



– amixon® whitepaper –

Cellulose Processing

Complex plant technology in cellulose processing



Pulp is the name given to the fibrous mass created by the chemical pulping of vegetable fibres. Pulp mainly consists of cellulose. The word cellulose is borrowed from Latin and means „small cell“. Cellulose is the structural backbone of all plant cells.

Cellulose is an all-rounder: The manufacture of paper would be inconceivable without pulp and, in a chemically modified form as a cellulose derivative, it made the development of photography possible, is an important constituent of textile fibres, helps when laying tiles, keeps bakery products fresh, maintains the consistency of mayonnaise and makes toothpaste supple.

However, the manufacture of the different cellulose derivatives works only with high-quality process apparatus.



There is hardly any other raw material with which the history of mankind is so closely interwoven as with cellulose. Without paper, human history would be different. Even rags were used for making paper in the beginning, because they were made of cotton, in whose fibre the cellulose is present in a particularly pure form. The development of the chemical utilisation of cellulose began in 1846 with the manufacture of nitrocellulose, also called cellulose trinitrate. It was initially used for military purposes and was also referred to as gun cotton. It is formed when cellulose is treated with nitrating acid, a mixture of sulphuric and nitric acid. In further process steps, the nitrocellulose is washed, ground and dried. In addition to military use as a blasting agent, the civilian use of nitrocellulose also began in the 19th century. Low-nitrated nitrocellulose (cellulose dinitrate) is mixed with camphor and, under the name celluloid, formed the basis for the first technical plastics. Celluloid served as the carrier for photographic films until 1951. Even table tennis balls were made of nitrocellulose till 2014. The property of being particularly flammable led to its replacement by other materials. The first plastic film was also based on cellulose. In the 1920s, cellulose glass (trade name cellophane) was produced for packaging purposes. It is particularly brilliant and, unlike modern packing films, can be permanently bent. It was used for sweet wrappers, for example, as it could be simply twisted at both ends. Cellophane has now been largely replaced by oil-based plastic films for technical and cost reasons. However, cellophane might well undergo a renaissance in future due to its excellent biodegradability.

Cellulose is an organic macromolecular molecule. It is tasteless, odourless, hydrophilic and insoluble in water and most organic solvents. It is also non-toxic and biodegradable as well as inexpensive and of unlimited availability as a renewable natural product.

The cellulose content of cotton is approximately 84-91%. Due to its long fibres, it is mainly processed as a textile raw material.

The cellulose content of wood is only about 40-45% and it needs to be isolated by chemical pulping, which is very complex. Sawmill residues and lower-quality coniferous trees are the main raw materials for industrial paper production. However, higher quality coniferous and deciduous timber qualities, mostly from plantations, are also used for the application as chemical cellulose.

When using the sulphite pulping process, a particularly pure cellulose is obtained from wood, called Dissolving Pulp or Specialty Cellulose. However, the cellulose must first be extracted from the wood. To do this, the tree trunks are chopped into wood chips of a uniform size. These are cooked with acidic chemicals for several hours in pressure-resistant reactors under the influence of heat and pressure. Associated cellulose materials such as lignin and hemicellulose are dissolved in the acid and are separated out with the filtrate. The filtrate, which is also called black liquor because of its colour, further contains lignin frag-

<i>Product</i>	<i>Global production</i>	<i>Application</i>
<i>Regenerated cellulose</i>	3,300,000 t/a	Textiles
<i>Cellulose acetate</i>	900,000 t/a	Coatings and membranes
<i>Cellulose nitrate</i>	420,000 t/a	Coatings, membranes and explosives
<i>Carboxymethyl cellulose</i>	360,000 t/a	Food, cosmetics, pharmaceuticals, oil field, paper
<i>Methyl cellulose</i>	180,000 t/a	Food, pharmaceuticals and construction
<i>Hydroxylethyl cellulose</i>	80,000 t/a	Paints, varnishes, films and cosmetics
<i>Ethyl cellulose</i>	4,000 t/a	Pharmaceuticals, electronics

Commercially important cellulose regenerates, cellulose esters and ethers and their main applications.

ments, carbohydrates from the decomposition of the hemicellulose, sodium carbonate, sodium sulphate and other inorganic salts. Sodium, sulphur and calcium are recovered and recycled. From lignin, vanillin can be extracted in much the same way as from the tree bark. This is followed by several washing processes. The bleaching of the cellulose takes place in several steps, depending on the desired product quality.

The cellulose is subsequently dried mechanically and thermally. Depending on the fibre quality of the wood and the desired degree of purity of the cellulose, up to 400 kg of cellulose can be obtained from one tonne of wood. The cellulose is usually marketed as a roll (approx. 500 kg) or as baled goods (approx. 200 kg).

Of the approx. 150 million tons of pulp produced worldwide each year, 97% are used for paper production and only 3% for refinement in the chemical industry.

We encounter cellulose derivatives almost everywhere

With the advances in macromolecular chemistry, different cellulose derivatives having valuable properties were created.

Cellulose ester: Celluloid, the first thermoplastic, has been manufactured from nitrocellulose and camphor since 1856 and processed to make table tennis balls or film material. Cellulose acetate, as the second thermoplastic, is processed to make textile fibres, cigarette filters, films and transparent moulded parts (cubes, screwdriver handles, etc.).

Cellulose ethers: Since the beginning of the 1930s, this group of cellulose derivatives has gained in industrial importance – a triumphal march that still continues today with an ever increasing number of applications.

Cellulose ethers are non-toxic, mostly water-soluble products, that are usually marketed as white powders or granulates. The special properties of the individual cellulose ethers depend on the type, number and distribution of the substituents that are introduced by a chemical reaction following the activation of the cellulose molecule with caustic soda. They are named according to the names of the substituents, e.g.: methyl cellulose (MC), hydroxypropyl-methyl cellulose (HPMC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), ethyl cellulose (EC), etc.

They are used in the construction industry as additives for the optimisation of various properties in mortars, tile adhesives or fillers (HEMC or HPMC). Wallpaper adhesive mostly consists of methyl cellulose (MC) or carboxymethyl cellulose (CMC).

Cellulose derivatives are used as lubricants in metal forming and as viscosity regulators and binders in the manufacture of paints and lacquers. In dishwasher tabs as tablet disintegrants, or in agriculture, when pesticides are to develop their effect with a delay. Some cellulose derivatives are approved as food additives and for use in cosmetic compositions. Among other things, the behaviour of the various cellulose ethers in an aqueous environment at different temperatures is used for these applications. Often they are indispensable additives in emulsifiers, stabilisers and preservatives. They improve the flowability of instant sauces and soups. In ice cream, they influence the melting behaviour and the mouthfeel and make it taste creamy with less cream. In the food and pharmaceutical industries, they influence the quality, shape, structure and consistency of liquid and semi-solid goods. Their range of applications extends from toothpaste to covering masses for pharmaceuticals. In cosmetics, they are viscosity adjusters and stabilisers, and they determine the rheology of ointments, suntan lotion and makeup. Their potential is far from being exhausted and continues to be subject of intensive research.

The price for “simple” cellulose derivatives such as carboxymethyl cellulose (CMC) starts at €1.50/kg, rising to more than €50/kg for special cellulose derivatives in pharmaceutical applications. As cellulose ethers in many applications are hardly replaceable by oil-based products, the market and quantities produced will grow in parallel with the application industries, whether in pharmaceutical applications or as food additives, especially for fast food and convenience products.

<i>Name</i>	<i>Abbreviation</i>	<i>Production</i>	<i>Application</i>
<i>Carboxymethyl cellulose</i>	CMC	Converted to alkaline cellulose with caustic soda. Alkylation with chloroacetic acid.	oil industry, textile industry, detergent additive, binder, thickener, paper glue (wallpaper paste), protective colloid, food additive E 466 (ice cream, mayonnaise, jelly, bakery products), tooth paste, crosslinked to a tablet disintegrant
<i>Methyl cellulose</i>	MC HEMC HPMC	Converted to alkaline cellulose with caustic soda. Alkylation with methyl chloride. Etherification with propylene oxide.	Additive in various building materials (concrete, mortars, tile adhesives, fillers, plasters, etc.), wallpaper adhesives, thickeners, gelling and glazing agents, emulsifiers, stabilisers in foods (MC: E 461, HPMC: E 464), meat substitute products, ice cream, bakery products, mayonnaise, instant products and frozen goods and cosmetics. In the pharmaceutical industry as "synthetic tears", laxative, negative contrast agent, active ingredient retarder, tablet coating, material for hard capsules.
<i>Ethyl cellulose</i>	EC	Converted to alkaline cellulose with caustic soda. Alkylation with ethyl chloride.	Thickener, binder, adhesive, as well as film former and water-repellent barrier layer. Main component of lightfast cellulose ether coatings, packaging materials, thermoplastics, artificial snow for Christmas trees, cable insulation, protective skins and seals. As an additive of synthetic resins and waxes for lacquering dyed Easter eggs and as an additive for stamping inks in the food industry (E 462). In pharmaceuticals, as an excipient for increasing viscosity, as a binder for tablet granulates, as a builder and disintegrant for tablets and in particular as a film former (e.g. protected by the trademark Surelease®) for lacquer tablets
<i>Hydroxyethyl cellulose</i>	HEC	Converted to alkaline cellulose with caustic soda. Etherification with ethylene oxide.	In the building materials industry in water-soluble paints and dispersion adhesives as well as plaster and fillers. In pharmaceuticals as an excipient and in toothpaste.
<i>Hydroxypropyl cellulose</i>	HPC	Converted to alkaline cellulose with caustic soda. Etherification with propylene oxide.	Use as a pharmaceutical excipient, binder for ceramic masses, for coatings and adhesives, in cosmetics, in printing inks and in polymerisation technology. In food as a stabiliser, protective layer and gloss coating.

Cellulose ethers and their areas of use in industry



At the end of the amixon® granulator, a balance between grain build-up and grain destruction has been created. If operated ideally, the apparatus produces a soundly compacted granulate within narrow grain size boundaries.

Complex reaction processes

The most important cellulose ether in terms of quantity is carboxymethyl cellulose (CMC). Purified cellulose from wood or cotton is ground to a fine powder (particle size approx. 100 to 200 μm) and pneumatically transported into a large pre-mixer (10 to 30 m^3). The downstream reactor is filled from the cellulose filtered premix. After adding the solids, 50% caustic soda is injected into the reactor. This exothermic activation reaction results in sodium cellulose, which is subsequently converted into carboxymethyl cellulose with liquid chloroacetic acid. The CMC synthesis can be done either with or without a solvent (isopropanol or ethanol) using the slurry method.

Other cellulose derivatives (e.g. hydroxypropyl-methyl cellulose) are produced in a similar way. Here, however, no solvents are used as a rule and the reaction chemicals are gaseous (methyl chloride, propylene oxide or ethylene oxide). This results in significantly higher pressures (up to 20 bar) and the danger potential is considerably higher.

Reactors for the production of cellulose derivatives have a pressure-resistant design to ensure that gaseous components remain in the system at high temperatures. They are also provided with a double jacket in order to be able to heat or cool the contents. Larger reactors also have further cooling systems in the superstructure as well as parallel to the reactor.

Furthermore, there are some particular challenges that must be taken into account when designing the reactor. For example, the container material must be very strong and highly resistant to corrosion, because the resulting chlorides of the salts are particularly aggressive at high temperatures in conjunction with water (from the cellulose and the caustic soda). Due to high system pressures during the reaction, there is also a risk of stress corrosion cracking. The handling of the reagents and reaction by-products also requires a lot of know-how. Ethylene oxide (manufacture of HEC or HE mixed ethers such as HEMC) has the greatest danger potential: It is explosive and must be stored in a nitrogen atmosphere. During the production of methyl celluloses (MC, HEMC or HPMC), a side reaction produces dimethyl ether, which is highly flammable, explosive and toxic. On completion of the reaction, it must be discharged together with unreacted methyl chloride. In the industrial process, the gas mixture is collected under pressure and partly reused in the process.

The reaction result is a moist cellulose derivative, which still contains table salt and some by-products (higher alcohols). The raw product is discharged into water with a temperature of 90°C and suspended. Salts and by-products dissolve in hot water, but the cellulose ether doesn't. MC, HEMC and HPMC are insoluble in water at temperatures above 50 – 60°C.

The hot washing water is subsequently filtered off and the filter cake washed to be salt-free. The heated washing water can be used several times during cleaning, because it absorbs up to 30 percent table salt. This process design saves energy and water. The residual moisture content of the purified product downstream the filter and washing stages is still about 50 to 60 percent. The cellulose ether, which still contains the powder bulk density of the ground cellulose after washing (approx. 150 g/l), is now carefully cooled to its approximate dissolving temperature in water (approx. 45°C) in a continuously operating ring-layer mixer granulator, also by means of the addition of cold water or crushed ice. The objective is to achieve an increase in the bulk density (350 - 400 g/l) by partially dissolving while at the same time kneading.

The methyl cellulose and the crushed ice are continuously poured into the ring layer mixer-granulator and accelerated in a rotating movement. A ring layer is formed on the wall. This layer is intensively mixed, deagglomerated, compressed and conveyed by the pin tools. Therefore, solid and liquid bridges form between the particles. Granulation seeds are created and grow to a certain size. If the granules grow beyond a certain size, they become fragile and disintegrate. Fine aggregate content formed in this way clings again and is rounded. A balance is created between grain build-up and grain destruction. If operated ideally, the RMG produces a stable, compacted granulate within narrow grain size boundaries.

In the last process step, the product is ground and dried in flow dryers. The dry product is collected and homogenised in large mixers before being packed in sacks or big bags.



amixon® supplies smaller vertical reactors for special cellulose derivatives and offers extremely large heat exchanger surface areas



Final homogenisation

The raw material cellulose is a natural product. Like all natural products, the raw material is subject to variations resulting from the season and the place where the tree was harvested. In addition, the material is processed in batches. Here, too, there are slight differences in the quality from batch to batch. One of the main tasks of the final mixer is to balance these differences. Three methods of final mixing are described below.

Two opposed flows meet in the amixon® mixer. At the outside, the mixtures are transported upwards in spiral fashion, while a downward flow prevails in the centre. All particles change their neighbourhood in the border areas. The shovel-shaped mixing tool arms create supplementary transverse flows. Technically ideal mixing qualities are achieved despite slow rotational speed. These mixtures are practically impossible to improve any further. The total flow described sets all particles continually in motion relative to one another. It is universally present, regardless of whether the filling level is 5% or maximum. The special shaping of the mixing device helix with its „SinConvex®“ design guarantees virtually 100% residue-free emptying. The particularly gentle processing of the mixture is derived directly from the low drive power. The mixture particles are neither ground, nor rounded and/or broken.



40 m³ final mixer. amixon® manufactures various vertical mixers up to 100 m³ and guarantees ideal mixing qualities with a minimum input of energy. The result is a homogeneous product of equal grain size distribution and chemical composition.



amixon® continuous mixer AMK

Continuous final mixing

Interesting here is that this kind of mixture – regardless of the size – can optionally be operated batch-wise or continuously. What's even more interesting is that the discharged mixtures correspond to the ideal mixing quality right from the start. There are no „startup losses“. This is explained below:

Operation at start of production:

The discharge device of the mixer is closed. All the gravimetric working dosing components are started simultaneously with small mass flow and tune themselves automatically in relation to one another. The level of the mixing container fills up continuously, starting up the mixer drive when it reaches half filling quantity. Tuning is completed once the mixer is filled to about half its capacity. The discharge device opens slowly once the desired filling level (approx. 40 to 90 % of the usable capacity) has been reached. A constant filling level is ensured. The dosing flows are increased up to the maximum mass flow while maintaining a constant tuning.

Operation at end of production:

All dosing devices gradually slow down the mass flow and then switch off and close at the same time. The mixer discharges the mixture continuously until it is completely empty. Free-flowing goods flow out completely.

These are the user benefits at a glance:

- technically ideal mixing quality
- choice between operation as a batch mixer for premixes, or as a continuous mixer
- adjustable mixing intensity (from gentle homogenisation to intensive deagglomeration)
- defined dwell time based on the vessel flow – regardless of the rotary speed of the mixing tool
- no product loss at start of production
- no product loss at end of production
- ideal residue-free emptying
- defined filling level from 10% to 100% of cubic capacity
- micro-fine admixture of liquid material without contamination of the mixer
- extended processes such as humidifying, tempering, drying, reaction execution possible
- highest health standard (GMP Standard); safe cleaning; dry or wet
- Mixing device is only supported and driven from above.

Final mixer for particularly large batches Gyraton®-mixer

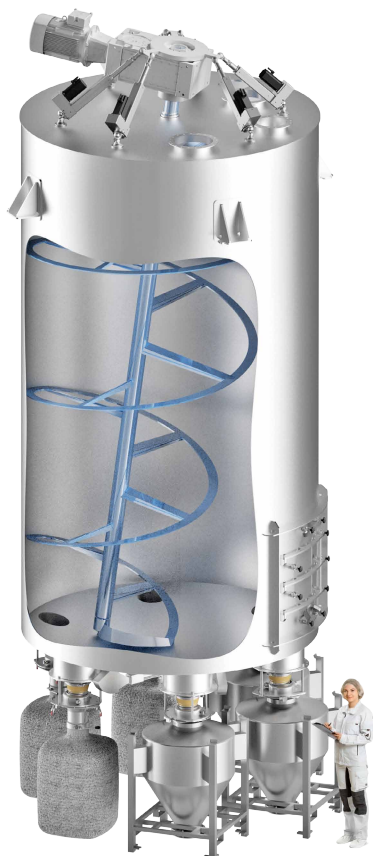
For the homogenisation of particularly large batches, amixon® has created an interesting new development in the form of the Gyraton® mixer:

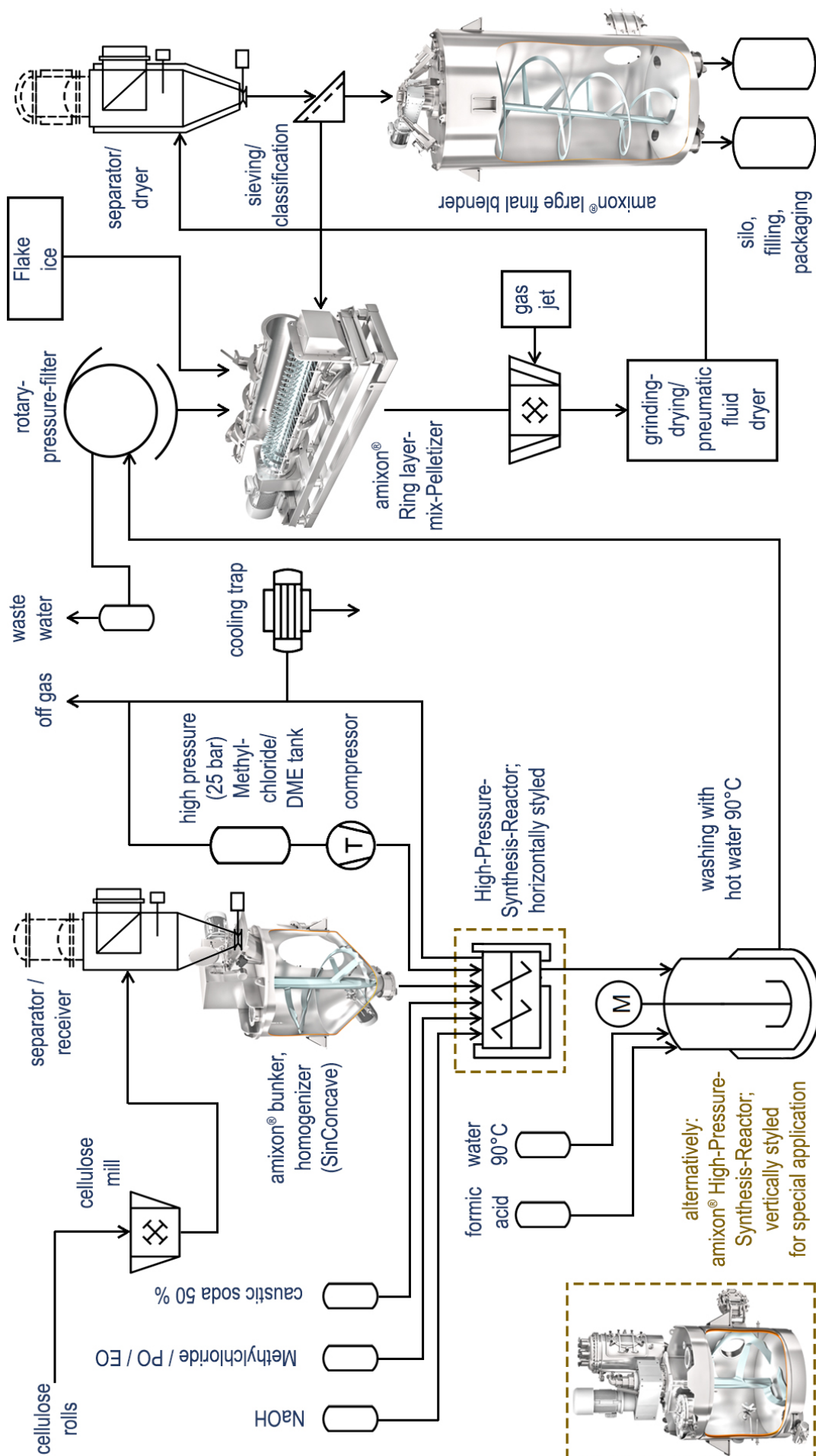
The mixing tool helix rotates clockwise and transports the mixtures upwards. The mixing device gyrates around the shaft seal and seizes all volumetric parts intermittently but free of dead spaces.

This mixer is used for dry, moist or even suspended bulk materials too if the materials are sufficiently free-flowing. Liquid admixtures can optionally be mixed in as well. The sizes are freely selectable from 10 m³ to 100 m³. Best mixing results are already achieved from a filling level of 10%. Mixing is extremely gentle with a low energy input. The mixer is fed from above via one or more standard nozzles. The mixtures are discharged downwards through a standard nozzle when the floor flap is open. Emptying can also take place simultaneously via two, three or more outlet nozzles in order to fill several big bags or containers at the same time, for example.

Special features:

- space-saving, compact
- safe and fast emptying
- convenient to inspect or clean with large inspection door
 - wet (automatic)
 - manually drying with vacuum cleaner
- optionally pressure-resistant or vacuum-resistant, in any case gastight
- The mixing process is particularly gentle with minimum energy input.
- The rotational speed of the mixing tool and the gyratory movement are adjusted according to the mixing time, which the customer can specify. The energy consumption is accordingly low.
- The temperature of the mixing chamber and the entire mixing tool can optionally be controlled. The mixing system can be used as paste bunker, vacuum dryer or heat exchanger.





System diagram of a HPMC process



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