Integrated devolatilization processes. Efficient solutions for polymers.

> compounding & extrusion > materials handling > service

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confidence through partnership

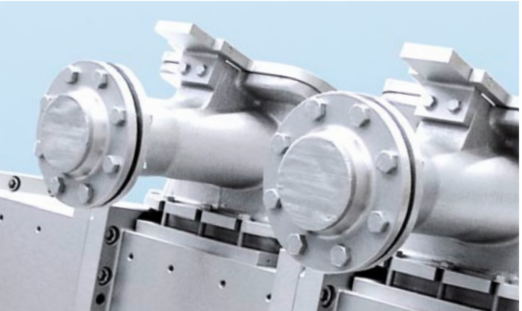
Integrated devolatilization solutions. Devolatilization is a common process task in many polymer producing and compounding operations.

Depending on the process small (< 0.2 %) to large amounts (ca. 50 %) of volatiles have to be removed from the polymer melt rsp. solution or the solid polymer pellet. Required residual volatile levels depend on type and application of polymer. Volatiles could be monomers, moisture, gases e.g. air or solvents. The type of volatile depends on polymer and way of polimerization. The table below shows initial and final (in pellet) volatile levels of different polymers.

Devolatilization of volatiles from polymers

Polymer	Type	Initial content	Final content; extruder devolatilization
LDPE	Ethylene	< 3,000 ppm	< 1,000 ppm
LLDPE	Hexane, Cyclohexane	10 - 15 %	< 500 ppm
		3 %	< 250 ppm
EPDM	Hexane, Cyclohexane	10 - 15 %	< 1,000 ppm
POE, PP	Hexane, Cyclohexane	5 - 15 %	< 1,000 ppm
EVA	Vinylacetate	5,000 ppm	< 50 ppm
PS	Styrene	3,000 - 5,000 ppm	< 300 ppm
ABS	Acrylonitrile (AN)	20 ppm	< 4 ppm
PC	Methylenchloride	20 %	< 50 ppm
PA 6	Caprolactame	< 8 %	< 0.8 %
SBR, SBS	Hexane, Cyclohexane	15 - 70 %	< 1,000 ppm
Acrylic adhesive	Acetone	50 %	< 1,000 ppm
Polyimid	Chlorobenzene	70 %	< 500 ppm
PP	various	approx. 1,000 ppm	< 50 ppm
PMMA	MMA	10 - 40 %	< 0.3 %
POM	CH_2O	5 %	< 100 ppm

VENT DOME OF ZSK MEGAvolume PLUS

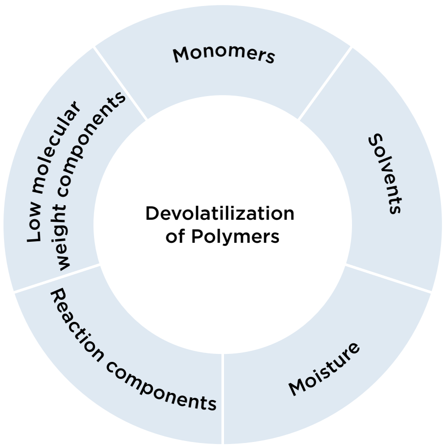


ZS-EG SIDE DEVOLATILIZATION

VENT PORT OF STS advanced

Basics of devolatilization of polymer melts, powders and pellets

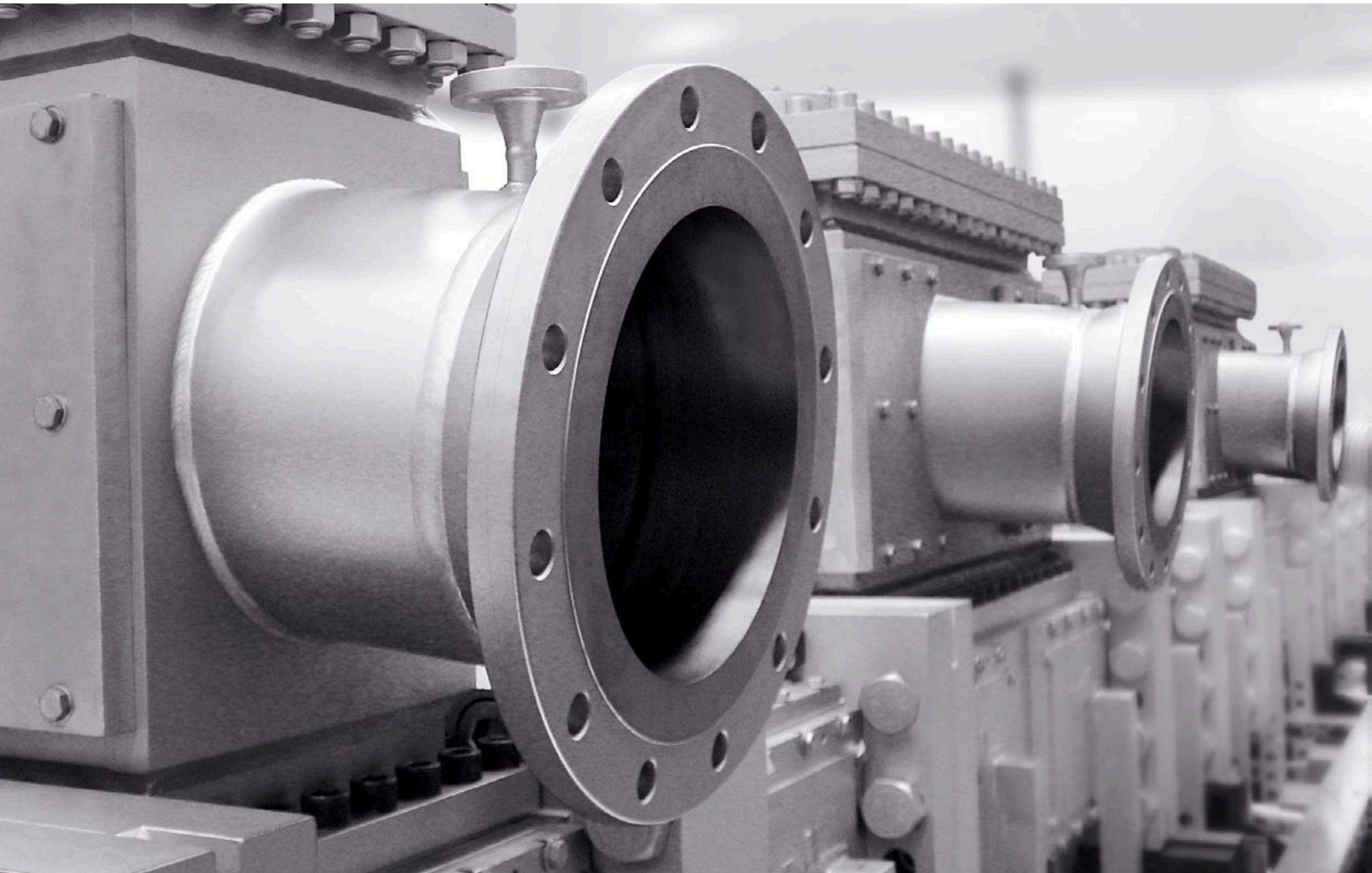
Polymers are polymerized in different processes from monomeric components. All processes have in common that not all monomers can be completely polymerized to the requested chain length. A certain amount of monomers and oligomers will remain in the end product. Depending on the chain length of these short-chain molecules and the application conditions (e.g. temperature) the volatiles will, by diffusion, come to the melt or particulate surface after a certain time.
Therefore these volatiles have to be removed to meet legal requirements of the final product or, during plant operation, could cause local accumulations of the lightly volatile substances and thus lead to an explosive mixture. Such explosions could result in local fires (causing agglomerates in silos) or even damage a complete silo with considerable potential for damage to operating personnel. The devolatilization process can be simulated using diffusion coefficients of the critical volatiles, operating conditions and extruder/plant layout data. Thus a forecast for the commercial plant can be made.



> DIFFERENT TYPES OF VOLATILES TO BE EXTRACTED FROM POLYMERS BY DEVOLATILIZATION

Extruder devolatilization – highest efficiency with adequate residence time. ZSK twin screw compounders form an excellent concept for devolatilization whether low or high amounts of volatiles, volatiles with low or high boiling point, have to be removed. This results from more than 50 years of experience on small and large ZSK extruders, low and high output rates. Calculations and trials form the basis for the transfer/scale-up to commercial operations and are backbone of the wealth of practical experience.

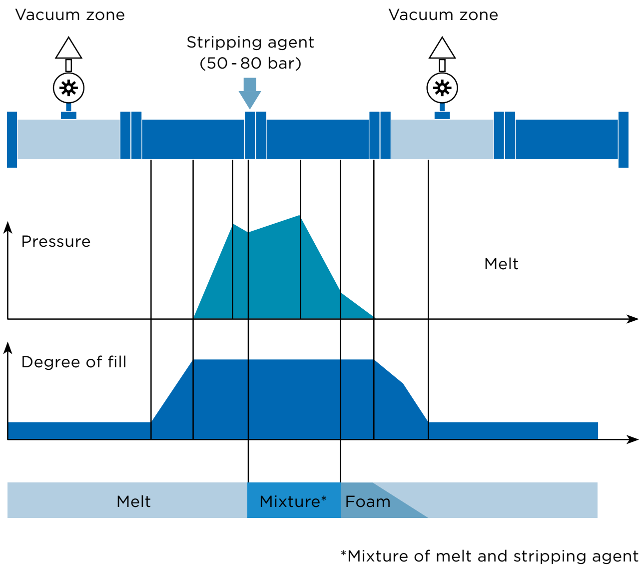
VENT PORTS OF ZSK EXTRUDER



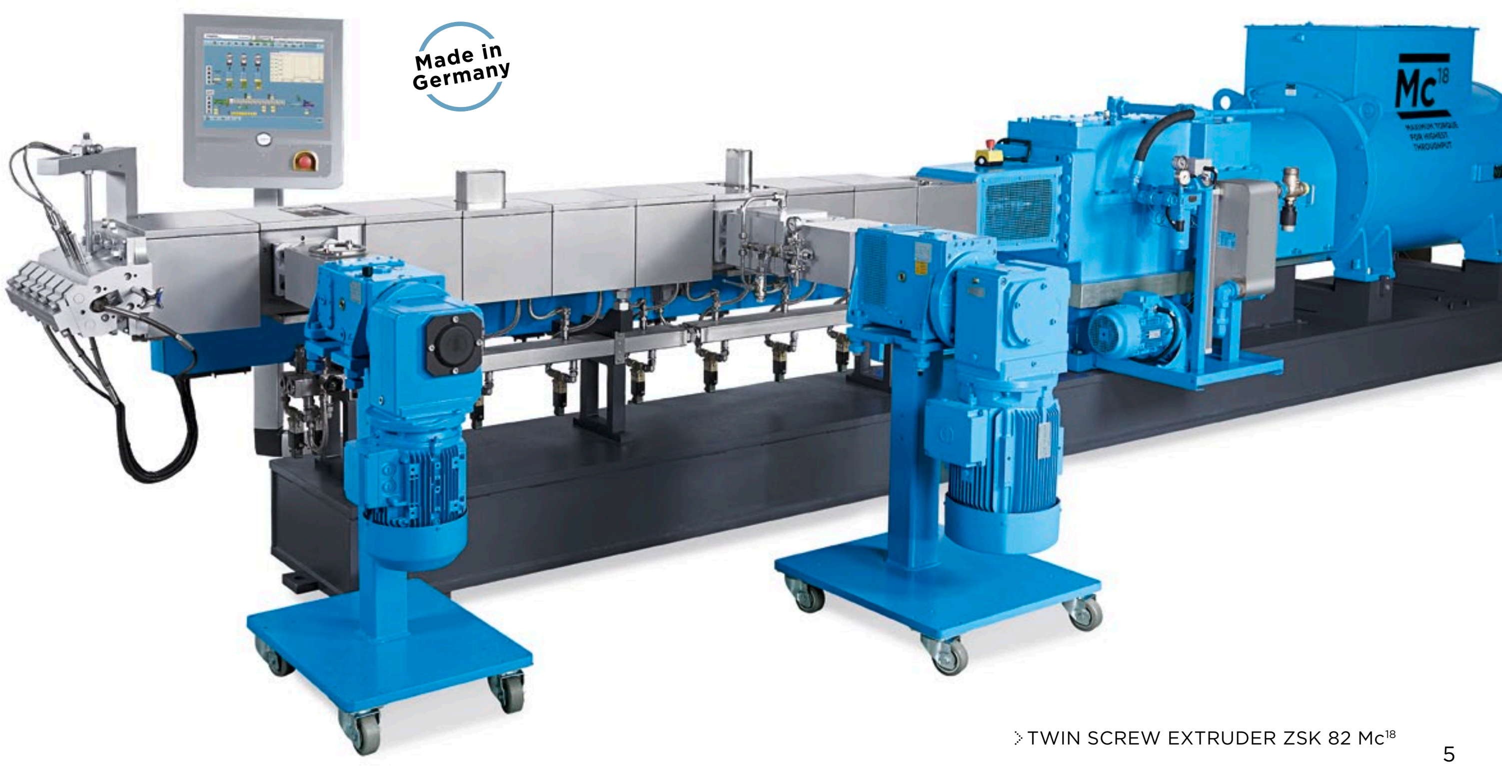
Modular building concept allows to adjust ZSK extruder to the need of each devolatilization process

Important are the following features of the ZSK extruder:

- Several parallel and continuous screw channels inside the process section
- The proper design of screw pitch and selection of operating conditions allow for partial filling of the screw channels
- Staged vacuum along the process section ensures balance between volatile amount and gas velocity thus providing safety of venting operation
- Possibility for adding stripping agents: Using stripping agents such as water, N_2 or CO_2 further enhances the devolatilization process. Such stripping agents will reduce the partial pressure of the volatile or they will, together with the solvent or monomer form an azeotrope. Typically up to 1% of such stripping agent is introduced into the closed, pressurized portion of the barrel section. It has to be incorporated under pressure still as a liquid. It will later on turn into steam and create bubbles inside the melt pool to further increase the surface devolatilization.



INCORPORATION OF STRIPPING AGENTS

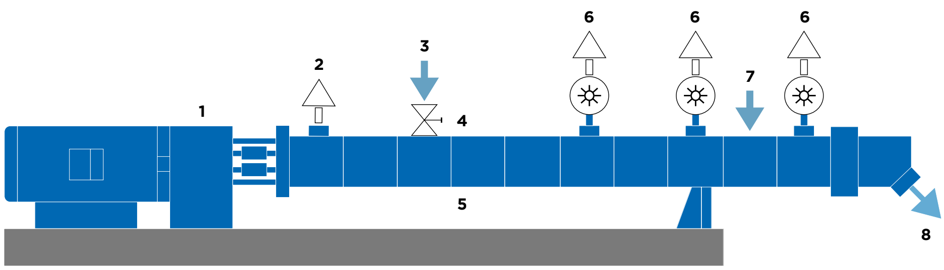


TWIN SCREW EXTRUDER ZSK 82 Mc[18]

Multiple processing tasks. Individual extruder configuration to meet the devolatilization requirements.

Devolatilization of SBR or LLDPE

Here in this case the process task asks for the removal of up to 50 % of solvents out of an SBR solution that is introduced into the feed barrel of the ZSK. The solution fed to the ZSK is overheated and then flashed into the feed port. Thus a large portion of the solvent will vaporize and escape in a counter current flow in the up-stream direction through the rear vent. The remaining solution will then be conveyed downstream through several devolatilization stages where at different vacuum levels then the desired residual volatile level is achieved.
Screening and subsequent pelletizing will then be a normal and routine processing procedure.
A similar application is the removal of solvents out of LLDPE. Here output rates of up to 20 t/h are achieved on commercial operations on a ZSK 320.



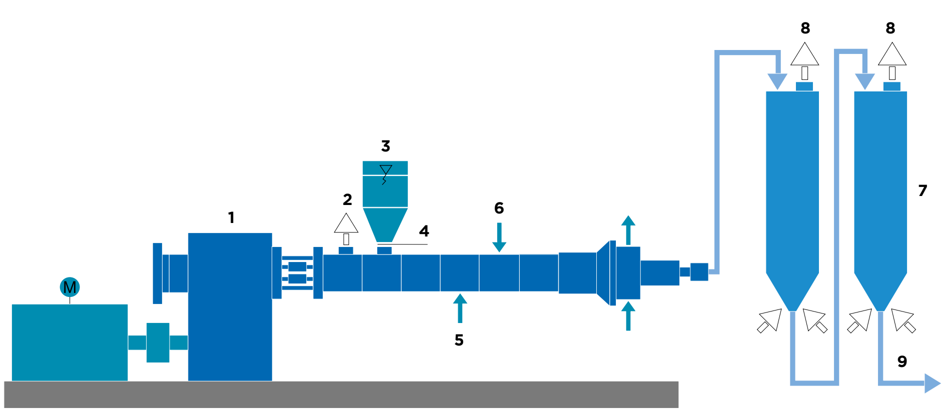
1. Drive
2. Rear vent
3. Overheated solution with $p > p_{vapour}$
4. Flash valve
5. Kneading section
6. Vacuum
7. Stripping agent
8. Discharge/Pelletizing

Devolatilization of polycarbonate

Solvent or monomer devolatilization of PC, starting from melt or melt solution, is an additional field of ZSK applications.
It is state-of-the-art to remove up to 20 % Methylene chloride out of a PC solution down to a few ppm final content in one step and to subsequently pelletize the PC melt. It is also possible to remove up to 30 % Chlorobenzene to less than 100 ppm. ZSK extruders for the concentration of PC solutions have been in successful operation since many years. Throughput rates of up to 5 t/h are achieved.

Devolatilization of LDPE

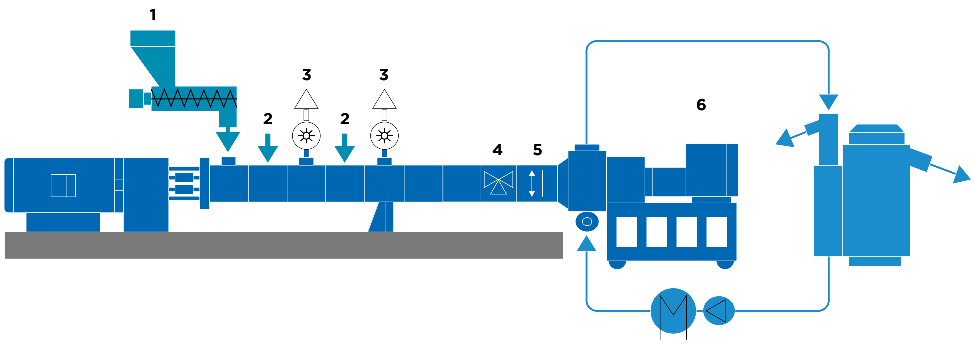
This is a typical example where both extruder devolatilization and solids devolatilization will be applied. Here typically the LDPE melt with monomer levels of around 2,500 ppm, depending on the pressure level in the low pressure separator, will be fed into the discharge extruder. Through a rear vent Ethylene is removed. Operating conditions such as screw speed and feed valve setting will determine feed rate. This will influence the partially filled screw length and thus devolatilization area. With such ZSK extruders a residual Ethylene level of 800 to 1,000 ppm is reached. In the same operation additives are incorporated into the melt, which is then pelletized with an underwater pelletizer.
These pellets still containing some Ethylene which will be conveyed to devolatilization silos where the residual level of Ethylene is reduced to ≤ 50 ppm in silo devolatilization.



1. Extruder
2. Venting
3. Low pressure separator
4. Slide gate for level control
5. Lateral extruder
6. Liquid additives
7. Silos with pellets
8. Silo devolatilization, several steps possible (pellets)
9. Pneumatic conveying to storage silos

Stabilizing and devolatilization of polyoxymethylen

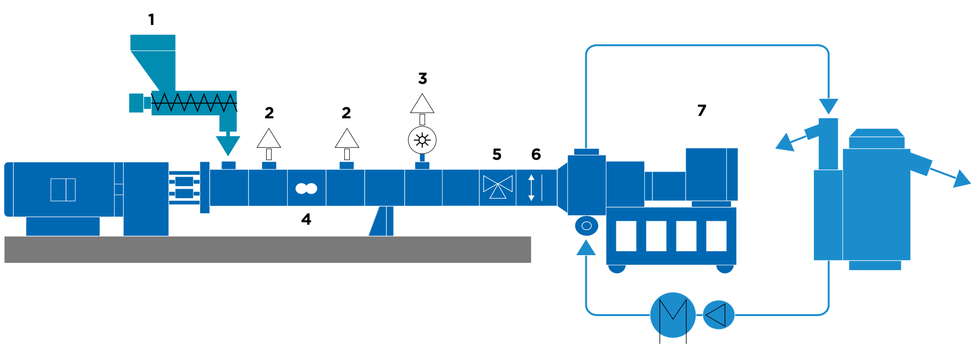
The devolatilization of residual monomers out of POM is another field of application of the ZSK extruders. The unstabilized POM-powder is stabilized in the ZSK machine and in the same process step the residual monomers are devolatilizated. A low residual content (measured in ppm) of monomer is obtained. The input concentration of monomer can be up to 5 %. ZSK extruders up to the size of ZSK 250 are applied for this process. POM is very sensitive concerning depolymerisation; this means that pressure build-up and extrusion/ pelletization zones in the extruder have to be designed very carefully.



Devolatilization of POM
1 POM + additives
2 Stripping agents
3 Vacuum
4 Start-up valve
5 SWZ screen pack changer
6 WRG waterring pelletizer

Alloying and blending in one step

In this process SAN-melt or SAN-pellets rsp. -powder is fed into the inlet port of the ZSK extruder and melted. Downstream rubber, containing water, is introduced into the process section. The moisture is evaporated and removed in up- and downstream direction out of the process section. Concurrently SAN and rubber are thoroughly homogenized. The remaining volatiles are removed through additional vent openings. Throughputs of up to 9 t/h are reached with ZSK 133 or ZSK 177, depending on recipe and process.



Producing a polymer alloy with simultaneous removal of large amounts of water
1 Alloying component (SAN)
2 Atmospheric venting
3 Vacuum venting
4 Alloying component (wet rubber introduced with side-feed screw)
5 Start-up valve
6 SWZ screen pack changer
7 UG underwater pelletizer

Wide experience with devolatilization processes on ZSK extruders

Product	ZSK	Volatiles	$C_{IN\ volatile}$	C_{OUT}	Rate [t/h]
LDPE	380	C_4	2,500 ppm	< 1,000 ppm	55
LLDPE	250	Hexane	10 - 15 %	< 500 ppm	4 - 5
LLDPE	320	Hexane	10 - 15 %	< 500 ppm	15 - 20
SBR	250	Cyclohexane	15 %	< 1,000 ppm	4 - 5.5
SBR	320	Cyclohexane	30 - 50 %	< 1,000 ppm	6 - 7.5
Polyolefin	177	C_4 - C_{20}	7 - 30 %	< 300 ppm	1 - 4
Polyolefin	420	C_4 - C_8	5 - 10 %	< 1,000 ppm	15 - 35
POM	250	Formaldehyde	1.5 - 4.5 %	< 100 ppm	4
ABS	133	H_2O	10 - 15 %	< 500 ppm	4.5 - 6
ABS	177	H_2O	10 - 15 %	< 500 ppm	6.5 - 9
PC	177	Diphenylcarbonate	600 ppm	< 300 ppm	4 - 5
PC	250	Diphenylcarbonate	120 ppm	< 60 ppm	4 - 5
PC	250	Chlorobenzene, $MeCl_2$	3 - 5 %	< 50 ppm	4 - 5

Silo devolatilization for bulk materials. Silo devolatilization is required in two main fields of application: explosion protection and product quality improvement with regards to taste and odor.

Certain products contain a level of residual volatile material which, as it evaporates from the pellets, may lead to explosive atmosphere in the silos or in other containments. A devolatilization process step in the materials handling plant is required in order to eliminate this risk. Dilution with ambient air has proven to be an economic solution for this task. For this purpose a sufficiently high air flow is fed to and distributed in one or more silos for a sufficiently long time such that the concentration of volatile material is safely kept below the Lower Explosion Limit (LEL).

Other products may contain a certain amount of volatile material, which although it does not pose an explosion hazard, can cause unpleasant smell and taste emanating from the finished product. This is considered a quality criteria in many industries (e.g. automotive, food packaging, etc.). A devolatilization process step may be required in order to increase product quality. Also for this process step the product is typically stored in a silo for an appropriate time and ambient air is fed to the silo to reduce the volatiles content. Silo devolatilization can be included in new plants but can also be retrofitted in existing plants.

Devolatilization for

- Explosion prevention
- Prevention of local smoldering
- Reduction of taste and odor
- Quality improvement

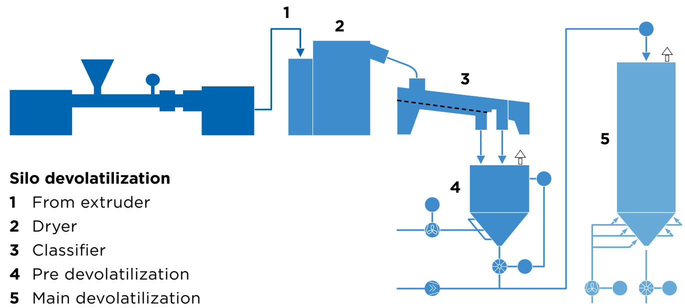
Typical products requiring silo devolatilization

- LLDPE
- HDPE
- LDPE
- EVA
- PP

Characteristics of silo devolatilization

Silo devolatilization takes place at considerably lower temperatures with significantly longer residence time compared to extruder devolatilization. The required devolatilization time depends on the specific product criteria and the devolatilization temperature. The process parameters differ between the devolatilization process to avoid explosive atmosphere and the devolatilization process to improve product quality. Two step silo devolatilization is often applied. In new plants the devolatilization concepts of extrusion and materials handling can be integrated.

	Extruder	Silo
Temperature	< 350 °C	70 - 80 °C
Residence time	< 2 min	10 - 30 h



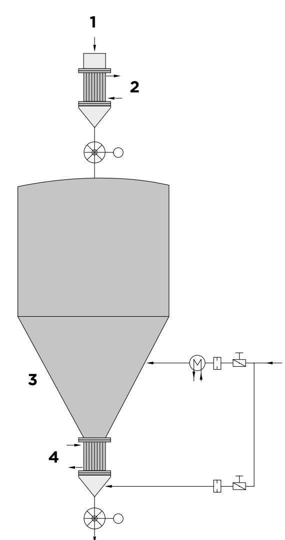
Silo devolatilization
1 From extruder
2 Dryer
3 Classifier
4 Pre devolatilization
5 Main devolatilization

The way to reliable devolatilization

As a first step the required devolatilization concept has to be established. Working together with the customer the objective and the basic parameters are defined. Important data such as product criteria, diffusion coefficient, volatiles content, LEL (lower explosion limit), batch or continuous operation, silo dimensions etc. influence the calculation results. Based on these data the devolatilization parameters, e.g. devolatilization time, required purge air flow, required temperature, heating time, cooling time etc. are established in a study. With the results of this study the details of the plant are specified. These include the air supply equipment, the heating/cooling concept as required, the air inlet arrangement, the air distribution arrangement in the silo, instrumentation, controls. A safety concept has to be defined which later will typically be assessed in a HAZOP analysis. The safety concept has to consider all related adjacent equipment with adequate system redundancy and an emergency plan. Start-up and shut down situations must be taken into consideration because threshold values can be exceeded in these non-stable situations. During detail engineering all equipment and supplies will be designed, sized, specified, purchased and finally shipped. Several patents with regard to devolatilization are registered by Coperion.

Coperion's services for silo devolatilization

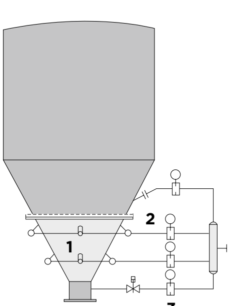
The first and foremost task for every plant is safe and economic operation. As Coperion is usually already involved in projects during the planning phase, competitive multi-stage concepts can be developed by a combiniation of extruder devolatilization and silo devolatilization. A devolatilization in several levels in the solid phase (powder, granulate) can also be favorable and in combination with the Coperion Bulk-X-Change® for heating and cooling of the product is very efficient. Coperion's unique know-how provides a single source for the degassing study, engineering, supply of equipment and materials including assembly, commissioning and start-up. As a matter of course we can also assist in the analysis of incidents and damages.



Devolatilization with heating and cooling
1 Product
2 Bulk-X-Change® heating
3 Devolatilization
4 Bulk-X-Change® cooling

Silo devolatilization also easily to retrofit

In existing plants the requirement for new products with increased devolatilization demand (softer products, higher PE-portion, etc.) is to preserve safety of plant and quality of product. As a result of construction and modular assembly silo devolatilization can be inexpensively retrofitted by Coperion.



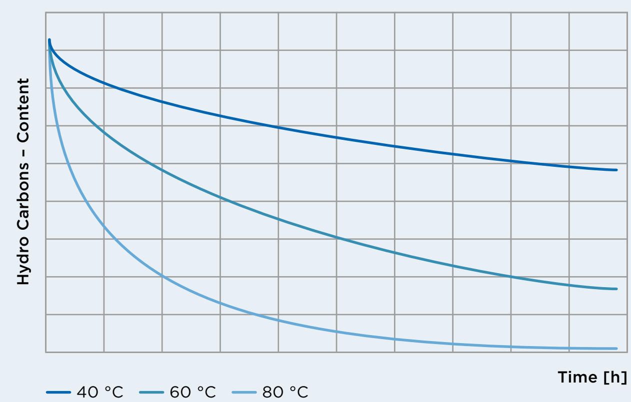
Devolatilization system can be retrofitted
1 Injection nozzle
2 Purge gas distribution
3 Purge gas regulation

Product quality and plant safety. The devolatilization concept is adapted to product and system requirements.

Plant Safety by right devolatilization

For example in LDPE plants for safety reasons the residual volatile material (ethylene) has to be removed in order to avoid potentially explosive atmospheres. The volatiles concentration in the product and in the silos is not constant but varies over time. If several unfavorable factors exist simultaneously local fires, smoldering up to silo explosions could occur. All operating conditions of the plant, silo filling, storage in silos, silo emptying have to be taken into consideration in order to ensure a sufficiently low volatiles concentration and to maintain a sufficient safety margin to the LEL (lower explosion limit). Using simulation programs Coperion can define the required parameters for purge air flow, air distribution and design of the air feeding arrangement.

Devolatilization at different temperatures



Highest requirements to the end product

Not only in the field of packaging of food and animal feeds there are stringent requirements to the devolatilization of remaining monomers. For example an odor disqualifies certain polymer types for these applications if they have not been devolatilized sufficiently. For certain applications the requirements are such high that classical methods of analysis are not sufficient. Odor experts are employed in such cases who detect residual traces of residual monomers by smell. A silo devolatilization is highly suitable for retrofitting an existing plant concerning the increasing requirements for polymers.

Devolatilization of controlled rheology polypropylene

During extrusion of polypropylene, for some grades, organic peroxide is used in order to influence the rheology of the product. Usually the molecular weight is reduced and the molecular weight distribution becomes more narrow. During the extrusion process the peroxide decomposes partly into volatile organic components (VOC) like Acetone, TBA and others. These do not undergo a chemical reaction with the PP molecules and eventually will diffuse out of the PP. The VOC is removed in a devolatilization process, which is carried out in downstream silos and can take up to 30 hours due to the low diffusions coefficients. The volatile material at a certain concentration (lower explosion level LEL) together with ambient air can generate an explosive atmosphere. By selective purge gas feeding explosive atmosphere can be avoided by maintaining a volatiles concentration well below the LEL. Appropriate amount, conditioning and monitoring of the purge gas flow and the correct arrangement of the air feed points are crucial to achieve this. Depending on the legal regulation a secondary treatment of the purge gas emission (e.g. by thermal oxidation) might be necessary.

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