Proprietary process technology

HCBR

High Cis Polybutadiene Rubber polymers

Versalis proprietary process technologies available for licensing

Our company

Versalis - the petrochemical subsidiary of Eni - is a dynamic player in its industry sector facing the multifold market needs through different skills.

With a history as European manufacturer with more than 50 years of operating experience, Versalis stands as a complete, reliable and now global supplier in the basic chemicals, intermediates, plastics and elastomers market with a widespread sales network.

Relying on continuous development in its production plants as well as in its products, strengthening the management of the knowledge gained through its long industrial experience, Versalis has become a worldwide licensor of its proprietary technologies and proprietary catalysts. The strong integration between R&D, Technology and Engineering departments, as well as a deep market expertise, are the key strengths for finding answers to customers requirements.

Our commitment to excellence, in quality of our products and services, makes our company an active partner for the growth of customers involved in petrochemical business.

Through engineering services, technical assistance, marketing support and continuous innovation, our knowledge is the key strength to customize any new project throughout all phases.

Customers can rely on this strong service-oriented outlook and benefit from a product portfolio that strikes a perfect balance of processability and mechanical properties, performance and eco-friendliness.

Introduction to Versalis HCBR technology

High Cis Polybutadiene rubber (HCBR) was first developed by Eni in the 80s with the aim to produce rubber grades with specific properties in tyre sector as well as in other industrial applications. HCBR offers higher abrasion resistance and display lower heat build-up under dynamic load, meaning that they reduce rolling resistance. Furthermore, tyre sidewalls made with HCBR are less susceptible to cracking. Neodymium is used to manufacture a Ziegler-Natta catalyst. The Neodymium Catalyst reacts with a chlorine donor as well as an aluminium activator. Typical Versalis HCBR line is based on one reaction section, one finishing line and one packaging line.

Key features of Versalis HCBR production technology are:

- high flexibility in terms of product mix and good quality constancy and reproducibility;
- use of hexane or chexane as solvent, in comparison with theconventional processes where aromatic solvent are used. Non aromatic solvent brings several advantages in terms both of economics (lower steam consumption) and of environmental health (toxicity of hexane is lower than aromatics);
- polymerization reaction is carried out adiabatically bringing many advantages concerning energy consumption, investment cost and easier operations;
- due to the fact that neodymium is not an oxidation catalyst, normal antioxidants easily protect HCBR from oxidation during processing and storage, while troubles may occur in conventional processes where Cobalt and Nichel are normally used;
- no purification operations are necessary to remove toxic metals residuals from catalyst;
- optimized configuration of the stripping section with three stages arrangement to minimize steam consumption without impact emissions of VOC;
- small quantity of volatile organic compounds (solvent) enter finishing section (low release during extrusion).

Versalis can always provide appropriate solutions to different client's needs thanks to its capabilities and experience in the following fields:

Research & Development

The presence of a strong R&D team, established in Ravenna since the early 70s, qualifies Versalis as an outstanding owner of know-how in the field of elastomers. Reliable and updated facilities (pilot plants, synthesis and analytical labs, equipment for elastomer processing), allow Versalis to continuously up-to-date the technology in order to support the elastomers business in a very competitive and demanding market scenario. Additional services are then available for potential Licensees, such as technical assistance, training, development of analytical methods, site assistance for start-up and follow up, development of tailor made products on demand.

Process design & operational experience

Process design is flexible and able to face different conditions and constraints. Any project is individually evaluated to offer the best solution, tailored to specific customers needs. Thermal and fluodynamic analysis (CFD) can be applied to the design of key equipment such as reactors, agitators and strippers.
The design takes also advantage of the Versalis long-term manufacturing experience.
New technological solutions are first tested in production plants and the acquired experience transferred to the licensed technology, in order to reach not only the best process performances, but also a safe and reliable plant arrangement.

Mechanical design

Versalis Engineering Dept. has been working in close coordination with the Process Dept. since a long time. This fact has allowed to develop unique and well sound engineering solutions for critical equipment, that guarantee the best results in terms of mechanical reliability and process performances.

Versalis HCBR technology allows to provide with a single line a fairly broad range of economically feasible capacities: up to 40 kt/y per reaction unit with a single finishing line.

Wastes and emissions

The design of the plant is carried out taking into account the target of the minimization of the effluents as this means more efficiency and lower environmental impact. The process produces oily waste water which can be treated in a standard bio-treatment. Large waste air emissions from finishing require only a scrubbing process (dedusting). Some selected exhaust streams from finishing section are usually sent to a regenerative-type thermal oxidizer (ISBL) in order to minimize the environmental impact of the process. Normal process venting are collected and can be sent to flare or other OSBL systems. Solid waste material, during normal operation, is limited to small amounts of filtering elements, plastic cans used as chemicals' package and rubber cleanings from paved areas.

Industrial applications

The first production plant (25 kton/year) was build in 1985 at the Versalis site in Grangemouth (UK). In 1993 a new plant was started up in Ravenna site (Italy) with a capacity of 40,000 ton/year, which was then modified and impoved step by step according to experimental results as well as to the continuous market feedbacks. In 2008 the Ravenna plant has been revamped increasing the capacity at 80,000 ton/year.

Main process parameters

	per MT of HCBR
Raw Materials (Butadiene)	1,020 kg
Electricity	0.52 MWh
Steam (Medium Pressure + Low Pressure[1])	6 MT

[1] 10 barg and 6 barg respectively.

The Europrene® HCBR polymers portfolio

Versalis HCBR technology enables the production of two different viscosity grades of Dry polymer. Changing the polymer viscosity is possible to obtain products characterized by:

- a medium viscosity grade highly suitable to be used in tyre industry; due to relatively high molecular weight compounding results easy, while the high cis level allows to increase both mechanical as dynamic properties. In trade wear applications the use of HCBR with sSBR guarantees important reduction in rolling resistance while its use in tyre sidewall permits to reach incomparable fatigue and tear resistance;
- a high viscosity grade suitable to be used when mechanical properties are strongly requested. The combination of high molecular weight and high cis content allows increasing recovery with excellent results in terms of fatigue and tear resistance. Such portfolio of products is continuously improved by our R&D centers through market feedback.

All polymer grades are stabilized with a specifically designed antioxidant package.

Process description

Polymerization of butadiene in aliphatic solvent is achieved by means of Neodymium based catalyst; this kind of catalyst was firstly developed in the middle of 70s by Assoreni (Eni owned company), and recently developed in Versalis Research Centre of Ravenna.

The rare earth based polymerization is a way to polymerize dienes that permits a strong control of 1-4 cis isomer content in polymeric chain. Due to the ability of 1,4 cis sequences to crystallize under deformation, high level of cis greatly improves mechanical properties like tear strength and abrasion.

The process includes purification of solvent and monomers through distillation and adsorption operations as well as blanketing with dry nitrogen of all chemical mix and feed tanks, in order to ensure the lowest level of poisons detrimental to polymerization reaction.

Catalyst is easily prepared in a specific section of the plant mixing a Neodymium salt with an aluminium alkyl and an organic chloride; after a brief period useful to reach the completeness of the reaction, it is fed to the first reactor of the continuous train of polymerization.

The dry mix feed (butadiene and hexane) coming from the purification systems is fed to the reactor together with the catalyst solution. Butadiene polymerization takes place in continuous in two stirred tank reactors operating in series.

Molecular weight is easy to be controlled using an appropriate chain transfer which is fed directly in reactors during the polymerization: the easiness of this control results in a high Mooney stability of the production over long periods.

The polymer solution leaving the reactors is mixed with the stopping agent to destroy the catalyst and then is discharged into blend tanks in order to homogenise the product. Vapour coming from blend tanks are condensed and sent to light's column to separate and recycle the non-reacted monomer.

The blended solution with the antioxidant agents is fed to the stripping section where the solvent is removed by steam distillation in the presence of a dispersing agent aimed to control the crumb size in the slurry.

The crumb slurry is then pumped to the finishing unit where the crumb is dewatered on a shaker screen, being the water partly recirculated to the strippers and partly sent to waste water treatment.

The vapours obtained from the stripping section are otherwise condensed and the solvent, separated from water by a decanter, is sent to the wet solvent tank.

The dewatered crumbs are dried in two mechanical extruders in series, cooled with air, weighed and baled. Catalyst is able to built a molecular architecture which avoids any cold flow phenomenon; bales are dimensionally stable and its automatically made handling is highly appreciated; other that the high activity of the catalyst permits to be used at very low concentration; the process technology grants for no yellowish hue or colour appearing.

Process design advanced features

- Very good control of impurities level through a special design in purification section that leads to market required product quality.

- Special design of continuous and adiabatic section in order to minimize reactors fouling, to lower investment costs and to save energy.

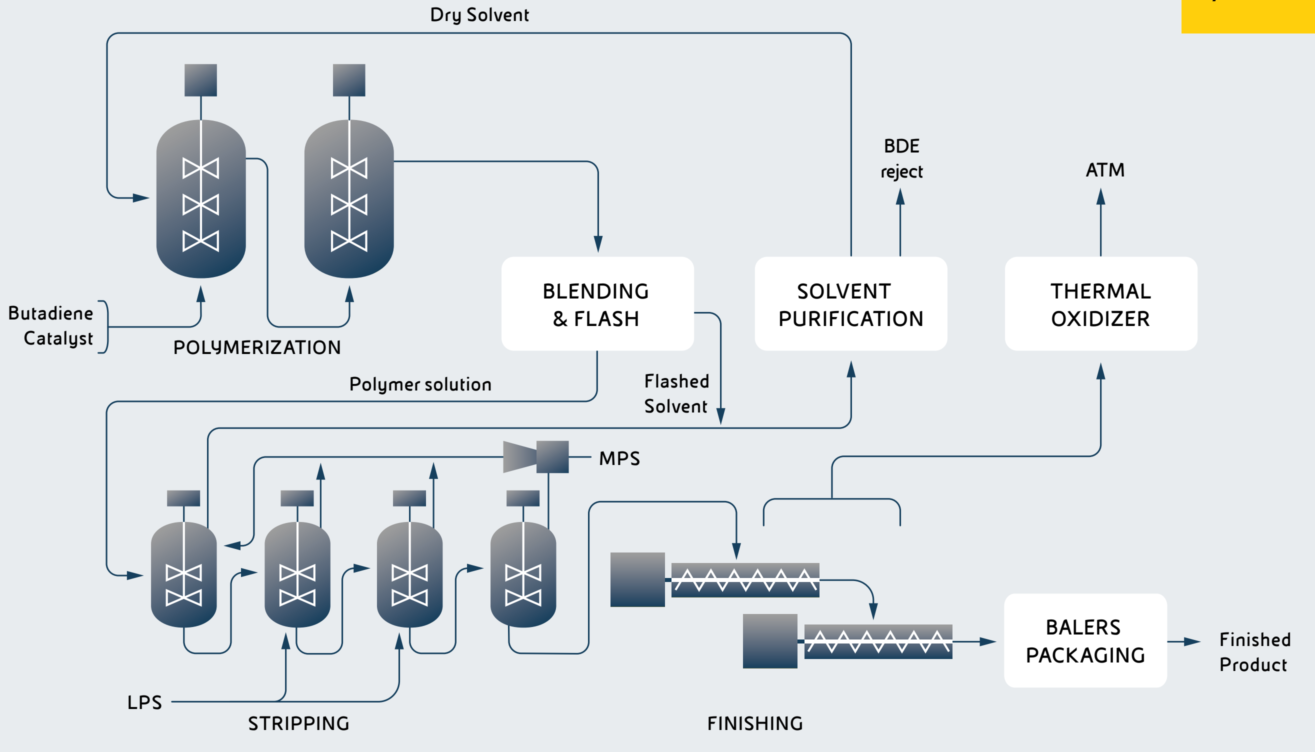
- Recovery and recycle of non-reacted monomers which enhance the raw material consumption figues.

- Polymerization is carried out adiabatically. This feature gives many advantages concerning energy consumption, investment cost and ease of operation, since:
  - use of heat exchange fluid (cooling water or refrigeration fluid) in polymerization is not required;
  - the high heat content of polymeric solution (cement), available at about 100 °C at the end of the polymerization train, is recovered increasing the solid content of cement, allowing to decrease the consumption of stripping steam;
  - heat exchange operation on cement and related problems (viscous system, scaling of surfaces, etc.) is avoided;
  - problems of products quality, that would arise in other processes in case of troubles in removing of polymerization heat, are avoided.

- Special purification section brings raw material impurities to negligible level, avoiding detrimental effects on both the process and structural parameters of the product.

fig. 1

HCBR • process scheme



Proprietary process technologies portfolio

Biotech

PROESA® 2G Ethanol and Cellulosic Sugars

Phenol and derivatives

Cumene (with PBE-1 zeolite based proprietary catalyst)*
Phenol, Acetone, Alphamethylstyrene*
High selectivity Cyclohexanone
Acetone hydrogenation to Isopropyl Alcohol*
Isopropyl Alcohol to Cumene**
Ammoximation (with Titanium silicalite based proprietary catalyst TS-1)

DMC and derivatives

Dimethylcarbonate (via Carbon Monoxide and Methanol)*
Diphenylcarbonate*

Proprietary catalysts

Titanium silicalite
PBE-1 Zeolite
PBE-2 Zeolite

Styrenics

Ethylbenzene (with PBE-1 and PBE-2 zeolite based proprietary catalyst)
Styrene
GPPS
HIPS
EPS suspension polymerization
ABS continuous mass polymerization
SAN

Polyethylene

LDPE
EVA

Elastomers

Emulsion-SBR
HSL Latices
Solution-SBR
TPR
LCBR
HCBR
NBR
Carboxylated latices
EP(D)M

* Co-licensing in cooperation with Lummus Technology (a McDermott International Company).
** Close to commercialization.

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