC industry the Input-Output table appears more comprehensive than for other polymers. This cannot be seen as an indicator of the higher environmental relevance of the production of PVC.

Main Product	Quantity	Unit	Remark
S-PVC	1	kg	
Energy carriers			
Electricity	approx. 0.2 a)	kWh	/3/, 1)
Steam (medium pressure)	0.95 - 1.05 b)	kg	/3/, /32/, 1)
(Fuel (preferably natural gas))	(approx. 0.3) a)	MJ	1)
Materials			
Vinyl chloride monomer	1.005 - 1.02	kg	/7/, /3/, /32/, 1)
Deionised water	0.9 - 1	kg	/2/, /32/, 1)
Initiator	0.0003 - 0.0008	kg	/2/
Inter gas (nitrogen) process material	no data a)	kg	
Protective colloid/Emulsifier, methyl-cellulose	0.0005 - 0.0015	kg	/2/, 1)
Cooling water (process material)	100 - 200 d) a)	kg	/3/, 1)
Process materials: e.g. soda lye, hydrogen chloride	0.0015 - 0.004	kg	/32/
Air (process material)	1- 2 c)	kg	1)
Process water	3 - 5	kg	/32/
Emissions to air			
VOC	5E-5 - 2E-4	kg	1)
of which VCM	bis zu 1.9E-4 e)	kg	/7/, /32/
other VOC	1E-5 - 5E-5	kg	/32/
Particles	6.5E-5 - 1.5E-4	kg	/7/, /32/, 1)
Waste air	1 - 2	kg	1)
CO	negligible f)	kg	/32/
CO2	negligible f)	kg	/32/
SOx	negligible f)	kg	/32/
NOx	negligible f)	kg	/32/
NH3	no data g)	kg	
Emissions to water			
Chemical oxygen demand (COD)	0.00015 - 0.00075 a)	kg	/5/, /7/, 1)
Biological oxygen demand (BOD)	5E-5 - 3.75E-4 h)	kg	/5/, 1)
(Adsorptive organically bonded halogens (AOX))	(3.8E-6 - 5E-6) i)	kg	1)
NH4+	0.000002 a)	kg	/5/
Solids (suspended)	0.00006 - 0.0005 a)	kg	/5/, /7/, 1)
Other nitrogen compounds	no data j)	kg	
Phospate as P2O5	no data j)	kg	
VCM	1E-6 - 5E-6	kg	/32/
(Chromium unspecific)	(2E-7 - 7E-7) k)	kg	/7/, 1)
Waste water	1.15 - 4	kg	/2/, 1)
Cooling water	100 - 200	kg	/3/, 1)
Wastes			
Near-domestic industrial waste	0.002 - 0.003 l)	kg	1)

1) Figures based on IKP estimates

The German PVC industry is trying the evaluate the power consumption data (a) in more detail. The figure quoted would appear to be sensible.

The ratio between electricity (a), steam (b) and natural gas input (c) can vary depending on the drying process used (flash dryer, fluidized bed dryer, rotary drum) and the respective energy input for the drying process.

The material input of air (c) is environmentally irrelevant. The energy effects of compression have been taken into account in the energy input. The value represents a technical characterisation.

Approx. 90% of the input water (d) is used in a cyclic system so that only a negligible share of the cycle water is consumed.

The range warranted for a "Best Available Technology", which in some cases is already applied, is 70 mg_{VCM}/kg_{PVC} (e).

Process-specific emissions (f) of CO and CO_2 are negligible sine the goal of the reaction is to prevent free oxygen in the reactor. This prevents the formation of CO and CO_2 in the reaction area. CO and CO_2 emissions can occur depending on the dryer operation and its energy supply (e.g. operated with natural gas).

The PVC industry is investigating the relevance of ammonia emissions (g) which may be caused by the use of ammonia compounds. The probability that such emissions can be recorded in relevant quantities is slight.

The key parameter to measure water emissions is COD (h). The BOD measurement depends on the specific approval procedure and is not required in Germany.

The goal of measuring AOX (h) is to determine the "mobile" (i.e. not chemically bonded) halogens. There is a risk of "incorrect measurements" if the value is interpreted as a mobile halogen share since the immobile, bonded halogens in the polymer are also measured. Thus, this parameter and the measurement results are questionable and need further investigation.

The PVC industry will check whether eutrophic emissions (j) occur.

According to discussions with experts from industry, no chrome emissions (k) are known or possible from processes since a chrome-free catalyst is used. Any measurements are probably due to abrasion from plant components made of chromium-alloyed steel.

The large share of near-domestic industrial waste (l) is due to packaging, dispatch, etc..

We would at this point like to point out that interdependencies may exist between the quoted figures. This means it would be wrong to conclude that a plant may only be evaluated as BAT if it complies with the minimum limits for all quoted values. As becomes clear if one takes energy carriers as an example (electricity, steam, fuel), the electricity demand can be reduced by using natural gas burners to supply power to the dryer. This naturally leads to a certain demand for natural gas which has to be won and supplied.

9.1.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

9.1.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

9.1.4.2 Technical parameters

Polymerization pressure	3-10 bar
Polymerization temperature	45-75 °C
Catalyst efficiency	1200 - 3300 $g_{S\text{-}PVC} / g_{Initiator}$
Polymerization time	5-8h
Conversion rate	approx. 90%

9.1.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	120,000 t
Investment costs	approx. 76 million euro
Raw materials costs	approx. 685 euro / $t_{S\text{-}PVC}$
Initiator / Initiator costs	approx. 15 euro / $t_{S\text{-}PVC}$
Energy costs	approx. 11 euro / $t_{S\text{-}PVC}$
Personnel costs	approx. 12 euro / $t_{S\text{-}PVC}$
Maintenance costs	approx. 19 euro / $t_{S\text{-}PVC}$

The personnel costs have been calculated on the basis of 25 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

9.1.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Reaction preparation

VCM should be stored in cooled tanks at atmospheric pressure or in pressure tanks at ambient temperature. The tanks should be connected to the VCM-recovery system.

In principle one can differentiate between two possible methods of raw material supply. Integrated plants supply the raw materials in the vicinity and are directly connected to the production plant via pipelines. Integrated plants exist in Germany which range from chlorine production through to the finished PVC. The initial chain from the fossil energy carriers to ethylene is not normally integrated. In integrated plants ethylene is partly supplied via a pipeline. The conversion to dichloroethane and further to vinyl chloride can take place in combined production.

Both integrated and isolated plants have advantages. Integrated plants display fewer transport processes and diffuse emissions from supply processes. Larger isolated plants to produce initial products which supply a number of production plants can lead to a more efficient production of initial products since the concentration of larger material and energy flows may allow more efficient processes.

Reaction

Fouling of the reactor should be prevented. The "closed reactor technology", i.e. the process control and cleaning of the reactor in a closed system can be seen as the BAT for all new and future plants.

Possibilities for a BAT are thus:

- clean-wall-technology through the use of coatings in the reactor
- encapsulated high-pressure cleaning systems and
- recipe improvements to minimise caking

The implementation of these technologies allows the aforementioned closed process control since the system does not have to be opened to clean the reactor, inspection and maintenance after every batch.

Thus, opening of the reactor can be limited to approx. once every hundred batches. This reduces the emission of volatile substances (VCM) and other process chemicals. This contributes to reducing the pollutant load at workplaces.

Possibilities for an effective removal of residual VCM from the reactor before opening for cleaning, inspection and maintenance may:

- reduce the pressure in the reactor during VCM recovery
- displacement of the VCM by introducing fluid components in the closed tank
- rinsing and cleaning the reactor with water, draining this water into the waste water treatment
- steam input or rinsing the reactor with inert gas to remove VCM traces and forwarding of this to VCM recovery.

On account of the interim emptying of the polymerization reactor waste water flows should be collected in an equalizing reservoir.

It must be ensured that the reactor is completely freed from polymer between batches because this is the main cause of material faults, which in this connection are also called "fisheyes".

The PVC solution at the inlet to the dryers should not have more than a maximum of 20 g residual VCM per ton S-PVC (annual mean) for consideration as BAT /11/.

Substance	Quantity
VCM (residual monomer conc. in the suspension at the dryer inlet)	20 g/t S-PVC

Polymer separation and monomer recycling

Fluid flows which are to be connected to VCM recovery:

- vents for inert rinsing facilities in the reactor or other tanks and pumps in the polymerization unit.
- uncondensed steam from the head of the slurry stripper
- flows from the waste water stripper which contain monomers
- vents from the VCM tanks

All vent lines should be connected to the waste gas treatment or VCM recovery. The following may be exceptions:

- vent lines containing an explosive mixture of organic compounds and oxygen.
- main vent lines (safety vents), which would extinguish the flames in the combustion units due to their high mass flows
- exhaust gas from the PVC dryer (low concentration of VCM in high volume flows)

Diffuse emissions

The following measures can be taken to reduce or prevent leaks which may lead to volatile, airborne emissions:

- Valves: for example the use of diaphragm, double seals or similar effective fittings.
- Pumps: for example double seals with fluid stop, magnetically operated or encapsulated.
- Compressors and vacuum pumps: for example double seals with fluid stop, magnetically operated or encapsulated.
- Agitator: for example double seals with fluid stop, magnetically operated or encapsulated
- Flanges: for example minimisation of the number, use of high-quality seals.

Process control and quality management

The process control to avoid extraordinary discharges to the environment can be ensured by recording environmentally relevant parameters which can be continuously called by engineering and management.

Batches which do not come up to the required specification should be prevented by quality management systems. Examples include automatic weighing and dosing of substances. It is also very important to ensure that different grain sizes of various products are not mixed in subsequent processes such as suspension treatment, stripping, drying and storage.

To prevent contamination with foreign substances adequate metals must be chosen for the construction and design. Stainless steel, for example, can be used for PVC polymerization.

What to do in the event of an accident

Additional precautions to prevent the discharge of VCM into the atmosphere can include:

- Computer-aided monitoring of the reactor input and operating states
- Emergency power supply for the agitator
- Emergency cooling units for the reactor, emergency condensation
- Controlled emergency venting for VCM recovery
- Chemical e-stop system (deactivation of the reaction).

Waste gas treatment

The VCM emissions can be minimised if the plant is run in "closed-lid operation".

One source which must be subjected to VCM gas cleaning is the waste gas from VCM recovery. The removal and recovery of VCM is achieved by absorption with organic solvents or absorption on activated carbon. Combustion under defined conditions is an additional or alternative solution.

VCM is mainly emitted in the dryer waste air. One way to reduce these emissions is thermal afterburning of the dryer waste air.

Modern continuous stripping columns display VCM emissions of less than 10 ppm /8/.

Substance	Quantity
VCM (after stripping column)	< 10ppm in waste gas

Older stripping columns which work with batches cannot reach these values since they cannot be used to achieve the low residual VCM content in the product.

One possible and documented maximum for long-term average emissions from an S-PVC plant listed for BAT is 70 g_{VCM}/t_{PVC} , taking into account volatile emissions /11/.

Online-monitoring of emissions after waste gas purification should include VCM, CO, O_2 and the temperature.

Monitoring volatile emissions as regards workplace concentrations should include:

- Continuous, online recording of VCM using instruments at all relevant points in the plant's air system.
- Individual measurements of VCM using hand-held devices (to look for leaks)
- Personal control devices (e.g. control buttons with activated carbon)

PVC can be lost, for example in separators and if silos are overfilled. It is thus important that all drains which could contain PVC are fitted with separators (e.g. filter). This ensures that flows leaving the system are free from PVC. The PVC powder losses from drying (through overflows) can be prevented if the cyclone design is matched to the air mass throughputs.

Modern plants use, e.g. cloth filter systems or wet washers to comply with the PVC powder loss limits. These are around 10 mg/m^3 air /8/.

Substance	Quantity
PVC powder (losses)	< 10 mg/m^3 air

Moist or wet production residues can be collected and input into non-critical applications as second or third class quality materials.

Waste water treatment

Process water flows which contain VCM and are collected in closed units for forwarding to a washer (removal and recovery of VCM) include:

- condensate from the suspension stripper (if present)
- condensate from VCM recovery
- water from the VCM-water separation unit
- cleaning water used to clean the reactor
- rinsings from pumps or gas tanks
- waste water from vacuum systems

VCM is removed to less than 1 mg VCM per litre of waste water with steam strippers. The cleaned waste water are forwarded to a system to remove suspended or emulsified solids or to a biological waste water stage. PVC particles can be removed by filtration, flocculation or precipitation. If residual additives have to be removed from the waste water a biological waste water treatment can be integrated downstream to reduce the biodegradable organic compounds in the waste water.

Possible discharge quantities:

Before biological waste water treatment	1 mg VCM/litre
At waste water drain	125 mg COD/litre
Particles at waste water drain	30 mg PVC/litre

These figures do not mean that biological waste water treatment is compulsory.

The values can be monitored by a continuous monitoring of the waste water flows and random sample analyses for VCM, COD a dissolved solids.

Wastes

It should initially be checked whether PVC wastes can be used as raw materials for products. Wastes which cannot be used can be dumped on landfill sites or burnt.

Residual monomer content

Food packaging	<1 g VCM/t PVC (< 0.5 g in practice)
Most common qualities	<5 g VCM/t PVC
Special qualities	< 10 g VCM/t PVC

9.1.6 Assessment

The introduction of the closed reactor technology can be seen as being environmentally positive and should apply as a standard for all new plants. VCM emissions can be effectively and technically reduced with this technology.

Although the encapsulation of cleaning systems calls for a certain apparative input, it should also be rated as positive due to the reductions in emissions which it brings.

The consistent return of monomers from vent systems, spray facilities and strippers should be rated positively from an environmental point of view since it cuts VCM emissions and thus increases the resource input efficiency.

An important condition for the achievement of lower VCM emissions in dryers is the lowest possible VCM concentration in the product or slurry. Low residual monomer contents, not only in the final product but also in the interim stages of the process, should thus be rated positively.

The waste gases from the dryer containing VCM are not used for recycling since the volume flows of waste air are too large and the concentration of VCM too low. It would appear to be technically possible to concentrate the VCM content. However, the environmental improvement potential of a recovery is estimated as being slight since the energy and material flows which have to be input for such concentrations would cancel out the positive effects of the emission reduction.

Process control in an almost closed system („closed lid operation“) can be assessed as very effective in terms of emission reduction and resource saving.

The reduction of diffuse emissions through suitable sealing systems reinforces this effect (see also Chapter 14).

As for particle emissions, cloth filters or wet washers in particular are rated as effective and advantageous from an environmental point of view since the fine particle emissions can be minimised.

The collection of waste waters containing VCM in closed units should be rated as positive since the efficiency of the washers is improved through the concentrated removal and recovery of VCM.

10 Process for the synthesis of polystyrene

Polystyrene is mainly produced by continuous polymerization processes. Solvents such as toluene or ethyl benzene are often added in small amounts to enable a better control of the rate of polymerization and the viscosity of the polymer melt. This is then a solvent polymerization. If no solvents are used we are dealing with a mass polymerization. The polystyrene is hereby dissolved in styrene (monomer). Solvent and monomer have to be removed from the polymer by degassing.

There is also suspension polymerization, where the styrene is dispersed as small beads in water by stirring. Suspending agents such as polyvinyl alcohol or alkaline-earth phosphates have to be added in this case. The reaction must be started by radical initiators since the process temperatures are lower than in mass polymerization. The main advantage of suspension polymerization is that the heat of reaction can be easily dissipated through the aqueous phase. However, the PS has to be granulated again after separation of the water to meet market requirements. During this granulation additives and dyes can be added, e.g. to set mechanical properties of the product. The suspension process, which is mainly used to produce expandable PS, is gradually being ousted by the mass polymerization process. However, some plants are still in operation.

The more modern process of mass polymerization will be described in more detail in the following.

10.1 Mass polymerization

10.1.1 Process description

All industrial mass polymerization processes are carried out continuously and are relatively economical. The PS has a constant quality and a low residual monomer content.

Monomer and additives, possibly a small amount of solvent and in certain cases an initiator are continuously fed into a reactor. The reactors used differ in terms of the way in which the heat of reaction is drawn off and the reactor contents are mixed.

In CSTR the heat is removed by back-flow cooling. The heat of reaction leads to an evaporation of part of the styrene. The gaseous monomer is condensed in condensers with a large surface area and returned to the reactor. A condition for this type of heat dissipation is an effective mixing of the reactor contents. Anchor, impeller, paddle or helical ribbon agitators are used. The reaction temperature is the most important parameter in the reaction since it affects the molecular weight and thus the product properties. The temperature is set by changing the pressure and thus the boiling point of the styrene in the reactor. This leads to temperatures of 100°-170°C, corresponding to a pressure of 0.5-2 bar.

Tower reactors are equipped with special fittings through which coolant circulates to carry off the heat of reaction. Different temperature zones can be set in the reactor by adjusting the temperature of the coolant. Tower reactors are also fitted with agitators.

Adiabatic tube reactors are sometimes used for high conversion rates, the reaction temperature is not controlled.

The PS melt which leaves the reactor has a concentration of 60-90%. Unreacted monomer and solvent can be removed by degassing in extruders or falling film evaporators. However, the most common method is flash evaporation. The polymer is passed into a heated tank with a vacuum in which the volatile constituents evaporate. The mixture of solvent and monomer is returned to the reactor. However, a small part must be rejected so as to avoid an enrichment of impurities in the styrene.

Degassing of the PS melt is followed by granulation. The melt is first forced through a perforated disk. The force needed is provided by a conveyor pump or extruder. The strands are cooled in a water bath and cut into cylindrical parts. Lenticular granulate can also be produced by underwater granulation.

10.1.2 Process flow chart

This flow chart shows the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

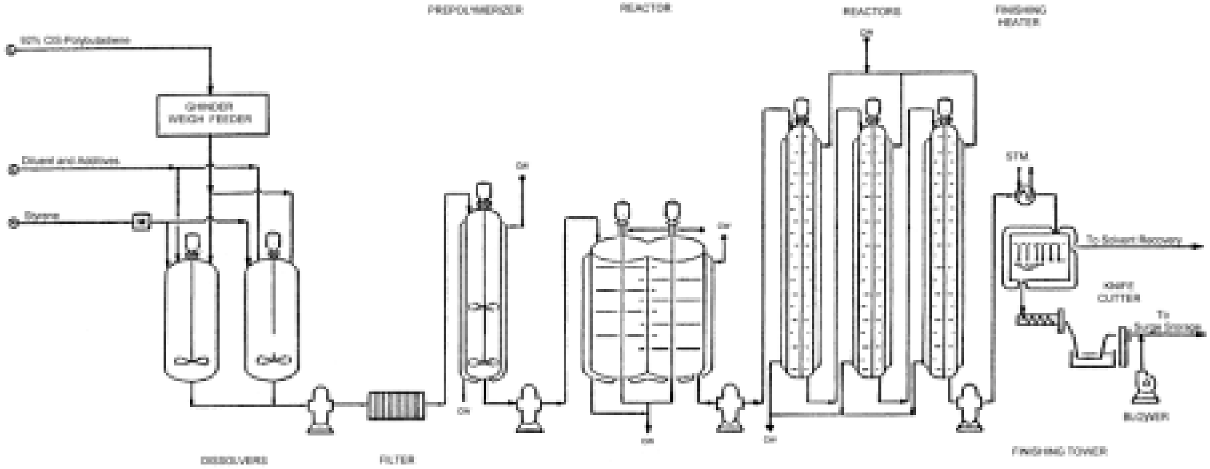


Figure 10.1: Mass polymerization of PS – synthesis and granulation /3/

10.1.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
PS	1	kg	
Energy carriers			
Electricity	0.06 - 0.2	kWh	/3/, 1)
Steam (total, no pressure data)	0.05 - 0.2	kg	/3/, 1)
Thermal energy	0.12 - 0.6	kg	
Materials			
Styrene	0.88 - 1.015	kg	/3/, 1), industry
Ethyl benzene	0.01 - 0.015	kg	/3/
Polybutadiene	0 - 0.12	kg	/3/, 1), industry
Inert gas (nitrogen)	0.01 - 0.02		industry
Mineral oil	0 - 0.08	kg	/3/, 1), industry
Cooling water	15 -45 (0.3 - 0.4 kWh)	kg	/3/, 1), (industry)
Process water	0.05 - 8	kg	/3/, 1)
Air	0.15 - 0.2	kg	1)
Stabilisers and additives	0 - 0.01	kg	industry
Emissions to air			
Waste air	0.15 - 0.2 (1.5 - 2)	kg	1) , (industry)
VOC	5E-5 - 4E-4	kg	1)
of which styrene	4.7E-5 - 3.9E-4		1)
Particles	2E-6 - 2E-5	kg	1)
Emissions to water			
Waste water	0.05 - 0.1	kg	1)
Cooling water	15 -45	kg	1)
Chemical oxygen demand (COD)	3.6E-6 - 1.7E-5	kg	1)
Biological oxygen demand (BOD)	4.5E-7 - 1.7E-6	kg	1)
Solids (suspended)	2.9E-6 - 5.2E-5	kg	1)
Hydrocarbons	6.9E-7 - 5.4E-6	kg	1)
Wastes			
Near-domestic industrial waste	1.7E-3 - 4E-2	kg	1)

1) Figures based on IKP estimates

In the case of polystyrene, process-specific information is also available from APME /5/, which although it relates to the entire process chain (i.e. not simply the polymerization stage), the shares for fuel production and delivery, fuel use, transport and biomass input have been calculated out of the figures. These figures can thus be used for validation.

Ethylbenzene, although we are dealing with a mass polymerization process, refers to small quantities of solvent added to the process.

Polybutadiene is added to obtain "High Impact"“ polystyrene. Other qualities are produced without the addition of polybutadiene.

Since various PS types can be produced the polybutadiene rubber demand fluctuates. The standard polystyrene types which have a very high dimensional stability under heat normally contain no mineral oil.

Stabilisers and additives are normally added in quantities below 1 %-weight.

The compressed-air demand is for air conveyance.

The data from industry as regards the waste air quantities are in brackets. A high exchange of air must be guaranteed at the nozzle heads, i.e. those points where the polymer melt is pressed into strands. Large air volumes are also required for pneumatic conveyance. The air load is naturally lower due to the higher air demand (relative to mg/m³).

The VOC value of "General Purpose" PS is estimated at approx. 0.0166 kg VOC/kg PS over the life cycle. This value is quoted at 0.0028 kg VOC/kg PS in /5/. "High Impact" qualities are estimated in the range of approx. 0.017 kg VOC/kg PS, whereby /5/ quotes 0.0038 kg VOC/kg PS.
The differences (HI to GP) result from the different initial products. The polymerization itself is comparable. The production of the initial products and the power supply account for >98% of the load. The VOC from the polymerization are thus < 2%.

Apart from styrene, polybutadiene, VOC from the use of mineral oil and solvents may be emitted depending on the recipe (HI or GP). If one compares input amounts, the styrene emissions can be estimated.
High-impact PS:
- Minimum input styrene: 0.93 kg
- Maximum input ethylbenzene 0.015 kg
- Maximum input mineral oil 0.03 kg
- Sum total of inputs: 0.975 kg
- Minimum ratio styrene/HC total = 95.4 %

General purpose PS:
- Maximum input styrene: 1.015 kg
- Minimum input ethylbenzene 0.01 kg
- Minimum input mineral oil 0.02 kg
- Sum total of inputs: 1.045 kg
- Maximum ratio styrene/HC total = 97.1 %

This leads to the estimated range of styrene emissions of 4.7E-5 – 3.9E-4 kg/kg PS.

The life cycle emissions of the particles are mainly caused by the initial chains. Differences (HI to GP) result from different initial products (polymerization comparable). With a 1% share of polymerization, this corresponds to an emission due to polymerization of 2E-5 kg/kg PS on the basis of /5/ at 2E-3 kg (High Impact).

The amount of cooling water which has to be drawn off depends on the cooling water in the system. According to data from industry, these values are also optionally quoted in kWh so that consumed energies (taking into account the difference in temperature of the water) can be characterised. However, this is ignored in our study.

Data for the life cycle emissions of COD fluctuate between 0.00037 kg according to /5/ and 0.0016 kg. Initial products and energy again play the main role with >99%. COD from polymerization is estimated at < 1% share of the life cycle emissions.

The same applies for BOD and particles whereby the estimate for BOD of 0.000045 kg/ kg PS to 0.0001 kg/kg PS and for solids of 0.00034 kg/kg PS to 0.0052 kg/kg PS in terms of the life cycle emissions is adequate.

10.1.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

10.1.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

10.1.4.2 Technical parameters

Polymerization pressure	0.5-2 bar
Polymerization temperature	100°-170°C
Catalyst efficiency	no data
Polymerization time	1 d
Conversion rate	<95%

10.1.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	100,000 t
Investment costs	approx. 45 million euro
Raw materials costs	approx. 1316 euro / t_{PS}
Initiator / Initiator costs	approx. 15 euro / t_{PS}
Energy costs	approx. 5 euro / t_{PS}
Personnel costs	approx. 17 euro / t_{PS}
Maintenance costs	approx. 13 euro / t_{PS}

The personnel costs have been calculated on the basis of 30 workers (22,200 euro p.a.), 10 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

10.1.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Reaction

In the categories of carcinogenic substances, styrene is classed in category 5. The LTL and BAT values list has this to say about category 5:

Substances with a carcinogenic and genetically toxic effect whose strength is so slight that if the LTL limit is observed no significant contribution to the cancer risk for humans can be expected. Great care must thus be taken to ensure that all plant parts are adequately sealed to guarantee the LTL values. This is particularly true of the agitator shafts.

Around 95% of the monomer has been converted after the various reactions. However, a dwell time of 1-2h in a further reactor ("finishing tower") should be observed so that the unreacted monomer is consumed and the product quality increased. Otherwise the monomer should be recovered.

Polymer separation and monomer recycling

The solvent is recovered after the so-called "finishing tower" by flashing in a reactor with a number of plate fixtures or in a number of reactors. The residual monomer is removed from the polymer during solvent stripping. Steam or methanol are sometimes used as process materials during stripping to make this easier. These substances then have to be separated from the flow. The solvent and the monomer therein are recycled.

10.1.6 Assessment

The almost complete conversion of the styrene and recovery of unreacted monomer must be rated as positive, which is why high conversion rates can apply as key parameters. Due to the toxicity of styrene emissions, safety at the place of work is increased through the high efficiency of the conversion from monomer to polymer. The amounts of styrene which are converted do not have to be separated from the polymer, nor recycled nor treated. The second positive aspect is the concomitant increased resource efficiency.

A trade-off situation can arise between the alternatives of on the one hand a more complicated polymerization to maximise the conversion rates (avoidance of residual monomer) and on the other a more complicated (recycling of residual monomer).

The solvent separation and its recycling is rated as positive and efficient. Since the substances are low-toxic (such as ethylbenzene), the solvent always requires special treatment. Since the separated solvent-monomer mixture can be returned to the polymerization reactor without further separation, this recovery system can be rated as efficient.

The closed cycle system for the water used in granulation reduces the demand for this resource and the efficiency of its use.

If the outwardly transferred solvent flows are subsequently burned and the heat recovered this is rated as being positive in view of the reduction in emissions. If the concentrations of solvents in the extracted gas are however low, environmental compensation effects can arise from the input of energy for the thermal combustion.

11 Process to produce acrylonitrile-butadiene-styrene (ABS)

ABS polymers are two-phase systems in which chemically different polymers co-exist as separate phases. All ABS particulate composites have a continuous phase (matrix) of copolymers of styrene and acrylonitrile. The second phase is an elastomer on the basis of butadiene which is embedded in the matrix with a characteristic morphology.

Apart from the choice of the polymerization process (emulsion process, mass process, solution process) the manufacturer can decide whether and ABS particulate composite is produced directly using polybutadiene and the monomers styrene and acrylonitrile in one reaction stage or whether the two necessary polymer components are produced separately. The second method offers a greater choice for adjusting the individual parameters. Both of these processes has advantages and disadvantages as regards product properties, ecology and costs. Since fields of application and product features are often closely related the quality requirements frequently determine the production process.

The ABS production processes can be classified according to two aspects:

- differentiation according to type of elastomer components, i.e. between the copolymer and graft polymer and accordingly between ABS blend types and ABS graft types.
- Classification according to the polymerization process employed.

Whereas the separate production of rubber copolymer and SAN matrix is imperative for ABS blend types, there are two possibilities for ABS graft types:

- the separate production of rubber and SAN copolymer with subsequent compounding stage and
- the production of the overall particulate composite (rubber and matrix) in one reaction stage.

The desired product quality determines which of these two methods is employed.

ABS graft copolymers with a rubber content of 5 - 85 % by weight can be produced by emulsion polymerization. In the case of mass or solution methods the rubber content is limited to a max. of 20 % by weight for viscosity reasons.

A separate production of graft rubber and matrix has production technology advantages inasmuch as the properties of both individual components can be separately controlled and different processes used to produce the rubber phase and the matrix. The advantages of an integrated process lie in the fact that it enables a fully continuous process control. However, the range of product variations is restricted in this case.

11.1 Emulsion/suspension polymerization

11.1.1 Process description

The emulsion process is the standard process to produce ABS on account of its wide-ranging applicability. The process is split into three stages:

- Production of the graft base, i.e. a polybutadiene or butadiene-comonomer-latex with a defined particle size and distribution.
- Performance of the graft reaction through polymerization or a monomer mixture of styrene and acrylonitrile (and possibly further monomers) in the presence of the graft base.
- Processing of the grafted polymer through coagulation, washing and drying of the powder which is produced.

In the first stage a polybutadiene-latex is produced, possibly with further comonomers. The monomer(s) is/are hereby mixed in water at a mass ratio of between 1:0.6 and 1:3. Anionic active emulsifiers (alkaline soaps of abietic acid or fatty acid) are used to disperse the monomers and stabilize the resulting polymer particles. The molecular weight of the polymer is set by regulators. After rinsing with nitrogen, butadiene is impressed and activated with a peroxide starter system (e.g. potassium peroxodisulphate solution). The reaction speed in this batch process is controlled by the heat dissipation in the reactor. The polybutadiene components are produced in a temperature range from 5° - 75°C and at a pressure of <12 bar In depending on the activation system. The reaction speed drops at conversion rates of approx. 80-90%. The monomers are largely consumed, crosslinking reactions start. The reaction is stopped by lowering the temperature, unconverted monomers are drawn off. So as not to disturb the subsequent reaction, no shortstoppers are used apart from pure reducing agents.

In the second stage, the actual ABS production stage, the following components are metered into the reaction zone: monomer including molecular weight regulator, soap solution, initiator and accelerator solution and the polybutadiene-latex. At a temperature of 50°-90°C the mean dwell time is approx. 120 min. The graft reaction is normally carried out a temperatures between 30° - 75°C and without pressure. The choice of initiator greatly affects the ratio of SAN copolymerization to the graft reaction. Organic peroxides which dissolve monomers are preferably used.

To obtain ABS powder from the polymer-latex, the emulsifier has to be deactivated after polymerization. This is done by adding acids and/or salts.

The latex can then be freed from the residual monomers by stripping with water steam. Once it has passed through a stabilisation tank the polymer is coagulated in a so-called powder line and the powder then washed and dried before being forwarded to a compounding stage. After adding lubricants, colorants and other additives the polymer leaves the process as a granulate.

11.1.2 Process flow chart

These flow charts show the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

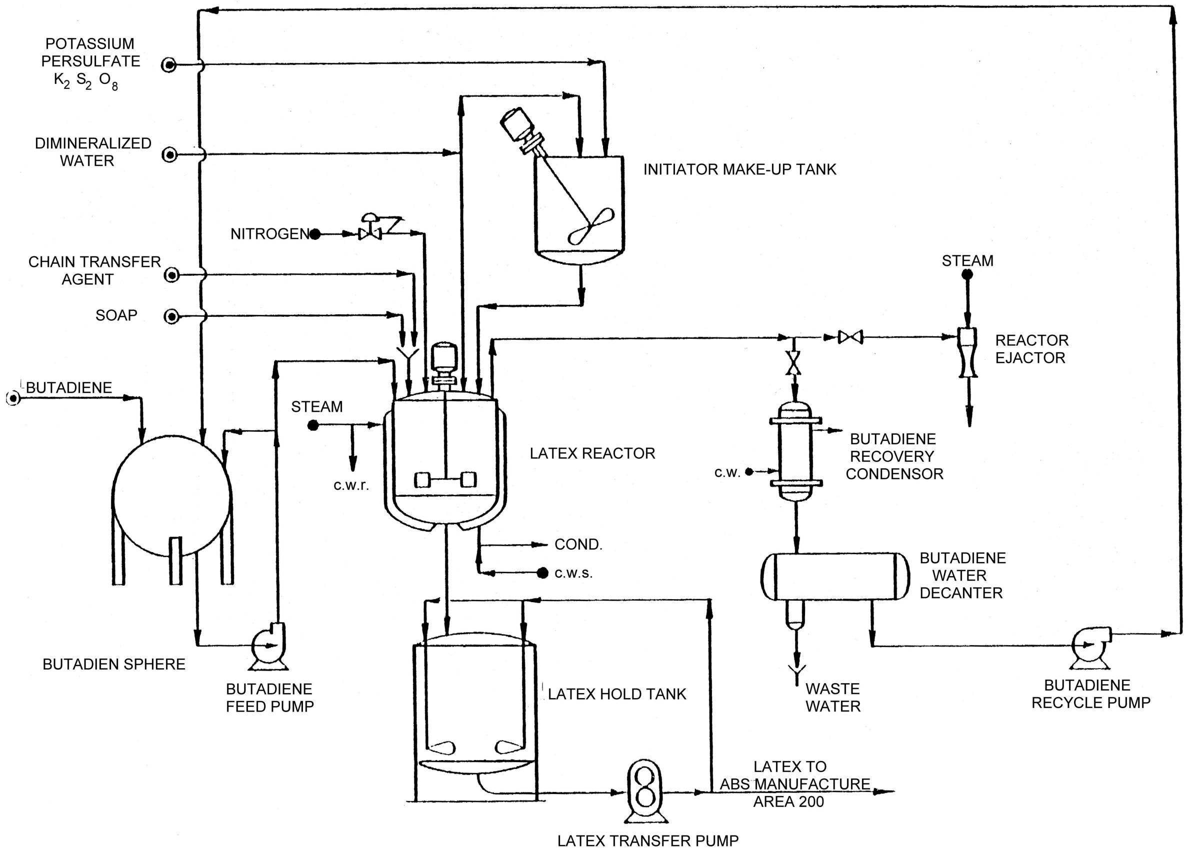


Figure 11.1: Producing ABS – production of the polybutadiene-latex /3/

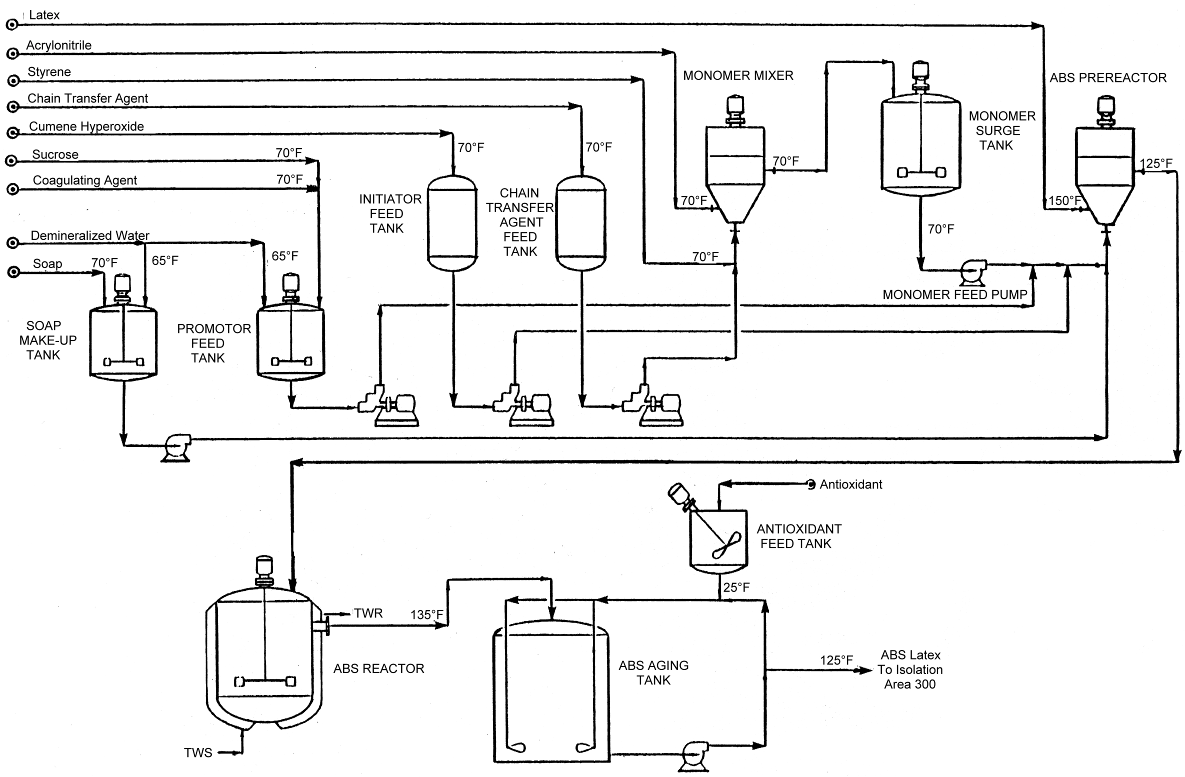


Figure 11.2: Producing ABS – synthesis /3/

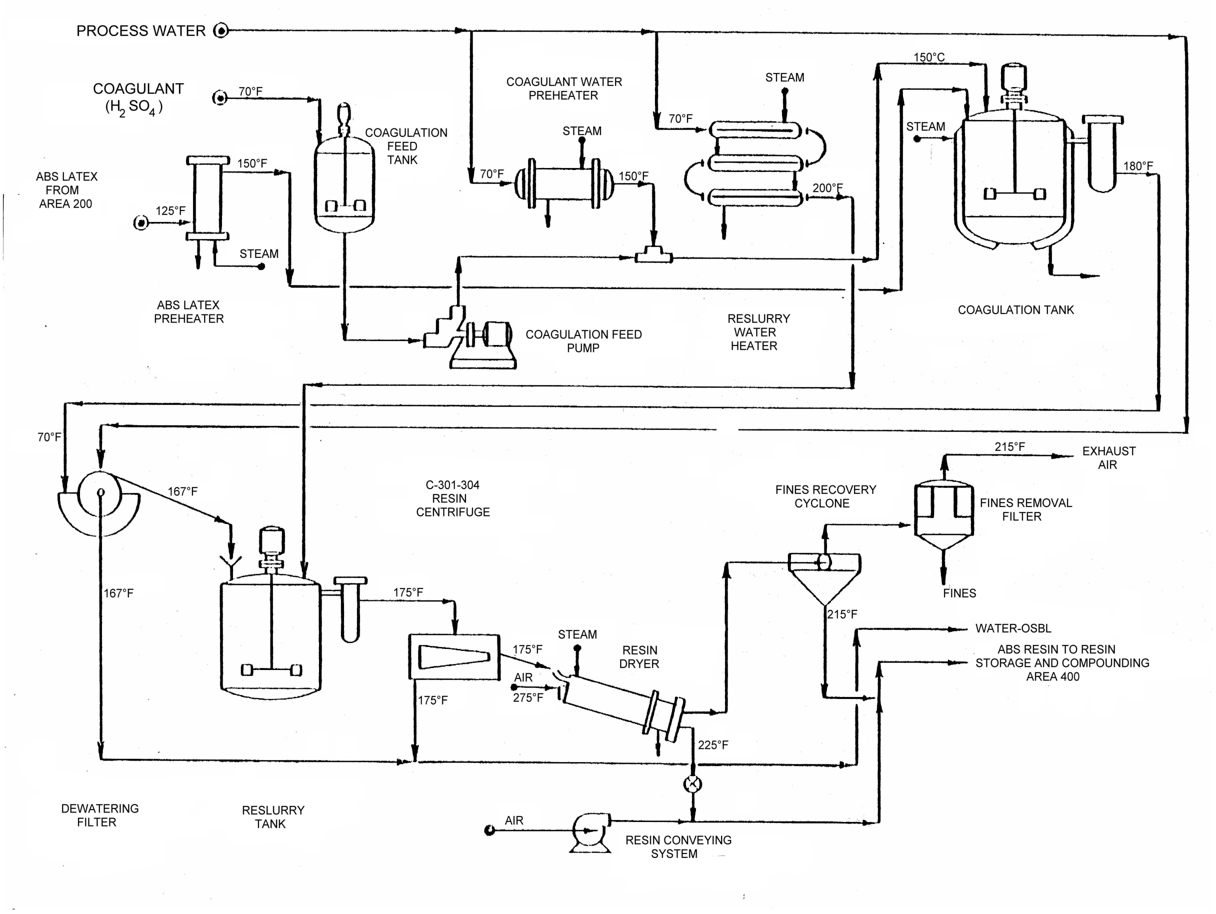


Figure 11.3: Producing ABS – polymer separation /3/

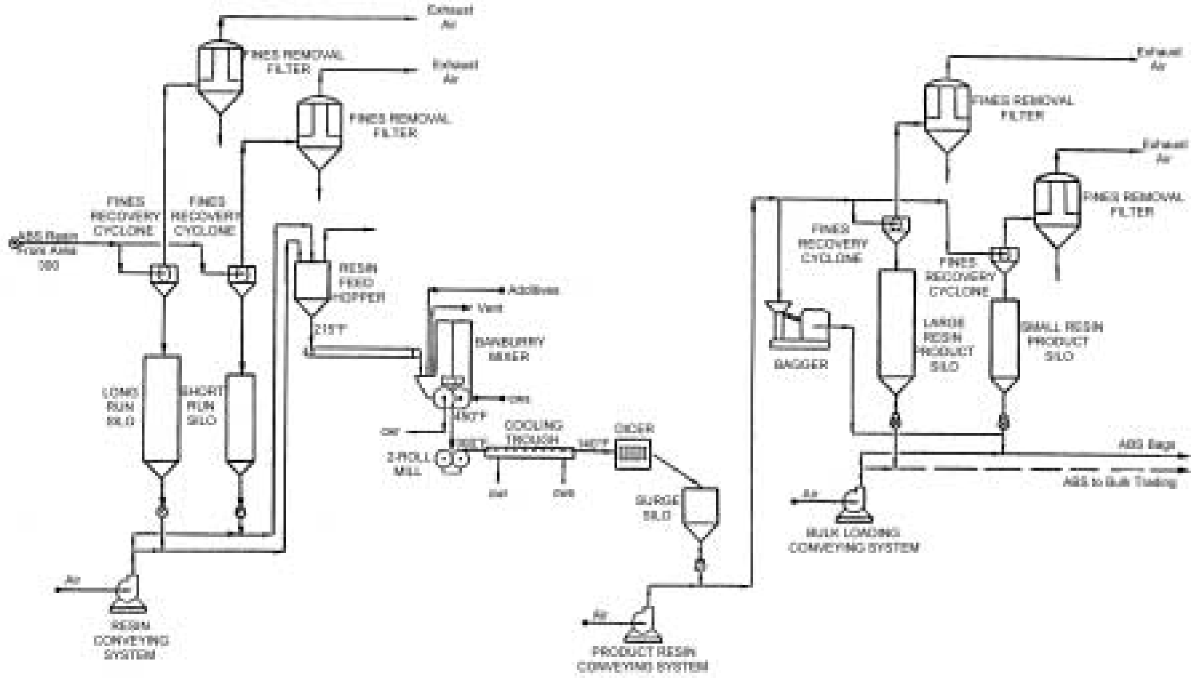


Figure 11.4: Producing ABS – compounding and packing /3/

11.1.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
ABS	1	kg	
Energy carriers			
Electricity	0.35 - 0.65	kWh	/3/, 1)
Steam (total, no pressure data)	01.05.02	kg	/3/, 1)
Fuel (natural gas)	0.05	kg	/3/
Materials			
Styrene	0.52 - 0.62	kg	/3/, 1), industry
Acrylonitrile	0.21 - 0.28	kg	/3/, 1)
Butadiene	0.15 - 0.26	kg	/3/, 1), industry
Emulsifier	0.02	kg	/3/
Inert gas (nitrogen)	0.02 - 0.05	Nm3	/3/, 1)
Chain transfer agent (Mercaptan)	0.006	kg	/3/
Cooling water	18 - 50	kg	/3/, 1)
Process water	3 - 12	kg	/3/, 1)
Air	02.05.03	kg	/3/
Emissions to air			
Waste air	02.05.03	kg	1), industry: irrelevant
VOC	3E-3 - 5E-3	kg	1)
of which styrene	0.0013 - 0.0032	kg	1)
of which acrylonitrile	0.00055 - 0.00152	kg	1)
of which butadiene	0.0005 - 0.00142	kg	1)
Particles	3.6E-5 - 2.7E-4	kg	1), industry: irrelevant
Emissions to water			
Waste water	3 - 12	kg	1)
Cooling water	25 - 35	kg	1)
Chemical oxygen demand (COD)	1.5E-3 - 8.3E-3	kg	1)
Biological oxygen demand (BOD)	2.8E-5 - 3E-3	kg	1)
Hydrocarbons (acrylonitrile)	5E-5 - 1E-3	kg	1)
Wastes			
Near-domestic industrial waste	0.0037 - 0.03	kg	1)
Hazardous waste	< 3.3E-3	kg	1)

1) Figures based on IKP estimates

In the case of ABS, process-specific information is also available from APME /5/, which although it relates to the entire process chain (i.e. not simply the polymerization stage), the shares for fuel production and delivery, fuel use, transport and biomass input have been calculated out of the figures. These figures can thus be used for validation.

The life cycle emissions of VOC were estimated at between 0.0031 kg/kg ABS /5/ and 0.023 kg/kg ABS. Under German conditions, production of the initial products (relative to the input quantities) already causes 0,0076 kg VOC. The APME calculations however relate to European conditions which in this case apparently differ greatly from the German conditions.

The waste air data are not from industrial sources (not regarded as relevant by industry).

The initial products styrene, acrylonitrile, butadiene and energy cause more than 78% of the VOC emissions. Polymerization is thus estimated at < 22% of the aforementioned life cycle value.

The styrene, acrylonitrile and butadiene shares in VOC were determined as follows:

- Total input of styrene, acrylonitrile and butadiene is min. 0.92 kg and max. 1.13 kg.
- The styrene share is min. 0.52/1.13=46% and max. 0.59/0.92=64%.
- The acrylonitrile share is min. 0.21/1.13=18.6% and max. 0.28/0.92=30.4%.
- The butadiene share is min. 0.19/1.13=16.8% and max. 0.26/0.92=28.3%.

The share of styrene emissions is thus estimated at 0.00138 – 0.0032 kg, the share of acrylonitrile emissions at 0.00055-0.00152 kg and the share of butadiene emissions at 0.0005 – 0.00142 kg.

APME quotes 0.003 kg particle emissions for the total life cycle. According to /5/ the initial products account for at least 0.002726 kg. In other words, the polymerization causes a maximum of 0.000274 kg (9.1% of life cycle). Relative to German conditions for initial products this leads to an approx. 9% share 3.64E-5 kg particle emissions. These data are not from industrial sources (not regarded as relevant by industry).

The polymerization stage is clearly involved in COB emissions. The life cycle estimates vary between 0.0022 kg /5/ and 0.011 kg.

The initial products (styrene, acrylonitrile, butadiene) and the energy supply cause approx. 24% of the loads, i.e. polymerization is estimated at 76% (<0.0083kg). If this is related to APME one arrives at 76% 0.00159 kg emissions.

Hydrocarbon emissions in water fluctuate over a wide range. The life cycle estimate varies between 4.1E-5 kg according to /5/ and 0.001375 kg. The value according to /5/ is regarded as too low for German conditions since the production of the initial products according to German conditions is already estimated at approx. 3.6E-4.

On the basis of German conditions, the share for the production of initial products and the energy supply is <27% with the marginal conditions assumed here This leads to a polymerization share of > 72% and an estimate of > 0.0009kg.

11.1.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

11.1.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

11.1.4.2 Technical parameters (graft reaction)

Polymerization pressure	pressure-less
Polymerization temperature	30 – 85 °C
Catalyst efficiency	no data
Polymerization time	100 – 500 min
Conversion rate	80-97%

11.1.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	50,000 t
Investment costs	approx. 46 million euro
Raw materials costs	approx. 1016 euro / t_{ABS}
Initiator / Initiator costs	approx. 138 euro / t_{ABS}
Energy costs	approx. 36 euro / t_{ABS}
Personnel costs	approx. 50 euro / t_{ABS}
Maintenance costs	approx. 26 euro / t_{ABS}

The personnel costs have been calculated on the basis of 85 workers (22,200 euro p.a.), 20 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation. The cost table should serve as a rough estimate.

11.1.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs. This also includes alternative processes and process variants.

Production of polybutadiene-latex

The stability of the emulsion must be ensured by regular checks. This permits an optimum control of the process.
At the end of polymerization the unconverted monomer is separated in a degassing stage and recycled.

Graft reaction to ABS

To prevent the monomer styrene from escaping it is important that all apparatus in the plant carrying the monomer, in particular the agitator shafts, pumps and fittings, be adequately sealed.

The polymer is precipitated after the graft. The solution of water, possibly salts and/or acids used for this then has to be removed from the polymer. The mixture extracted from the precipitation has a polymer share of around 10% and is initially dehydrated in a filter and then washed with water. The water share drops to 30-50% during filtration. The water separated from the polymer still contains fine particles and residues of unreacted monomers, mainly acrylonitrile. The fine particles can be separated and recycled by suitable processing techniques. However, it must be ensured that the waste water treatment effectively removes any residual monomers from the water.

The filter cake is again slurried with water and then centrifuged; alternative techniques are allowed. The separated water should also be treated as waste water.

The moisture residues are removed in the subsequent dryer. However, care must be taken to ensure that the polymer is not damaged in the dryer. This means: no remixing and minimum dwell times in the dryer.

The entrained particles in the dryer air must be separated, e.g. with a cyclone and superfine filter.

Compounding

The transport air must be cleaned of superfine particles with a cyclone and cloth filter.

A twin-screw extruder is generally used for compounding. A degassing facility in this extruder can remove water and monomer residues.

11.1.6 Assessment

The condensation of the residual monomer content during the production of the polybutadiene-matrix after a pressure drop when the reactor is opened and the monomer recovered can be assessed as environmentally favourable if the waste water is forwarded for waste water treatment. This increases the efficiency of the initial product input and reduces butadiene emissions.

A "trade-off" situation may arise between the procedure for the 2nd stage of monomer separation and the environmental performance of the further process. The residual monomer contents are so low that a concentration and recovery of the remaining monomer amount cannot be practically estimated from an environmental point of view. The energy inputs would probably cancel out the positive effect of the emission reduction.

The use of separators such as cyclones with downstream cloth filters or wet washers to remove fine particles during compounding is assessed as environmentally effective since the apparative, material and energy inputs are low, particularly with a cyclone/cloth filter system. These are higher with a wet washer, but finer particles can be separated.

The outlay for special sealing systems during the graft reaction to ABS can be assessed as an environmental advantage since the monomer styrene is a carcinogenic substance. The improvement in the environmental performance is thus accompanied by improved safety at the workplace.

The separation of fine ABS particles with subsequent recycling is assessed positively since a relatively low input leads to an effective separation. The recovery of acrylonitrile can be assessed as rather ineffective. However, acrylonitrile is a toxic substance so that if no recovery system is installed a suitable waste water treatment must be ensured.

11.2 Mass polymerization

The production of ABS by mass polymerization consists of three stages:

- A suitable rubber substrate is dissolved in the monomer mixture.
- The rubber-monomer mixture is polymerized up to a conversion rate of between 15 and 30 % by weight in a pre-polymerization stage with continuous mixing.
- In the third stage of the process the polymer-monomer mixture is either suspension polymerized in water or mass polymerized. One can differentiate between a mass suspension and a purely mass process depending on the design of this third stage.

Unlike the emulsion process, no rubber particles exist at the beginning of the graft reaction. This consequently also results in a different distribution of the elastomer phase in the SAN matrix.

Whereas in the emulsion process the distribution is largely determined by the particle size of the graft base, in the mass polymerization process it is determined by the choice of reaction conditions for the graft reaction and by the resulting crosslinking and phase separation effects. The phase separation and phase inversion processes which begin during pre-polymerization are thus also important for the technological properties of the products. SAN droplets carrying monomers are emulsified in the rubber solution by simultaneously forming SAN polymers. With an increasing SAN formation there is a steady change in the phase-volume ratio. As polymerization progresses, the styrene-acrylonitrile-monomer phase becomes the continuous and the polybutadiene rubber the disperse phase. After phase inversion, polymerization is continued to a conversion rate of 25-30%. The viscosity of the polymerizing mass is then already high enough to fix the phase distribution.

11.3 Solution process

The production process for ABS by means of solution polymerization is one variant of the aforementioned mass polymerization. It is as yet not important on an industrial scale.

The solution polymerization process starts from a solvent in which the rubber used as the graft base and the resulting SAN copolymer can be completely dissolved and in which the resulting crosslinked graft polymer is dispersed in a swollen form. The advantages of such a process control are that:

- rubbers can also be used which can only be produced by solution polymerization or are insoluble in a styrene-acrylonitrile-monomer mixture.
- the solvent significantly reduces the viscosity problems which are otherwise present during mass polymerization.
- the waste water pollution is also reduced compared to the emulsion process due to work in a non-aqueous system. Distillation or evaporation can be employed to recycle the solvent.
- more simple apparatus are needed than with purely mass polymerization.

These advantages are set off by the disadvantage that it is very difficult to obtain defined rubber particle sizes and a simultaneously high level of crosslinking of the graft base by means of solution polymerization.
Since this process is not relevant on an industrial scale it will not be considered further.

11.4 Process combinations

The comparison of the emulsion production process and mass production process for ABS shows that these processes have both advantages and disadvantages in terms of the process engineering, ecology, product quality and economic efficiency. Numerous tests have thus been carried out to combine individual process stages from the two approaches.

12 Process for the synthesis of polyamide 6.6

12.1 Polycondensation from AH salt

The first stage is the preparation of pure AH salt (salt from adipic acid and hexamethylene diamine HMDA) in an aqueous solution. The stochiometric equilibrium is ensured by pH-measurements. Excess diamine is normally added to compensate losses due to the higher relative volatility. The equivalent pH value for aliphatic salts is 7.6.

The salt has to be decoloured with activated carbon if the diamine has not been carefully refined and in particular if its is not free of cis-1,2 diaminocyclohexane. Rinsing the activated carbon bed with inert gas prolongs its useful life.

In continuous processes, a two-stage recycling method is used to process the salt. The two-stage addition to diamine with water evaporation as an interim stage leads to a concentrated saline solution. Various mixing processes using molten acids and diamine have been patented. A 50% saline solution is normally produced to prevent precipitation during storage at 25°C.

Discontinuous production of PA 6.6

The saline solution is concentrated to 65-80% at overpressure before being fed into an autoclave. The basic design of a reaction cycle is as follows:

- Heating to 210°C at a pressure of 17.5 bar
- Gradual increase of temperature to 275°C under a constant pressure
- Reduction of pressure to prevent cooling
- The autoclave is kept under atmospheric pressure until the desired molecular weight has been reached
- The polymer is then extruded in an inert gas atmosphere

This reaction process ensures that there is enough water in the reactor to prevent the tank from freezing before the melting point is reached. This also prevents an excessive loss of diamine. Tanks with agitator fittings are normally used.

The extrudate produced is a wide strip that is cooled in a water bath. The water is then removed by fans. The strip is cut into a granulate which is then mixed and packed. Hermetically sealed containers are used to prevent water absorption which can lead to hydrolysis of the polymer and thus a reduction if molecular weight during subsequent processing. Typical pack sizes range from 10-500kg and also up to container size. The PA compounders and processors have drying equipment if the moisture content of the granulate is too high for further processing.

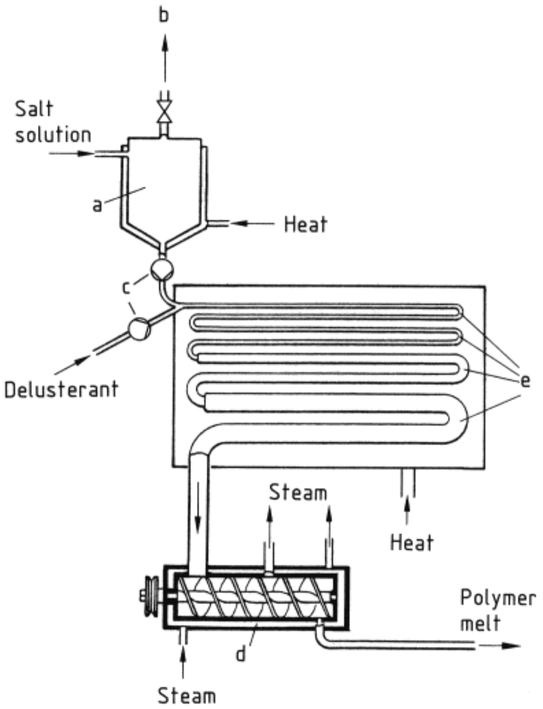
Although discontinuous production is still important for certain applications it is of minor interest for this study due to the small production quantities and will thus not be taken into further consideration here.

Continuous production of PA 6.6

The same considerations as regards the removal of water and loss of diamine exist for continuous production.
A first stage typically involves an evaporation/reaction with a controlled loss of water to produce a pre-polymer and minimise the diamine loss. Further reactions occur in subsequent stages during the controlled evaporation in apparatus known as separator and flasher. The desired molecular weight is achieved in a finisher. There are various patents dealing with an improvement to one of these apparatus or special combinations of these. One example is shown in Figure 12.1

The dimensions, dwell times, temperatures and pressures vary with each special design, though the direction of flow is always the same: A melt is produced with a high molecular weight and low water share which can be processed in an extruder or spinning machine to a granulate.

Serious restrictions to the functionality such as hot spots, exposure to oxygen, etc. must be strictly avoided in continuously operated high-temperature production plants with their polycondensation apparatus, extruders or injection moulding machines.



a) Evaporator/reactor ; b) Vent ; c) Pump ; d) Finisher ; e) Flash tubes

Figure 12.1: Continuous production of PA 6.6 /2/

12.1.1 Process description

The 63% AH salt is mixed with a small amount of hexamethylene diamine (HMDA) dissolved in acetic acid in a static mixer. In the first heated reactor (separator) the water evaporates in an inert gas atmosphere and overpressure. The polymer still contains approx. 18% water when it leaves the reactor. The conversion rate at this point is approx. 50%.

The separated steam contains HMDA and a small quantity of oligomers, is condensed and forwarded to that part of the plant where the HDMA is recovered.

The product then passes through the 2nd reactor (flasher). This heated tube reactor is equipped with static mixers and water or additives can be admixed. The conversion rate after this reactor is 98.5%.

The remaining water escapes in the 3rd reactor (finisher), which is operated with heat and overpressure.

The PA melt from the finisher is now extruded and granulated under water. The water is removed from the granulate in 2 stages with a blower dryer and a fluidized bed dryer operated with hot nitrogen.

The HMDA is recovered from the water which evaporates in the reactors using ion exchangers. Once an ion exchanger is charged with HMDA it is first rinsed with adipic acid and then with VE water and thus regenerated. The HDMA solution obtained can be used to produce the AH salt.

12.1.2 Process flow chart

This flow chart shows the process by way of example and should make for a better understanding of the process. Alternative designs can also fulfil the requirements of a BAT.

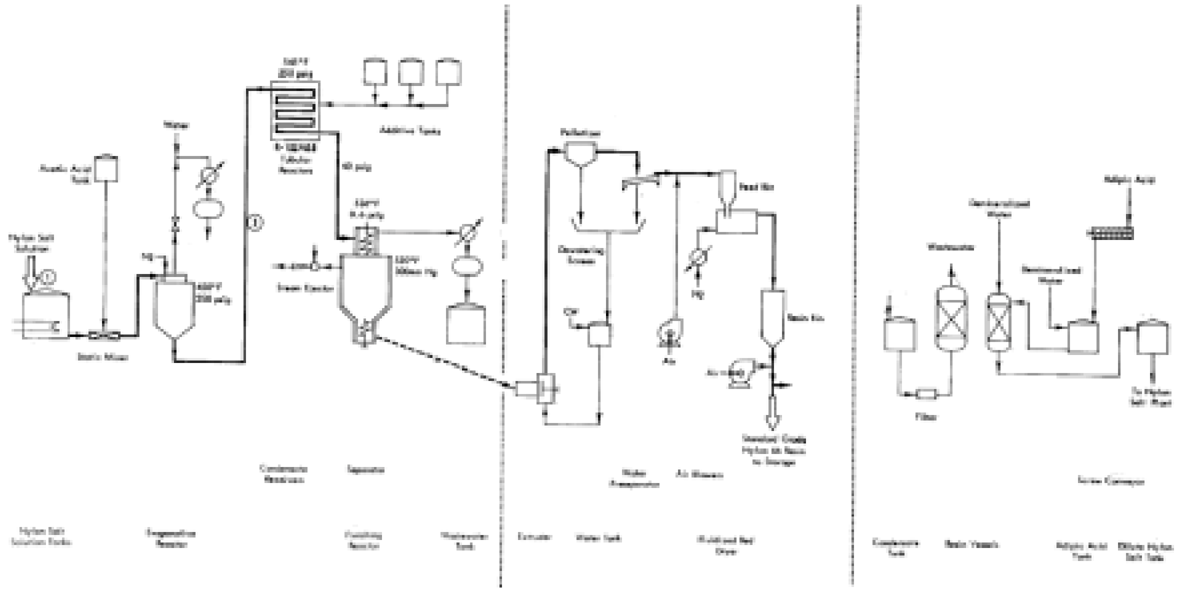


Figure 12.2: Process flow chart for the production of PA66 – synthesis and monomer recovery /3/

12.1.3 Input-Output table

General explanations can be found in Chap. 6.1.3.

Main product	Quantity	Unit	Remark
PA 6.6	1	kg	
Energy carriers			
Electricity	0.08 - 0.2	kWh	/3/, [1)]
Steam (total, no pressure data)	0.2 - 2.3	kg	/3/, [1)]
Thermal energy	0.15 - 0.3	kg	/3/, [1)]
Materials			
HMDA	0.46 - 0.57	kg	/3/, [1)]
Adipic acid	0.57 - 0.69	kg	/3/, [1)]
Inert gas (nitrogen)	0.001 - 0.002	Nm3	[1)]
Cooling water	100 - 200	kg	/3/, [1)]
Process water	2 - 6	kg	/3/, [1)]
Emissions to air			
VOC	< 2E-4	kg	[1)]
Particles	8E-5 - 2.7E-4	kg	[1)]
Ammonia	3.4E-7 - (3.5E-5)	kg	[1)]
Emissions to water			
Chemical oxygen demand (COD)	7.9E-4 - 1.8 E-3	kg	[1)]
Biological oxygen demand (BOD)	2E-4 - 2.2E-3	kg	[1)]
Solids (suspended)	k.A.	kg	
Hydrocarbons	4E-5 - 7E-4	kg	[1)]
Wastes			
Near-domestic industrial waste	0.02 - 0.072	kg	[1)]

[1)] Figures based on IKP estimates

The figures vary between 6.5 MJ – 12.98 MJ input of thermal energy. For extra light heating oil with a calorific value of 42.7 MJ/kg this means an energy carrier input of 0.15 kg – 0.3kg.

The VOC emissions over the life cycle are estimated at 0.0032 kg /5/ to 0.041 kg. The data according to /5/ can be seen as too low since under German marginal conditions > 0.039 kg VOC is released by the production of the initial products. The methane emissions from the natural gas route to produce adipic acid and HMDA via adipic acid account for 43% of the VOC. The estimated VOC emissions for polycondensation at < 0,5% mean < 2E-4 kg/kg PA 6.6.

The ammonia emissions are caused by the nitrogen input for HMDA. The life cycle emissions of 8.5E-6 kg to 6.9E-4 kg are dominated by the production of the initial products and energy supply (initial products > 50%, energy >45%). Polycondensation is thus estimated at < 4%. If one converts the APME data of 6.9E-4 kg in terms of the 4% share for polycondensation one arrives at 2.7E-5 kg/kg PA 6.6.

The COD value for the life cycle is estimated at between 0.0066 kg/kg PA 66 and 0.015 kg/kg PA 66. Production of the initial products under German conditions causes >88% of the loads. Polymerization is thus approx. around 12%. Converted for the data in /5/ this means < 7.9E-4 kg/kg PA66 for the polymerization.

The main share of industrial waste in the process chain is accounted for by polycondensation (packaging, filter dust, dispatch materials). Figures fluctuate between 0.021 kg and 0.08 kg /5/. The share of industrial waste from polycondensation in the life cycle is estimated at > 95%. The data in /5/ appear too high for German marginal conditions. The upper limit was thus estimated at a 90% share of the life cycle, corresponding to 0.072 kg.

12.1.4 Parameters

To round off the characterization of the processes, the Input-Output tables are also given general, technical and economic parameters /2, 3/.

12.1.4.1 General parameters

Location	West-Germany
Reference year	1988-1993
Production rate	100%

12.1.4.2 Technical parameters

Polycondensation pressure	17bar / 3bar – slight vacuum
Polycondensation temperature	230° / 280°
Polycondensation time	3 h / 40 min
Conversion rate	98.5%

12.1.4.3 Economic parameters

The economic parameters depend to a large extent on the process details and infrastructure and are dynamic according to the market situation. They are not an indicator of the environmental compatibility of a process.

Annual capacity	20,000 t
Investment costs	approx. 25 - 30 million euro
Raw materials costs	approx. 1900 - 2000 euro / t_{PA}
Energy costs	approx. 40 - 45 euro / t_{PA}
Inert gas	approx. 45 – 50 euro / t_{PA}
Personnel costs	approx. 60 euro / t_{PA}
Maintenance costs	approx. 70 euro / t_{PA}

The personnel costs have been calculated on the basis of 20 workers (22,200 euro p.a.), 5 technicians (26,800 euro p.a.) and 1 engineer (52,095 euro p.a.). 75% overheads have also been included in the calculation.

These calculated costs only serve as reference figures since data was only available for a discontinuous process and were adapted by estimation. The annual capacity quoted here as an example is partly exceeded by plants in Germany.

12.1.5 BAT options

The chapter on "BAT options" describes ways in which the effects of plants on the environment can be reduced. Wherever possible, figures are also quoted which are regarded as BAT and should be met by the plants. The chapter makes no claim to be complete since additional or alternative possibilities exist to implement the BAT depending on special plants or special plant designs.

Reaction preparation

HMDA is not stable during transport. It is thus sensible to produce AH salt (in a n aqueous solution.) and then transport this. The production of AH salt also offers the possibility of cleaning the input materials.

The concentration of the AH salt should be as high as possible. 63% solutions are common. This has the advantage that the steam amount needed to remove the water from the solution during the reaction can be significantly reduced (60% lower than with a 40% AH solution). The concentrated solution has to be transported while hot. The energy inputs needed for this are low compared to the energy advantages during the reaction, particularly if the plant producing the AH salt is near the plant producing the PA 6.6.

Reaction

The AH salt is only reactive in an aqueous solution. The basic task is thus a controlled extraction of the water without a simultaneous high loss of the relatively volatile diamine. The water is thus generally evaporated under pressure in a nitrogen atmosphere. Following conversion of approx. 98-99% the pressure is reduced to facilitate extraction of the remaining water. The water has to be cleaned of entrained diamines and oligomers. The water is firstly condensed. After passing through a filter to remove the oligomers the condensate then passes through an ion exchanger. The cleaned water which leaves the ion exchanger should nevertheless be passed through a water treatment plant. The HDMA collected in the ion exchanger is removed with a flow of deionised water and can be used elsewhere to dissolve the adipic acid for the production of the AH salt.

The product still contains approx. 18% of water when it leaves the reactor.

Since the reactors are pressurised they have to be carefully sealed, particularly the agitator shafts.

Polymer separation and monomer recycling

PA 6.6 has only a slight tendency to form oligomers. Oligomer contents in the polymer are below 1%. The polymer thus does not have to be cleaned of monomers and oligomers.

The conversion rate after leaving the tube reactor is 98.5%. Any water still in the polymer has to be removed in further separators. Although the water separated here still contains HMDA, it also contains other impurities and cannot be used for HDMA recovery. However, the waste water must be treated.

Following extrusion and underwater granulation the water should be removed as completely as possible from the granulate, cleaned and returned to a closed system.

Waste is produced when cleaning the plant or changing between different product qualities. This may be able to be mixed with regular materials depending on the quality of the waste.

12.1.6 Assessment

If waste air flows are checked for organic components and possibly burned with energy recovery, this can be assessed as environmentally positive. However, care should be taken to ensure that this is only carried out with relevant concentrations since otherwise the environmental improvements through emission reductions will be cancelled out by the increased input of energy.

The concentration of the solution before the reaction to at least 60% can be assessed as environmentally beneficial. The great reduction in the amount of steam needed to remove the water during the reaction justifies this measure.

Evaporation of the water under pressure can be assessed as environmentally since this reduces the diamine losses. The effect on the resource consumption and emissions is favourable if the pressure is only reduced after an almost complete conversion of the diamine to separate the remaining water. The water should be cleaned in an ion exchanger. The HDMA is enriched during extraction from the water after the evaporator. This is advantageous not only for emission reasons because the HDMA can be returned to the reaction as a material input (resource savings).

HDMA recovery from the tube reactor's waste water on the other hand is not seen as practical on account of the low quantity of HDMA. The outlay to recover the HDMA is to high, a waste water treatment appears more sensible.

13 Potentials of exiting and new technologies

13.1 Development trends in polymer consumption

Polyolefines made up the largest share of polymer materials consumed in the world in 1997 with 68 million t of a total of 100 million t. The following polyolefines were consumed in 1997 /13/:

Material	Consumption in million t
Polypropylene	23,4
Polyethylene PE-HD	18,7
Polyethylene PE-LD	15,6
Polyethylene PE-LLD	9,8

In the thermoplastic polymer class, polyvinyl chloride (PVC) with a consumption in 1997 of 22.8 million t and polystyrene (PS) with 9,6 million t are also important in terms of consumption quantities alongside the aforementioned polyolefines.

Significant changes in polyolefine production are expected from the use of new catalysts. Compared to conventional heterogeneous Ziegler catalysts (e.g. $MgCl_2$ supported Ti-catalysts) or Phillips catalysts (chromium (IV) oxide on SiO_2 or Al_2O_3 carriers), the possibility of new variations to the microstructure and resulting product properties are of decisive advantage. The performance of conventional $MgCl_2$ supported catalyst systems was drastically increased in the past with each new generation of catalysts from an initial 15-30 kg/g catalyst to at present 80-160 kg/g catalyst in the case of polypropylene /20/.

Potentials through new catalysts

The gas phase process, initially used only to produce polyethylene, today plays a dominant role in the production of polyolefines. This covers the production of polypropylene (PP) homo- and copolymers, ethylene-PP-rubber, ethylene elastomers, low-density linear PE (PE-LLD) and high-density homopolymer PE (PE-HD). The production process for polyolefines has been radically changed through the use of new catalyst systems. This includes the polymerization of PE-HD at a lower pressure and the development of "metallocene PE-LLD". The widespread commercialisation of the gas phase process by BP Chemicals and DOW has greatly accelerated the development of new catalyst systems. The latest estimates indicate a demand for the new packaging material PE-LLD in 2005 of 300,000 tons. This is three times the world's total polyolefine consumption in 1997. Around 30 % of this demand will come from the replacement of PE-LD and the rest from the development of new fields of application based on properties such as odourlessness and a higher transparency /18/.

The use of metallocene catalysts allows the separate control of molecular weight and stereoregularity over a wide range with a simultaneous lower polydispersity M_w/M_n of around 2.0. This is also the precondition for the production of syndiotactic polypropylene (sPP), a new class in the polypropylene family.

Metallocene catalysts have been known for over 20 years in the production of polyolefines, though they did not become commercially available as metallocene polyethylenes from homogeneous processes (Exxon Chemical, Dow Chemical) until 1991 /19/. These were followed by "Luflexene", a polyethylene (BASF 1995) and "Metocene", a polypropylene (Tagor GmbH 1998), further polyolefines on the basis of carrier-fixed metallocenes /21/. Neutral estimates assume a production share of around 20% of standard polypropylene on the basis of metallocenes /19/. Metal complexes of titanium, zirconium, hafnium as well as inorganic complex compounds of nickel, palladium and iron are currently being investigated as catalysts and cocatalysts /22/.

Product properties can be tailored to specific needs by varying the molecular weight and microstructure of the polymer chain if metallocene catalysts are used with methylaluminoxane (MAO) as a cocatalyst (single-site-Catalyst). During copolymerization the metallocene catalysts are characterised by the production of products with an homogeneous comonomer distribution independent of the molecular weight.

The immobilisation of the metallocene on inert carrier material permits the very profitable, solvent-free production of polypropylene with low investment and energy costs. By comparison: the majority of existing polypropylene plants use a catalyst in the gasp phase or in liquid propylene /19/.

The carrier material and the conditions under which the metallocene and/or the cocatalyst MAO are applied to the carrier decides the polymerization activity and morphology. There are great potentials here for improvements in production and the product properties, including the synthesis of completely new copolymers.

As for the use of metallocene catalysts in place of standard Ziegler-Ti catalysts, the following advantages/disadvantages can be listed /23/:

- much wider variety of polymer structures
- very homogeneous polymers
- new products for new applications
- new and easier way of functionalising polymer structures
- simplification of the production processes

It is hereby essential that metallocene catalysts can be used in former production facilities.

Current disadvantages of the use of metallocene catalysts such as lower processability (due to the closer distribution of the molecular weight) and the complicated morphology control should be compensated by new approaches to catalyst development /20/. In the case of polypropylene a new catalyst technology, called the Multicatalyst Reactor Granule Technology (M.R.G.T.) /24/, is favoured. This is a combination of heterogeneous Ziegler-Natta catalysis with homogeneous catalysis such as metallocene and other single-centre organo-metallic polymerization catalysts /20/. The progress in M.R.G.T. is being accompanied by the development of a new process technology for the polymerization of the alpha-olefin in a new reactor (Multi-Zone Circulating Reactor /25/).

The development of metallocene catalysts is still in early days. The optimum has only been reached for a few processes such as the isotactic polymerization of propene.

The future will almost certainly bring customised structures and a whole range of new polymers and oligomers. Metallocene synthesis will then have a firm place in plastic technology /26/.

13.2 Regenerative thermic oxidation

Regenerative thermic oxidation (RTO) is used for exhaust air carrying organic substances.

Temperatures of at least 750°C have to be maintained during regenerative thermic oxidation to ensure a safe decomposition of organic pollutants in the waste air flow. Since the organic substances themselves have a calorific value, only little extra energy is needed to reach these temperatures with higher loads. A normal gas burner is thus generally used.

With larger air volumes and lower concentrations of organic substances (reference value less than 1 g/m^3) a concentrator can be used which is followed by an activated carbon plant or a thermic/catalytic combustion. The concentrator reduces the air containing solvent by a factor of ten so that only a smaller combustion plant is needed. The concentrated mixture requires little or no input of external energy during combustion in the oxidator.

If there is more than around 1 g/m^3 solvent in the waste air regenerative thermic oxidation is recommended. The principle of this technology is based on passing the waste gas from the gas burner through a bed of inert material which largely absorbs the waste heat from the burner. Through a clever gas control, the energy stored in the inert material can be used to pre-heat the waste air flow up to shortly before its ignition point. The use of additional energy can thus be minimised.

Plants with capacities between 500 and 100,000 m^3/h are available in a compact design and with low pressure losses. Thermal efficiencies of 94 to 97% can be achieved, above all with large surface areas.

14 General BAT options

This chapter will summarise generally valid options for a plant to produce a polymer according to the BAT. The specific options for the individual processes have been described in the respective chapters. In general it can be said that different markets exist for the various polymer product qualities. Special processes are hereby used, each with specific levels of freedom. Thus, different production processes may be valid for one type of polymer according to BAT conditions.

Energy demand during polymer separation

An important part of the input energy is consumed during polymer separation. In liquid phase processes in particular, a good separation is only possible through the energy-intensive thermal drying processes. It is sensible to increase the solids share before thermal drying by using mechanical dryers. This is normally more energy efficient. The energy demand is shifted away from steam to electrical energy through the use of mechanical dryers. Of course, in the end the overall energy demand for drying is relevant. However, it should be remembered that in a combination plant where a lot of steam is available as "waste", a purely thermal drying may nevertheless have its advantages.

The use of heating gas for drying purposes can be assessed as environmentally positive if the input of electrical energy in flow dryers is substituted and a CO-NO_x co-ordinated firing control is used and regulated. Under German conditions, electricity has a primary energy efficiency of 33%, so that the efficiency of a natural gas firing and supply is much higher at 85-90%.

Process safety and quality control

An important demand on any industrial process is that it runs stably with no disturbances and supplies the desired quality for the products. The quality control measures taken by industry in this connection also lead to a reduction of environmental loads since a failure almost always leads to additional emissions.

Form the point of view of a BAT the quality efforts made by companies should be increased. There should be an automatic process control with continuous recording of quality, process and environmental parameters. This information can be called up by engineering and management and used to further optimize the process. Continuous recording or environmentally relevant parameters also allows an effective control of whether existing emission limits are being observed.

Batches which do not meet the required specifications should be avoided. This can be achieved, for example, through automatic weighting and the automatic feed of materials.

A further quality problem can arise through deposits in the reactor. These can be reduced by improving the recipes and high flow velocities. Nevertheless, the reactor still has to be cleaned from time to time. In order to reduce emissions when the reactor is opened, it can be cleaned when closed using suitable systems. This is particularly recommended for processes where harmful monomers or solvents can escape when the reactor is opened and can lead to problems of safety at the workplace. If the reactor nevertheless has to be opened for cleaning or maintenance, the following measures should be taken to reduce gaseous emissions:

- creation of a vacuum
- rinsing the reactor with inert gas
- rinsing the reactor with steam
- displacing the reactor contents with water

Diffuse emissions

Significant progress has been made over the past 15 years in the field of emission reductions from diffuse sources. The emission limits for organic substances have been reduced, for example at BASF in Ludwigshafen from approx. 400 t/a in 1987 to approx. 225 t/a in 1996. Since total emissions in this period could be cut above average through process improvements from approx. 3150 t/a to approx. 1250 t/a, the share of diffuse emissions rose from approx. 13% to approx. 17%. The importance of diffuse sources thus rose although their environmental significance has not risen in absolute terms /33/. The share of source groups for diffuse emissions is divided up as follows:

- 44% fittings
- 22% pumps
- 15% flanges in contact with fluids
- 6% sealing elements for compressors
- 3% flanges in contact with gaseous substances

Seals play a significant role in reducing diffuse emissions. The choice of a suitable seal can thus be seen as relevant for a BAT. The leak rates of selected asbestos-free seals are compared in the following /33/:

- Aramide fibres approx. 0.005-0.7 mg/(s*m)
- Graphite approx. 0.04-0.1 mg/(s*m)
- PTFE approx. 0.005-0.06 mg/(s*m)

The following measures can be taken to reduce or prevent leaks which may lead to volatile, airborne emissions:

- Valves: the use of diaphragm, double seals or similar effective fittings.
- Pumps: double seals with fluid stop, magnetically operated or encapsulated.
- Compressors and vacuum pumps: double seals with fluid stop, magnetically operated or encapsulated.
- Agitator: double seals with fluid stop, magnetically operated or encapsulated
- Flanges: minimisation of the number, use of high-quality seals

Monitoring volatile emissions as regards workplace concentrations should include:

- Individual measurements of VCM using hand-held devices (to look for leaks)
- Personal control devices (e.g. control buttons with activated carbon))

Continuous recording using instruments at all relevant points in the plant's air system may also be installed.

What to do in the event of an accident

Additional precautions to prevent the discharge of VCM into the atmosphere can include:

- Computer-aided monitoring of the reactor input and operating states
- Emergency power supply for the agitator
- Emergency cooling units for the reactor, emergency condensation
- Controlled emergency venting of the reactor through to plant parts for monomer recovery, blow down, controlled combustion
- Chemical e-stop system (deactivation of the reaction)

Integration of other plants

Both integrated and isolated plants have advantages. Integrated plants display fewer transport processes and diffuse emissions from supply processes. Larger isolated plants to produce initial products which supply a number of production plants can lead to a more efficient production of initial products. Location aspects play an important role (e.g. historical site or utilization/refining of by-products to extend the production plant).

Closed cycle system for water

Following underwater granulation the water should be separated from the polymer as fully as possible. The separated water can be run in a closed cycle system to avoid a waste water problem and spare resources. The cyclic water then has to be treated, e.g. through a filter, to avoid an enrichment of polymer particles and additives.

Conversion of plants to water cooling with a closed cycle water system and treatment of the cyclic water is sensible. This conversion has been almost completed in Germany.

Monomer recycling

Material flows which contain unreacted monomer occur at various points in a plant for the synthesis of plastics. There are various ways of dealing with these material flows depending on their volume flows and the monomer concentration:

- In the case of material flows with high monomer concentrations the monomer can be recovered in the reaction. Raw materials are saved and emissions avoided in this manner. However, the recovered monomer often has to be cleaned to prevent high concentrations of impurities in the system.
- Transfer of the flow to an integrated plant which uses this to produce a different product. Other production processes may be less sensitive to the impurities and this sometimes avoids the costly and energy-intensive cleaning of the flow.
- At high volume flows and low concentrations of the monomer thermal afterburning is often the only alternative. To reduce the energy-intensive heating of the high volume flow to ignition temperature it may be advantageous to concentrate the

monomer in the material flow before combustion. This can take place, for example, in absorption columns which remove the monomer from the flow. Only a lower volume flow which is used to regenerate the column then has to be thermally treated.

Waste heat utilisation

The waste heat from the plant, such as is produced e.g. in the reaction, the TNV or in high-performance compressors, should be used in combination plants wherever this is possible and can be implemented with few extra plant installations in the plant design.

Dust development

Granulation, transport, storage, blending and filling of the products vary and in some cases are quite complex depending on the product mix of the production plant. A common feature of all plants is that the granulate is conveyed pneumatically in these and that the waste air from the conveyor system contains plastic dust and monomer which escapes from the polymer as gas. The waste air thus has to be dedusted (cloth filter, washer, etc.) and thermally burnt depending on the monomer concentration. Another possibility is of course to clean the waste air and leave it in the closed cycle system. This is particularly sensible if an inert gas such as nitrogen is used for rinsing and conveying.

15 Summary

15.1 Low-density polyethylene (PE-LD)

15.1.1 High-pressure process in a tube reactor

Main product	Amount	Unit	Comment
PE-LD	1	kg	
By-product			
Ethylene (impure)	0.025 - 0.035	kg	1)
Steam (low-pressure)	0.8 - 1.0	kg	industry
Steam (medium-pressure)	0.1 - 0.2	kg	/3/
Energy carrier			
Electricity	0.825 - 1.05	kWh	/3/, /4/, 1)
Steam (very low pressure)	0 - 0.18	kg	/4/, industry
Kerosene	no data (not always used).	kg	(industry)
Substances			
Ethylene	1.01 - 1.05	kg	/3/, /4/, 1)
Cooling water	100 - 200	kg	/3/, /4/, 1)
Inert gas (nitrogen)	0.001 - 0.003	Nm3	/4/, 1)
Initiator	5E-5 - 0.002 (0.0002 - 0.001)	kg	/3/, industry
Process water	0.4 - 1.2	kg	1), industry
Compressed air	0.02 - 0.04	Nm3	1)
Emissions to air			
VOC	0.004 - 0.006	kg	1)
Particle	1.5E-6 - 7.5E-6	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	1.5E-5 - 8E-5	kg	1)
Biological oxygen demand (BOD)	1E-5 -1.5E-5	kg	1)
Solids (suspended)	<1E-4. 3E-4 - 4E-4 (not recorded)	kg	1) 2), (industry)
Nitrate	2E-5 - 3E-5 (not recorded)	kg	1), (industry)
Hydrocarbons	<7E-6 (not recorded)	kg	1), (industry)
Waste water	0.01 - 0.02	kg	1)
Cooling water	154 - 200 (not recorded)	kg	/3/, /4/, (industry)
Wastes			
Total waste	0.001 - 0.002	kg	industry
Near-domestic industrial waste	0.001 - 0.003	kg	1)

1) Figures based on IKP estimates
2) Figures from /5/ estimated by IKP

The conversion rate of the monomer per passage through the reactor is between 20 and 35%. Since the recovered monomer has to be compressed and heated before the next passage through the reactor the highest possible conversion rate (>30%) within the reaction conditions determining this parameter should be aimed at. The division of the reactor into temperature zones with quenching through the input of cold monomer contributes to higher conversion rates.

The majority of the monomer has to be separated from the mixture after the reactor in the high-pressure separator and recycled. The high pressure level of this monomer flow means that it only has to pass through one compression stage before re-entering the reactor. The monomer quantities separated in the low-pressure separator have to pass through both pressure stages. It is thus sensible to keep the share of monomer which is separated in the high-pressure separator as high as possible. A separation of >90% in the high-pressure stage appears possible.

Part of the monomer recycling flow is normally transferred outward to avoid an enrichment of impurities in the material cycle. This discharged share should best be returned to ethylene producers where it can be recycled and used as a raw material for other purposes. Primary ethylene can be replaced in this manner, which in turn takes a load off the environment.

15.2 High-density polyethylene (PE-HD)

15.2.1 Suspension process in an autoclave reactor

Main product	Quantity	Unit	Remark
PE-HD	1	kg	
By-product			
Ethylene	0.002 - 0.02	kg	1)
Energy carrier			
Electricity	0.3 - 0.45 (0.35)	kWh	/3/, /12/, 1)
Steam (total, no pressure data)	0.3 - 1	kg	/12/, 1)
Materials			
Ethene	1.01 - 1.06 (1.02)	kg	/3/, /12/, 1)
Inert gas (nitrogen)	0.030 - 0.11	Nm3	/12/, 1)
Cooling water	20 - 250	kg	/3/, 1)
Process water	0.5 - 4	kg	1)
Compressed-air	0.02 - 0.04	Nm3	1)
Hexane	0.004 - 0.015	kg	1)
NaOH 50%	0.01 - 0.015	kg	1)
Hydrogen	0.0001 - 0.0005	kg	/3/, 1)
Catalyst	8.33E-5 - 3E-4	kg	/6/, 1)
Emissions to air			
Waste air	0.04 - 0.06	kg	1)
VOC	0.0025 - 0.0035	kg	1)
Particle	1.5E-6 - 6.5E-6	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	6E-7 - 2.5E-5	kg	1)
Biological oxygen demand (BOD)	1.2E-6 - 8E-6	kg	1)
Solids (suspended)	< 2.5E-5	kg	1)
Nitrate	5E-10 - 9E-5	kg	1)
Hydrocarbons	1E-5 - 1.5E-5	kg	1) 2)
Heavy metals	6E-10 - 1E9	kg	1)
Wastes			
Near-domestic industrial waste	0.001 - 0.0035	kg	1)
Hazardous waste	0.00006 - 0.00075	kg	1)

1) Figures based on IKP estimates
2) Figures from /5/ estimated by IKP

Organic vapours are extracted from the reactor for purification. High and low-molecular impurities are separated in a multi-stage process. These impurities should be burnt and the waste heat used. The recovered solvent which contains ethylene residues can be recycled.

A higher concentration of solids in the polymer sludge when this leaves the reactor is advantageous to guarantee a more efficient production with respect to the energy and materials. This leads namely to a lower energy demand during separation of the solvent from the polymer. The goal should be solid concentrations of > 30%.

15.2.2 Suspension process in a loop reactor

Main product	Quantity	Unit	Remark
PE-HD	1	kg	
Energy carrier			
Electricity	0.3 - 0.5	kWh	1), industry
Steam (total, no pressure data)	0.16 - 0.25	kg	1), industry
Materials			1)
Ethene	1.01 - 1.03	kg	1)
Inert gas (nitrogen)	0.030 - 0.05	Nm3	1)
Cooling water	20 - 150 (100 - 200)	kg	1), (industry)
Process water	0.5 - 4	kg	1)
Compressed-air	0.02 - 0.04	Nm3	1)
Isobutane	0.004 - 0.006	kg	1)
Catalyst	0.0001 - 0.0002	kg	1)
Emissions to air			1)
Waste air	0.04 - 0.05	kg	1)
VOC	0.005 - 0.0075	kg	1)
of which isobutane	0.002 - 0.003	kg	1)
Particles	1.5E-6 - 6.5E-5	kg	1)
Emissions to water			1)
Chemical oxygen demand (COD)	6E-7 - 2.5E-5	kg	1)
Biological oxygen demand (BOD)	1.2E-6 - 8E-6	kg	1)
Solids (suspended)	< 2.5E-5 (not recorded)	kg	1), (industry)
Nitrate	5E-10 - 9E-5 (not recorded)	kg	1), (industry)
Waste water	3 - 4	kg	1)
Hydrocarbons	7E-6 - 1.5E-5 (not recorded)	kg	1), (industry)
Heavy metals	8E10 - 1.2 E9 (not recorded)	kg	1), (industry)
Wastes			1)
Overall waste	0.001 - 0.0035	kg	industry
Near-domestic industrial waste	0.001 - 0.0035 (not recorded)	kg	1), (industry)
Hazardous waste (solvent)	0.00004 - 0.0005 (not recorded)	kg	1), (industry)

1) Figures based on IKP estimates

A solvent with a low boiling point is used so that it can be easily separated from the polymer. This is favourable in terms of the energy demand. The low boiling point of the solvent means there is a risk of higher diffuse emissions. Since isobutane is not toxic, care should be taken to ensure that the measures to reduce emissions are economically justifiable.

The solvent is separated in a flasher after it leaves the reactor. Since the solvent has a lower boiling point a single-stage separation is generally adequate. Any solvent remaining in the polymer can be removed by rinsing with nitrogen in a dryer. It is sensible to treat the nitrogen and use it in a closed cycle. The solvent produced during nitrogen treatment should be recycled, this reduces the energy demand to separate the solvent.

15.2.3 Gas phase process in a fluidized bed reactor

Main product	Quantity	Unit	Remark
PE-HD	1	kg	
Energy carrier			
Electricity	0.3 -0.45	kWh	/3/, /4/, 1)
Steam (total, no pressure data)	negligible	kg	1)
Fuel	8E-6- 1E-5	kg	/3/
Materials			
Ethene	01.01.02	kg	/3/, /4/, 1)
Inert gas (nitrogen)	0.03 - 0.08	Nm3	/3/, /4/, 1), (industry)
Cooling water	60 - 140 (100 - 200)	kg	/3/, 1), (industry)
Compressed-air	0.04 - 0.06	Nm3	1)
Hydrogen	1.5E-4 -1.7E-4	kg	/3/
Catalyst	1.5E-6 - 1.0E-4	kg	/4/, industry
Emissions to air			
Waste air	0.1 - 0.15	kg	1)
VOC	0.003 - 0.005 (> 0.01)	kg	1), (industry)
Particles	3E-6 - 8E-5 (> 4E-4)	kg	1), (industry)
CO	4.8E-6 -6E-6 (not recorded)	kg	1), (industry)
CO2	0.024 - 0.031 (not recorded)	kg	1), (industry)
Emissions to water			
Chemical oxygen demand (COD)	negligible (< 0.12)	kg	1), (industry)
Biological oxygen demand (BOD)	negligible (< 0.04)	kg	1), (industry)
Solids (suspended)	negligible (not recorded)	kg	1), (industry)
Nitrate	negligible (not recorded)	kg	1), (industry)
Wastes			
Total waste	< 1.0	kg	industry
Near-domestic industrial waste	0.001 - 0.0035 (not recorded)	kg	1)
Hazardous waste	negligible (not recorded)	kg	1)

1) Figures based on IKP estimates

Compared to the two fluid phase processes a positive feature which should be stressed is that no solvent is used in the gas phase process. The possibility of doing away with a solvent has a number of advantages provided the specific process energy inputs do not rise significantly. No organic input material has to be provided, with corresponding consumptions of raw materials and energy, and there are no almost unavoidable diffuse emissions. Another positive aspect is that no work is needed to separate the solvent.

Conversion of the monomer per passage through the reactor is 2 – 3%, it should be as high as possible to keep the outlay for gas recovery low.

15.3 Polypropylene (PP)

15.3.1 Suspension process

Main product	Quantity	Unit	Remark
PP isotactic	1	kg	
Energy carrier			
Electricity	0.15 - 0.6	kWh	/3/, /12/, 1)
Steam (total,no pressure data)	0.15 - 0.5	kg	/3/, /12/, 1)
Heating gas	0.1 - 0.2	Nm3	1)
Materials			
Propylene	01.01.04	kg	/3/, /12/, 1)
Inert gas (nitrogen)	0.05 - 0.07	Nm3	1)
Cooling water	70 - 120	kg	/3/, /12/, 1)
Process water	2.5 - 3.5	kg	1)
Compressed-air	0.003 - 0.3	Nm3	1)
Hydrogen	3E-5 - 5E-3	kg	/3/, 1)
Catalyst	1.4E-5 - 1E-3	kg	/6/, 1)
Emissions to air			
Particles	1.5E-5 - 4E-5	kg	1)
NMVOC	1E-3 - 1.5E-3	kg	1)
CO	2E-6 - 1.5E-4	kg	1)
CO2	0.1 - 0.3	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	1.5E-4 - 2E-4	kg	1)
Biological oxygen demand (BOD)	2E-5 - 4E-5	kg	1)
Solids (suspended)	< 1.4E-5	kg	1)
Nitrate	1.8E-5 - 2.1E-4	kg	1)
Waste water	03.05.05	kg	1)
Hydrocarbons	1E-5 - 1.6E-5	kg	1)
Wastes			
Near-domestic industrial wastes	1.5E-3 - 1E-5	kg	1)
Hazardous waste	5.5 - 7.5E-4	kg	1)

1) Figures based on IKP estimates

The use of stereospecific catalysts reduces not only the amount of catalyst required due to the higher activity but also leads to higher yields of the desired product quality with a concomitant optimised resource efficiency.

The prevention of fouling (caking) through sufficiently high volume flow rates is should be assessed as positive in terms of the environment for two reasons. The use of coolant is reduced since the heat transmission would deteriorate though the fouling. Secondly, any openings in the system for cleaning purposes or the input of cleaning chemicals are minimised and thus emissions and the input of materials and energy (e.g. inert gas rinsing, steam rinsing) to avoid such emissions are reduced.

15.3.2 Gas phase process in a fluidized bed reactor

Main product	Quantity	Unit	Remark
PP isotactic	1	kg	
Propylene, impure	0.02 -0.04	kg	1)
Energy carriers			
Electricity	0.4 - 0.6	kWh	1)
Steam (total, no pressure data)	0.25 - 0.35	kg	1)
Materials			
Propylene	1.02 - 1.05	kg	1)
Inert gas (nitrogen)	0.04 - 0.05	Nm3	1)
Cooling water	40 - 60	kg	1)
Compressed-air	k.A.	Nm3	
Hydrogen	1E-4 - 2E-4	kg	1)
Catalyst	2.5E-5 - 3E-4	kg	/6/, /30/
Emissions to air			
Particles	3E-5 - 5E-5	kg	1)
NMVOC	3E-4 - 5E-4	kg	1)
Emissions to water			
Chemical oxyvgen demand (COD)	negligible	kg	1)
Biological oxygen demand (BOD)	negligible	kg	1)
Solids (suspended)	negligible	kg	1)
Nitrate	negligible	kg	1)
Wastes			
Near-domestic industrial waste	1.5E-3 - 1E-5	kg	1)
Hazardous waste	negligible	kg	1)

1) Figures based on IKP estimates

The Unipol process to produce PP can be regarded as being comparable to the PE-HD gas phase process except for the type of input monomer material (propylene instead of ethylene) and a special catalyst variant. The BAT options thus correspond to those mentioned in Chapter 15.2.3.

15.3.3 Gas phase process in a vertical reactor

Main product	Quantity	Unit	Remark
PP isotactic	1	kg	
Propene, impure	0.02 -0.04	kg	1)
Energy carriers			
Electricity	0.35 - 0.5	kWh	/3/, 1)
Steam (total, no pressure data)	0.25 - 0.35	kg	1)
Materials			
Propene, impure	1.015 - 1.055	kg	/3/, 1)
Inert gas (nitrogen)	0.04 - 0.045	Nm3	/3/, 1)
Cooling water	40 - 85	kg	/3/, 1)
Process water	0.2 - 2	kg	1)
Compressed-air	k.A.	Nm3	1)
Wasserstoff	1E-4 - 2E-4	kg	/3/, 1)
Catalyst	2.5E-5 - 3E-4	kg	/6/, /30/
Emissions to air			
Particles	3E-5 - 5E-5	kg	1)
NMVOC	5E-4 - 8E-4	kg	1)
Emissions to water			
Chemical oxygen demand (COD)	negligible	kg	1)
Biological oxygen demand (BOD)	negligible	kg	1)
Solids (suspended)	negligible	kg	1)
Nitrate	negligible	kg	1)
Wastes			
Near-domestic industrial waste	1.5E-3 - 1E-5	kg	1)
Hazardous waste	negligible	kg	1)

1) Figures based on IKP estimates

The reactor contains a filter to separate polymer from the gas phase (monomer). This filter should be regularly back-flushed with monomer so that the reactor does not have to be opened to clean the filter. This prevents monomer emissions.

Material recycling of the separated and heavily polluted solvent is assessed as being of little environmental advantage since the energy and material inputs for processing could cancel out or be higher than the advantages of saving fresh solvent.

15.4 Polyvinyl chloride (PVC)

15.4.1 Suspension process

Hauptprodukt	Quantity	Unit	Remark
S-PVC	1	kg	
Energy carriers			
Electricity	approx. 0.2 a)	kWh	/3/, 1)
Steam (medium pressure)	0.95 - 1.05 b)	kg	/3/, /32/, 1)
(Fuel (preferably natural gas))	(approx. 0.3) a)	MJ	1)
Materials			
Vinyl chloride monomer	1.005 - 1.02	kg	/7/, /3/, /32/, 1)
Deionised water	0.9 - 1	kg	/2/, /32/, 1)
Initiator	0.0003 - 0.0008	kg	/2/
Inter gas (nitrogen) process material	no data a)	kg	
Protective colloid/Emulsifier, methyl-cellulose	0.0005 - 0.0015	kg	/2/, 1)
Cooling water (process material)	100 - 200 d) a)	kg	/3/, 1)
Process materials: e.g. soda lye, hydrogen chloride	0.0015 - 0.004	kg	/32/
Air (process material)	1- 2 c)	kg	1)
Process water	3 - 5	kg	/32/
Emissions to air			
VOC	5E-5 - 2E-4	kg	1)
of which VCM	bis zu 1.9E-4 e)	kg	/7/, /32/
other VOC	1E-5 - 5E-5	kg	/32/
Particles	6.5E-5 - 1.5E-4	kg	/7/, /32/, 1)
Waste air	1 - 2	kg	1)
CO	negligible f)	kg	/32/
CO2	negligible f)	kg	/32/
SOx	negligible f)	kg	/32/
NOx	negligible f)	kg	/32/
NH3	no data g)	kg	
Emissions to water			
Chemical oxygen demand (COD)	0.00015 - 0.00075 a)	kg	/5/, /7/, 1)
Biological oxygen demand (BOD)	5E-5 - 3.75E-4 h)	kg	/5/, 1)
(Adsorptive organically bonded halogens (AOX))	(3.8E-6 - 5E-6) i)	kg	1)
NH4+	0.000002 a)	kg	/5/
Solids (suspended)	0.00006 - 0.0005 a)	kg	/5/, /7/, 1)
Other nitrogen compounds	no data j)	kg	
Phospate as P2O5	no data j)	kg	
VCM	1E-6 - 5E-6	kg	/32/
(Chromium unspecific)	(2E-7 - 7E-7) k)	kg	/7/, 1)
Waste water	1.15 - 4	kg	/2/, 1)
Cooling water	100 - 200	kg	/3/, 1)
Wastes			
Near-domestic industrial waste	0.002 - 0.003 l)	kg	1)

1) Figures based on IKP estimates

Fouling of the reactor should be prevented. The "closed reactor technology", i.e. the process control and cleaning of the reactor in a closed system can be seen as the BAT for all new and future plants.

VCM is mainly emitted in the dryer waste air. One way to reduce these emissions is thermal afterburning of the dryer waste air.

15.5 Polystyrene (PS)

15.5.1 Mass polymerization

Main product	Quantity	Unit	Remark
PS	1	kg	
Energy carriers			
Electricity	0.06 - 0.2	kWh	/3/, 1)
Steam (total, no pressure data)	0.05 - 0.2	kg	/3/, 1)
Thermal energy	0.12 - 0.6	kg	
Materials			
Styrene	0.88 - 1.015	kg	/3/, 1), industry
Ethyl benzene	0.01 - 0.015	kg	/3/
Polybutadiene	0 - 0.12	kg	/3/, 1), industry
Inert gas (nitrogen)	0.01 - 0.02		industry
Mineral oil	0 - 0.08	kg	/3/, 1), industry
Cooling water	15 -45 (0.3 - 0.4 kWh)	kg	/3/, 1), (industry)
Process water	0.05 - 8	kg	/3/, 1)
Air	0.15 - 0.2	kg	1)
Stabilisers and additives	0 - 0.01	kg	industry
Emissions to air			
Waste air	0.15 - 0.2 (1.5 - 2)	kg	1) , (industry)
VOC	5E-5 - 4E-4	kg	1)
of which styrene	4.7E-5 - 3.9E-4		1)
Particles	2E-6 - 2E-5	kg	1)
Emissions to water			
Waste water	0.05 - 0.1	kg	1)
Cooling water	15 -45	kg	1)
Chemical oxygen demand (COD)	3.6E-6 - 1.7E-5	kg	1)
Biological oxygen demand (BOD)	4.5E-7 - 1.7E-6	kg	1)
Solids (suspended)	2.9E-6 - 5.2E-5	kg	1)
Hydrocarbons	6.9E-7 - 5.4E-6	kg	1)
Wastes			
Near-domestic industrial waste	1.7E-3 - 4E-2	kg	1)

1) Figures based on IKP estimates

The almost complete conversion of the styrene and recovery of unreacted monomer must be rated as positive, which is why high conversion rates can apply as key parameters. The amounts of styrene which are converted do not have to be separated from the polymer, nor recycled nor treated. The positive aspect is the resulting increased resource efficiency.

15.6 Acrylonitrile-butadiene-styrene (ABS)

15.6.1 Suspension polymerization

Main product	Quantity	Unit	Remark
ABS	1	kg	
Energy carriers			
Electricity	0.35 - 0.65	kWh	/3/, 1)
Steam (total, no pressure data)	01.05.02	kg	/3/, 1)
Fuel (natural gas)	0.05	kg	/3/
Materials			
Styrene	0.52 - 0.62	kg	/3/, 1), industry
Acrylonitrile	0.21 - 0.28	kg	/3/, 1)
Butadiene	0.15 - 0.26	kg	/3/, 1), industry
Emulsifier	0.02	kg	/3/
Inert gas (nitrogen)	0.02 - 0.05	Nm3	/3/, 1)
Chain transfer agent (Mercaptan)	0.006	kg	/3/
Cooling water	18 - 50	kg	/3/, 1)
Process water	3 - 12	kg	/3/, 1)
Air	02.05.03	kg	/3/
Emissions to air			
Waste air	02.05.03	kg	1), industry: irrelevant
VOC	3E-3 - 5E-3	kg	1)
of which styrene	0.0013 - 0.0032	kg	1)
of which acrylonitrile	0.00055 - 0.00152	kg	1)
of which butadiene	0.0005 - 0.00142	kg	1)
Particles	3.6E-5 - 2.7E-4	kg	1), industry: irrelevant
Emissions to water			
Waste water	3 - 12	kg	1)
Cooling water	25 - 35	kg	1)
Chemical oxygen demand (COD)	1.5E-3 - 8.3E-3	kg	1)
Biological oxygen demand (BOD)	2.8E-5 - 3E-3	kg	1)
Hydrocarbons (acrylonitrile)	5E-5 - 1E-3	kg	1)
Wastes			
Near-domestic industrial waste	0.0037 - 0.03	kg	1)
Hazardous waste	< 3.3E-3	kg	1)

1) Figures based on IKP estimates

The condensation of the residual monomer content during the production of the polybutadiene-matrix after a pressure drop when the reactor is opened and the monomer recovered can be assessed as environmentally favourable if the waste water is forwarded for waste water treatment. This increases the efficiency of the initial product input and reduces butadiene emissions.

15.7 Polyamide 6.6

15.7.1 Polymerization from AH salt

Main product	Quantity	Unit	Remark
PA 6.6	1	kg	
Energy carriers			
Electricity	0.08 - 0.2	kWh	/3/, [1)]
Steam (total, no pressure data)	0.2 - 2.3	kg	/3/, [1)]
Thermal energy	0.15 - 0.3	kg	/3/, [1)]
Materials			
HMDA	0.46 - 0.57	kg	/3/, [1)]
Adipic acid	0.57 - 0.69	kg	/3/, [1)]
Inert gas (nitrogen)	0.001 - 0.002	Nm3	[1)]
Cooling water	100 - 200	kg	/3/, [1)]
Process water	2 - 6	kg	/3/, [1)]
Emissions to air			
VOC	< 2E-4	kg	[1)]
Particles	8E-5 - 2.7E-4	kg	[1)]
Ammonia	3.4E-7 - (3.5E-5)	kg	[1)]
Emissions to water			
Chemical oxygen demand (COD)	7.9E-4 - 1.8 E-3	kg	[1)]
Biological oxygen demand (BOD)	2E-4 - 2.2E-3	kg	[1)]
Solids (suspended)	k.A.	kg	
Hydrocarbons	4E-5 - 7E-4	kg	[1)]
Wastes			
Near-domestic industrial waste	0.02 - 0.072	kg	[1)]

[1)] Figures based on IKP estimates

The concentration of the AH salt should be as high as possible. 63% solutions are common. This has the advantage that the steam amount needed to remove the water from the solution during the reaction can be significantly reduced (60% lower than with a 40% AH solution). The concentrated solution has to be transported while hot. The energy inputs needed for this are low compared to the energy advantages during the reaction, particularly if the plant producing the AH salt is near the plant producing the PA 6.6..

Evaporation of the water under pressure can be assessed as environmentally since this reduces the diamine losses. The effect on the resource consumption and emissions is favourable if the pressure is only reduced after an almost complete conversion of the diamine to separate the remaining water. The water should be cleaned in an ion exchanger. The HDMA is enriched during extraction from the water after the evaporator. This is advantageous not only for emission reasons because the HDMA can be returned to the reaction as a material input (resource savings).

16 Sources

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Appendix A: Exemplary lists of apparatus for polymerizations

The lists of apparatus are to be understood as an exemplary choice. Alternative designs can be practical depending on the plant concept and may meet the requirements of a BAT.

A1 Low density polyethylene

Apparatus for reaction preparation, injection, reaction

Ethylene filter
Gas heater
Ethylene tank
Telogene drum
Telogene cooler
Telogene filter
Oxygen filter
Oxygen cooler
Low-pressure telogene compressor
High-pressure telogene compressor
Oxygen compressor
Co-monomer compressor
Co-monomer cooler
Co-monomer drum
Primary compressor
Primary compressor intermediate cooler
Various motors
Primary compressor aftercooler
Intermediate filter
Secondary compressor
Secondary compressor intermediate cooler
Reactor inlet cooler
Tube reactor (Autoclave reactor)
Product cooler

Apparatus for polymer separation

High-pressure-separator
Flow valve
Low-pressure separator
Recycle gas cooler
Wax separators
Wax pump
Wax drum
Low-pressure wax separator
Low-pressure recycle gas cooler
Equalizing reservoir
Recycle gas compressor
Motor

Apparatus for extrusion, packaging, dispatch

Extruder	Various air filters
Extruder motor	Various hoppers
Additive extruder	Various cyclones
Agitator motor	Scales
Water pump	Air heater
Water tank	Silos
Dehydrator	Bagging plant
Water cooler	Metal detectors
Water filter	Various conveyor belts
Classifier	Pelletizer
Magnetic separator	Shrink wrapping plant
Various compressors	

A2 High-density polyethylene

A2.1 Suspension process in an autoclave reactor

Apparatus for reaction preparation and reaction

Ethylene tank
(Co-monomer tank)
Solvent tank
Hydrogen tank
Catalyst tank
Solvent tank
Storage tank/mixing tank
Autoclave reactor (also a number in series)
Various agitator motors
Second polymerization reactor (Run-Down)
Agitator motor

Apparatus for polymer separation

Centrifuge
Motor
Fluidized bed dryer
Solvent condenser
Nitrogen compressor

Apparatus for extrusion, packaging, dispatch

Extruder
Extruder motor
Tank for crude polymer
Tank for granulate
Various feed pumps
Stabiliser tank

A2.2 Suspension process in a loop reactor

Apparatus for reaction preparation and reaction

Tank for fresh solvent
Tank for prepared solvent
Preparation for solvent
Tanks for ethylene
Tank for catalyst
Tank for co-monomer
Loop reactor
Agitator
Various motors
Compressor

Apparatus, materials and energies for polymer separation

Evaporation reactor
Various compressors
Various motors
Reactor for nitrogen rinsing
2 columns for solvent preparation
4 pulsed hot-air generators
Flare
Pump

A2.3 Gas phase process in a fluidized bed reactor

Apparatus for reaction preparation and reaction

Ethylene tank
Preparation for ethylene
Co-monomer tank
Catalyst tank
Distributing device for catalyst
Fluidized bed reactor
Intermediate cooler
Compressor
Motor

Apparatus for polymer separation

Cyclone
Filter
Flare
Surge tank
Compressor
Motor

Apparatus for extrusion, packaging, dispatch

Storage tank for crude polymer
Tank
Extruder
Dryer
Storage tank for granulated polymer
Tank
Filling plant

A3 Polypropylene

A3.1 Suspension process

Apparatus for reaction preparation and reaction

Lop reactor 2x
Agitator 2x
Motor 2x

Apparatus for polymer separation

Evaporation reactor
Pump
Various motors
Reactor for additive feed
Compressor

Apparatus for extrusion, packaging, dispatch

Silo
Metering plant for additive
Tank for additive
Flare
Gravimetric metering 2x with motor
Mixer
Various motors
Extruder
Granulation
Cooler
Filter
Pump
Tank
Centrifuge
Classifier
Magnetic separator

A3.2 Gas phase process in a fluidized bed reactor

Apparatus for reaction preparation and reaction

Fluidized bed reactor
Cooler
Compressor
Motor

Apparatus for polymer separation

Cyclone
Rinsing tank

A3.3 Gas phase process in an autoclave reactor

Apparatus for reaction preparation and reaction

Storage tank for catalyst
Storage tank for co-catalyst
Ball mill
Various motors
Conveyor belt
Storage tank for catalyst solution
Storage tank for co-catalyst solution
Various agitators
Various pumps
Dryer
Various coolers
Tank
Reactor
Evaporator

Apparatus for polymer separation

Separator
Demister
Cyclone
Various tanks
Dryer
Cooler
Heater
Compressor 2x
Motor 2x
Pump
Conveyor belt

Apparatus for extrusion, packaging, dispatch

Various tanks
Washing tower
Various coolers
Heater
Various pumps
Various filters
Dryer
Extruder
Various motors
Granulation
Flare

A4 Polyvinyl chloride

Apparatus for reaction preparation, reaction, stripping

Water tank
Initiator tank (cooled or stored as emulsion)
Initiator mixing tank with agitator
Initiator pump
Initiator metering system
Various shut-off valves
Protective colloid tank
Protective colloid mixing tank with agitator
Protective colloid pump
Autoclave reactor with agitator
Condenser for reactor cooling
Compensation tank
Pump for cooling system
Various waste water pumps
Reactor product transfer pump
Stripper tank with agitator
Stripper pump
Stripper column
Head condenser
Separation drum
Suspension pump

Apparatus for monomer recycling

Monomer filter	Monomer buffer drum
Various compressors	Monomer column
Mist collector	Base heater
Water pump	Column head condenser
Cooler	Distillate drum
Various waste water pumps	Solvent cooler
Gas tank	Column head cooler
Mist collector	Transfer pump
Primary condenser	Solvent heat exchanger
Primary separation drum	Solvent regeneration column
Secondary condenser	Base heater
Secondary separation drum	Coolant system

Various monomer pumps	

Apparatus for drying and dispatch

Centrifuge tank with agitator	Classifier/Screen
Centrifuge pump	Metering unit/hopper
Centrifuge	Store system cyclone
Centrifuges waste water pump	Bulk material silos
Feed screw	Bulk material loader cyclone
Dryer	Metering unit/hopper
Various air filters	Bagging material cyclone
Dryer blower	Metering unit/hopper
Dry polymer blower	Bagging machine
Store blower	Pelletisation machine
Dryer cyclone	Heater (films)
Various cloth filters/wet washers	Conveyor belts
Various waste air blowers	

A5 Polystyrene

Apparatus for reaction preparation and reaction

Autoclave reactor
Agitator
Motor

A6 Acrylonitrile-butadiene-styrene

Apparatus for reaction preparation and reaction

Tank for butadiene
Reactor for the latex with agitator and motor
Initiator preparation reactor with agitator and motor
Storage reactor for latex
Various pumps with motor
Butadiene monomer condenser
Decanter with motor
Preparation reactor for emulsifier
Various tanks for coagulation agent, initiator, chain-transfer agent, monomers
Mixer for monomers with agitator and motor
Preparation reactor for monomers with agitator and motor
Reactor for the initial reaction with agitator and motor
Reactor with agitator and motor
Tank for antioxidant with agitator and motor
Tank for improvement

Apparatus, materials and energies for polymer separation

Heat exchanger
Tank for coagulation agent with agitator and motor
Pump with motor
Heat exchanger
Reactor for coagulation with agitator and motor
Filter for dehydration
Slurry reactor with agitator and motor
Centrifuge
Dryer
Compressor with motor
Cyclone
Filter

Apparatus for compounding, packaging and dispatch

Various cyclones
Various silos
Various filters
Various compressors
Various motors
Filling hopper
Conveyor belt
Mixer
Mill
Heat exchanger
Shredder

A7 Polyamide 6.6

Apparatus for reaction preparation and reaction

Heated tank for the AH salt solution
Various tanks
Static mixer
Various reactors
Condenser
Tube reactor
Various separators
Reactor
Condenser
Ejector

Apparatus for polymer separation

Extruder
Underwater granulator
Separator
Tank
Blower dryer
Fluidized bed dryer

Heat exchanger
Tank
Blower

Apparatus for monomer recycling

Tank
Filter
Ion exchanger 2x
Tank 2x
Feed screw