SULZER

Biopolymer production technologies

# Leading the way for **renewable and biodegradable** materials

# Reliable biopolymer production starts with Sulzer Chemtech

In today's rapidly evolving market, the demand for renewable and biodegradable products is at an all-time high. Sulzer Chemtech stands at the forefront of this transformation, offering proven and guaranteed technology for biopolymer production. Our solutions not only help producers diversify their product portfolios towards greener plastics but also give them a competitive edge.

Our technology portfolio includes the biopolymer materials with the highest growing rates, including polylactic acid (PLA), biodegradable and derived from renewable feedstocks like sugars, starches, or agricultural waste, and polycaprolactone (PCL), a plastic known for its excellent biodegradability and biocompatibility properties.

## Why Sulzer

### 1 Leader in reaction and separation solutions with an established track record of excellence integrating technologies

Our comprehensive expertise in mixing, reaction and separation (synthesis, distillation, crystallization and devolatilization), combined with our unique ability to connect all processes, allows us to offer a fully integrated solution. From monomers to biopolymers, we deliver world-scale, innovative solutions, helping our customers at every step of their bioplastics journey.

### 2 Research-Driven

Our commitment to technology upgrades and a dedicated research facility allows our technology to constantly evolve while our experts explore different paths to find the most promising solution to meet demanding customer specifications.

### 3 Flexible capacity

With a unique ability to scale from a pilot plant to a large industrial capacity, Sulzer technology allows project customization to meet specific requirements. Sulzer Chemtech has installed plants from 1 kta to 75 kta.

### 4 Extensive product grade

Our innovation and technology center's testing capabilities redefine the boundaries of what can be achieved on biopolymer grades tailored to specific applications and its developments.

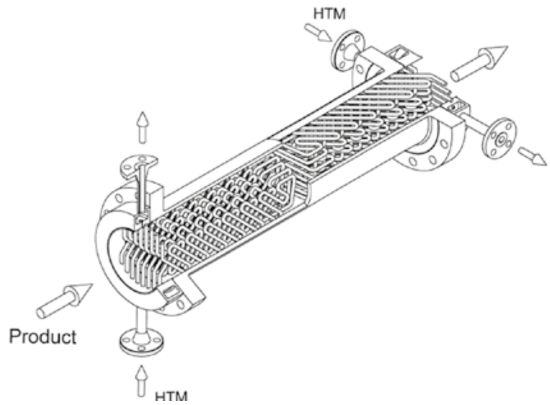
**Sulzer Chemtech's technologies integrate various key features to ensure efficient biopolymer production**. Here are the critical components that set our solutions apart:

- > Sulzer Mixing Reactor
- > Sulzer Static Mixers
- > Devolatilization
- > Crystallization
  - > Static
  - > Falling Film
- > Distillation

# Sulzer Mixing Reactor

The Sulzer Mixer Reactor (SMR$^{TM}$) stands out as a unique and superior equipment developed by Sulzer, leveraging years of testing, scaling-up, and experience in a variety of viscous applications. Its design, successfully proven in numerous industrial cases at different scales, from pilot plant to large polymer production, is a distinctive technology integrated into the licensed biopolymer process from Sulzer at the polymerization stage.

The distinctive tube layout is similar to that of a static mixer geometry, allowing a homogenous melt flow on the shell side and the formation of laminar layers in viscous streams at low shear rate at the expense of a small pressure drop, which is specially usefully for continuous bulk polymerization. This process enhances the heat transfer to and from the melt and combines well with the extraordinarily high surface area per unit volume, derived into an accurate control of heat transfer allowing high conversion and consistently high polymer flow. Moreover, the excellent radial mixing of the SMR ensures the optimal homogenization of local concentration and temperature gradients while avoiding channeling, maldistribution of for instance additive and catalyst, or dead zones. Having no rotating parts, the SMR design reduce the maintenance costs as well as the operating/energy costs. Regarding viscosity, the SMR performs with excellent results in a wide viscosity range, making it suitable for diverse polymer production or even multiproduct plants, such as PLA and PCL. In case of product switch, thanks to its high surface, any polymer grade change can be done quickly, reducing the amount of off-spec product.




All these features make the SMR one of the industry's highest-performing reactor/heat exchangers.

Hence, in the polymerization section the SMR is used for three different purposes:

**Loop Reactor**

Due to the relatively high exothermicity of the polymerization, individual SMRs are configured into a loop reactor to take advantage of its extraordinarily high heat exchange surface area, which provides reliable heat removal and temperature control. The purified monomer, such as lactide or caprolactone, is continuously fed to the loop while the semi-finished biopolymer is discharged and conveyed to the downstream plug flow reactor section. The loop reactor configuration allows a controlled polymerization at the monomer feed for various biopolymer grades.

**Plug Flow Reactors**

The SMR modules built in series behave like a plug flow reactor and allow the polymerization process to continue; hence, the monomer concentration decreases, leading to higher viscosity in the melt. The SMR secures a plug flow regime, even with high viscosity, which also features a narrow residence time distribution that promotes homogeneous biopolymer quality. This advantage is maintained throughout the spectrum of the changing polymer viscosity, even at high conversion levels. Moreover, the high conversion rate achieved in the SMR reduces the amount of by-products.

**Heat exchange**

Another use of the SMR in the Sulzer biopolymer technology is cooling the polymer melt. Once the polymerization has reached the highest conversion, the viscosity has increased to its maximum. The biopolymer must be cooled in a homogeneous way to avoid preferential flows through the multitube heat exchanger or even polymer degradation. Hence, the SMR design also accommodates optimum cooling conditions.

# Sulzer Static Mixers

When different fluids, usually in a liquid state, need to be mixed, static mixers are the most common device used in the industry. Mixing low-viscous additives into high-viscosity fluids is performed in various hydraulic regimes, ranging from laminar to transitional and turbulent.

The advantages of using a static mixer are significant for a biopolymer producer. Compared to dynamic mixing equipment like extruders, static mixing solutions are significantly lower in installation, operating, and maintenance costs. Low shear stress and short residence time in a device with a relatively low-pressure drop also makes the static mixer an ideal equipment for the biopolymer production.

With a proven track record, Sulzer has successfully integrated static mixers into our biopolymer technology. This practical application of the technology has significantly enhanced different sections of the polymerization process, demonstrating its effectiveness in the polymer industry.

### Dispersing additives

Additives can be perfectly mixed with static mixers. The Sulzer SMX™ or the SMX plus™ geometry has proven efficient in many industrial references for homogenization and dispersing tasks in laminar flow. In the Sulzer biopolymer process, static mixer is mainly used to homogenize additives, such as catalyst, initiation and chemicals, added into the melt.

### Melt homogenization / Upgrading solutions

After devolatization and prior to pelletization, additives can be mixed into the biopolymer melt to upgrade the final product. Sulzer's technology foresee the possibility to mix the melt with additives (like masterbatches, chemicals) to increase the properties of the final polymer. By doing it before pelletization, also the operation costs drop as the pelletized biopolymer is already formulated according to the market needs. Sulzer SMX and SMX plus show optimally equalized gradients of viscosity, temperature, and color.

# Devolatilization technology

In most polymer production, devolatilization is a crucial step since the polymerized product contains a certain amount of unreacted monomers, oligomers and other impurities that must be removed to enhance polymer quality before selling or further processing. In the case of biopolymers produced by the ring-opening polymerization, these reactions are typically equilibrium-limited. Hence, there is always a monomer to remove, such as lactide or caprolactone, in the cases of the PLA and PCL, respectively.

Sulzer Chemtech has developed a static devolatilization technology for removing these residual volatiles that uses less energy and reaches a very high removal of the volatiles, which is a key part of the biopolymer licensing technology. Apart from biopolymers manufacturing, this technology is already applied in other polymeric processes, such as polystyrene, polyolefins, or solvent-based recycling, from pilot plants to large-scale commercial lines. Sulzer Chemtech's proprietary degassing technology for biopolymers is based on a multiple-stage flash devolatilization process due to the amount of volatiles to be removed in order to achieve the desired final purity. The biopolymer degradation is reduced due to the relatively low residence time, no temperature overshoots and low shear rate. These units are static equipment, so they have low operating and maintenance costs.

For biopolymer production via ring-opening polymerization, Sulzer's devolatilization technology offers a series of advantages, which makes it the most suitable process with an already proven track record. The devolatilization system is composed mainly of a degassing chamber with customized internals accompanied by Sulzer's proprietary static mixers. Apart from the lower shear stress rate, this set-up based on static equipment is translated into relatively low capital expenditures, operational expenses, and maintenance effort. These advantages are noticeable, especially on large biopolymer plants, where the devolatilization vessels benefit from the economy of scale.

Creating conditions for optimum separation is a critical aspect of the devolatilization process. It involves careful control of liquid distribution, pressure, and temperature to ensure efficient mass transfer of the volatile component from the liquid to the gaseous phase. High available surface, low pressure, and high temperatures favor the transfer of solvent to the gas phase, underscoring the importance of excellent control over these parameters for acceptable product quality. The melt, composed of the biopolymer with the monomer and other residues, is heated up before entering the devolatilization process. The operating temperature, carefully controlled by optimized temperature loops, is defined to facilitate rapid evaporation is crucial for achieving the desired product quality. By designing the optimal internals for the degassing chamber, residence time can be controlled, and the desired biopolymer concentrations can be achieved, ensuring the quality and consistency of the final product.

# Distillation

Distillation is the most commonly applied separation technology in the industry, designed to bring diverse advantages to chemical producers such as improved product quality, increased capacity, and lower energy consumption. For almost a century several dozen thousands columns have been operating with Sulzer equipment and performance guarantees, in hundreds of different applications. The beforementioned coupled with an outstanding offer of different distillation technologies and solutions, makes Sulzer to become the leading expert in the industry. Sulzer’s distillation product portfolio includes column shells and state-of-the-art internals like distributors, collectors, random and structured packing (MellaPACK™), mist eliminators and trays plus other auxiliary equipment like heat exchangers and decanters among others.

The combination of Sulzer product portfolio in a distillation column ensures that the mass transfer effectively occurs at the surface of the packaging, ensuring, close contact between the liquid phase flowing downwards and the gas phase going upwards. Moreover, distillation column configuration are used also as reactors in the lactic acid to lactide synthesis step. Hence the biopolymer licenses include the supply of complete columns such as shells and internals, which are used as beforementioned as reactors in the lactide synthesis section in case of the PLA process and as monomer purification equipment for, respectively lactide to produce PLA and caprolactone to produce PCL.

Sulzer’s extensive experience and expertise in complex distillation, combined with computer simulations, proprietary sizing tools, and in-house pilot plant testing, are also applied to biopolymer production. This approach ensures that each project receives an optimal solution. The distillation columns in Sulzer's licensed biopolymer technology are of the multi-stage type, operating in continuous mode and serving various purposes.

As mentioned before, the distillation column configuration has different applications in the biopolymer process:

In the case of PLA manufacturing, the first step is the concentration of the lactic acid by removing its water in a distillation column prior to the oligomerization reaction.

This oligomerization step is the second application where a series of distillation columns act as reactors. By controlling process conditions such as pressure and temperature, the desired chain of the oligomer can be targeted.

Then, the next chemical reaction, the cyclization is also performed on distillation columns used as reactor, where, in case of the PLA production, its monomer the lactide is synthesized.

In case of lactide or caprolactone purification, a series of distillation columns eliminates light and heavy impurities, and separates the different isomers prior to the further purification at the downstream crystallization system.

# Crystallization

When distillation cannot further purify the chemical due to the risk of degradation, crystallization comes into play. It can remove any remaining impurities at low process temperatures when processing a mixture composed by chemicals heat sensitive.

The nature of bio-based materials makes their separation incredibly challenging. Biomaterial mixtures tend to have components with similar boiling points and are also heat-sensitive, which can undergo undesirable reactions, such as uncontrolled polymerization or thermal degradation. Therefore, a separation process that operates at low temperatures, such as crystallization, is preferred.

The Sulzer biopolymer licensed process integrates the Sulzer fractional melt crystallization technology. This robust purification solution, based on separation by liquid-solid phase transition via crystal growth by nucleation-cooling, is well established in the industry for many applications with the most demanding specifications in terms of product purity. Different chemical products like biopolymer monomers benefit from crystallization advantages such as being solvent-free, energetically efficient, and economically competitive. Moreover, the crystallizers contain no moveable parts such as stirrers or filters, making the equipment very reliable while drastically reducing the thermal stress applied to the monomer, therefore minimizing oligomerization or degradation.The process's environmental friendliness further enhances its appeal.

In the Sulzer biopolymer production process, the crystallizers are normally located downstream of the Sulzer distillation columns to further purify the monomer stream, such as lactide or caprolactone, by removing any unwanted chemicals. Two crystallization technologies can be applied: static and falling film, both based on the layer crystallization concept, where crystals are allowed to grow directly onto a cooled surface so that cooling is supplied through the crystal layer. In the case of PLA synthesis, the meso lactide is purified by the static and L-lactide by the falling film respectively.

### Static crystallization

The static crystallizer is similar to a plate heat exchanger with vertical plates except that the filled-in liquid product, like the meso lactide, remains stagnant in the crystallizer, i.e., it is not force-circulated or stirred. Molten product, fed into the unit, is partially crystallized on the plates so that the crystals adhere to the plate surfaces and form crystalline layers thanks to the cooling below the freezing point of the product. Impurities are rejected from the growing crystals and are concentrated in the remaining melt. Hence, the remaining liquid phase is drained, leaving the purer crystal layers that grow in the plates. Subsequent partial melting of the crystal, controlled by the heating fluid, which passes through the vertical plates, helps to remove trapped impurities and increase the purity of the reaming crystal before the final melting, draining into the product storage.

### Falling film crystallization

The falling film crystallizer comprises a bundle of vertical tubes, which are cooled or heated by a heating fluid, where the product to be purified falls by gravity on the walls of the tubes. The falling film inside the tubes starts to grow as cylindrical crystal layers. The crystals reject most impurities that concentrate on the remaining liquid phase with time. Since the crystal growth rate is slower than the falling flow, the bottom liquid recirculates. The homogeneous flow distribution in different tubes is considered one of the key design elements because it is essential for a good system functioning. Typical application in the Sulzer biopolymer technology is the purification of the L-lactide or caprolactone for producing PLA and PCL subsequently. Like static systems, after crystallization, the impurities are removed by partial melting, which raises the temperature slightly. In the case of the lactide, concentrations above 99.9% are achievable.

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**The Chemtech division is the global market leader in innovative mass transfer, static mixing and polymer solutions for petrochemicals, refining and LNG.**

Chemtech is also leading the way in ecological solutions such as biopolymers as well as textile and plastic recycling, contributing to a circular economy. Our product offering ranges from technology licensing to process components all the way to complete separation process plants. Customer support ranges from engineering and field services to tray and packing installation, tower maintenance, welding and plant turnaround projects – ensuring minimal downtime.