Proprietary process technology

STYRENE

versalis

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 Styrene technology

Versalis is in the position to offer a competitive styrene technology which has been developed by taking great advantages of Versalis long experience in both plant design and styrene manufacturing and sales. As in the present competitive styrene market even small differences in raw materials and utilities specific consumption can heavily influence the profit, the technology can be furthermore really tailored and customized to site conditions and customer needs. Styrene technology is reliable and proven at industrial scale, with the first plant come on stream in the early 90s and another plant with a 600 KTA capacity successfully started-up in early 2010.

Key features of Versalis styrene production technology are:

- low ethylbenzene consumption;
- high conversion/yield;
- high styrene quality;
- low energy consumption (high level of heat recovery);
- unique and patented solutions for EB/steam mixing and reactor effluents main condenser;
- long catalyst life;
- high plant reliability (due to thermal and mechanical analysis during design);
- optimized hot zone lay out (position of reactors and exchangers are settled in order to minimize residence time at high temperature in interconnecting pipelines, taking care either of pressure drop and piping elasticity);
- low maintenance cost;
- Versalis can also offer proprietary technologies which can be considered as option for a better integration of the styrene unit with site condition;
- proprietary technology for the up-grade of hydrogen off-gas to be used as raw material in hydrogenation process;
- proprietary technology for PA (phenyl acetylene) reduction;
- proprietary technology for benzene by-product treatment for its recycle to a liquid phase zeolite EB process.

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

Research & operation

Versalis background and expertise in Styrene technology comes both from manufacturing experience and the presence of a strong R&D team established in Mantova since the early 70s. A great and updated know how comes from continuous lab & pilot plant testing on dehydrogenation catalysts and polymerization inhibitors/retarders to be then applied on Styrene industrial plants.
A simulation program, suitable to optimise inhibitor/retarder dosage against polymer formation prediction, has been developed and applied since many years.

Process design

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) are applied to hot area reactors/exchangers and interconnecting piping to increase heat recovery, minimise pressure drop and reduce lack of homogeneity in distribution.
The great attention to minimise hot void volume, where low selectivity reactions take place, and the run of the reaction at very low pressure, has led to an improved design able to maximise catalyst performances and overall process selectivity.

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.
Thermal and mechanical analysis (including FEA) are applied to minimise temperature gradients, reach smooth discontinuity in wall thickness, improve stress distribution.

Wastes and emissions

The process produces oily waste water which can be treated in a normal bio-treatment.

As an option, a special treatment can be included in the plant in order to recover such liquid effluent as boiler feed water.
Other liquid waste and continuous / non-continuous vents can be sent to the steam super-heater furnace in order to lower all the plant emissions to a practically negligible amount. Spent catalyst at the end of its lifetime can be disposed in a normal landfill.

Industrial applications

Two styrene plants, based on proprietary technology, are on stream in Italy: a 430 kt/y, 2 reaction stages and a 190 kt/y, 3 reaction stages.
A styrene unit of 600 kt/y has been licensed by Versalis and started-up in early 2010.

Product quality

Styrene (dry)	99.95% wt

Main process parameters

Ethylbenzene consumption (MT per MT styrene)	1.051
Continuous run length	up to 36 months
EB conversion per pass	up to 71%

Process description

Reaction (hot Zone)

The gas phase ethylbenzene dehydrogenation occurs in two or three reactors used in series with interstage re-heater. The heat is provided by superheated steam, which, at the end of the cycle, will enter in the first reactor together with ethylbenzene.
The main reaction by-products are toluene and benzene; hydrogen rich off-gas is normally recycled in the steam superheater as fuel gas. Due to high operative temperature a small amount of heavy components are formed.

Condensation (cold Zone)

The reaction effluent, after heat recovery, is sent to the following section, where organic and steam are condensed and separated from off gases (hydrogen, carbon dioxide, methane, ethylene, etc).
Off gas is removed by a compressor that assures the vacuum pressure in the reactors. Water is purified and normally reused, whereas organic phase is sent to distillation section. With reference to such scheme, Versalis can offer different process solutions, in order to best fit customer need.

Distillation

Crude styrene (about 70%) with ethylbenzene, benzene, toluene and some heavy components, is fed to the first column where benzene and toluene are recovered as overhead. Such mixture can be fed to another column where benzene and toluene are separated. Ethylbenzene, styrene and heavies feed another column, where ethylbenzene is separated from styrene in vacuum conditions. The bottom is fed to the following column, where pure styrene is recovered from the top. The bottom is further processed in a finishing equipment, to recover additional styrene from the residue. In the overhead vapour of the styrene column p-tert-butylcatechol (TBC) is added, to prevent the polymerization of styrene in the storage.
Although distillation columns work in vacuum, bottoms temperatures can vary from 85 to 110 °C. For this reason it is necessary to add an inhibitor to avoid losses of styrene due to polymerization. Different substances as inhibitors or retarders can be used for this purpose as nitroderivatives, free radicals, etc; they can be used alone or in combination, to have a possible synergetic effect. Versalis can provide an up-to-date design including special arrangements suitable to achieve low material losses and energy consumption with very low inhibitor consumption.
A wide range of inhibitors and retarders have been tested and can be proposed.

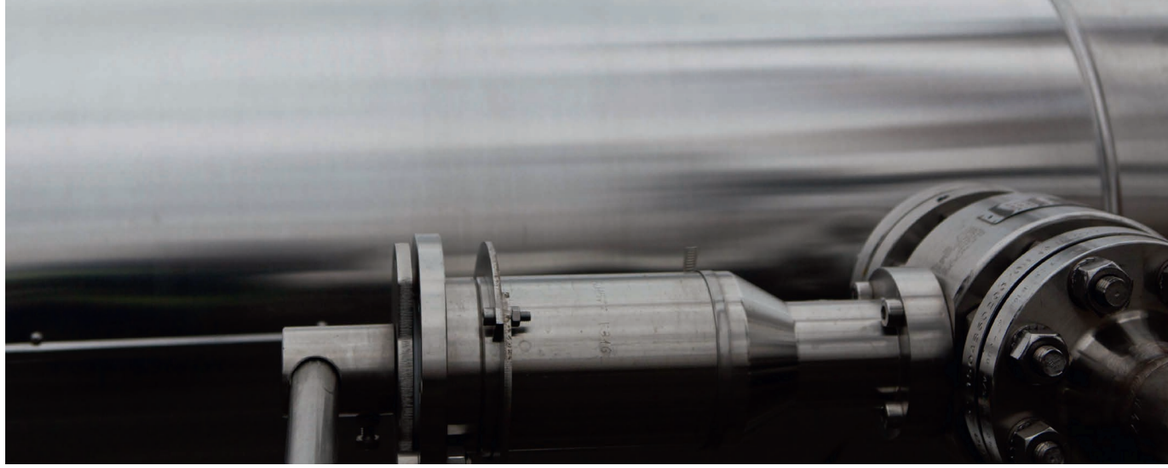
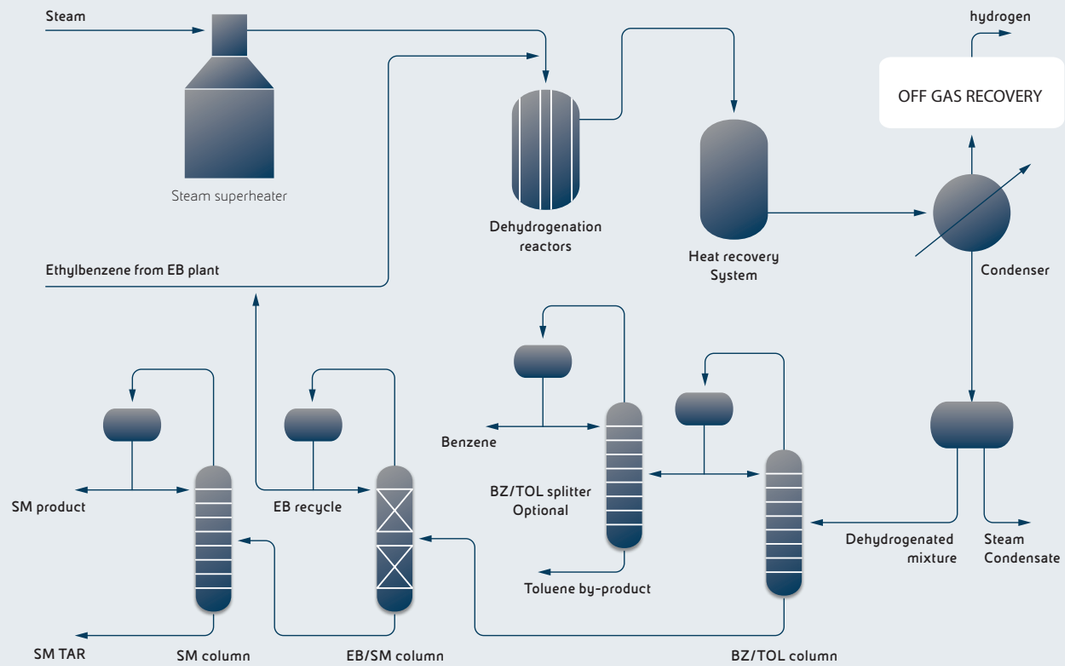


Fig. 1

Styrene • 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.

versalis

Versalis spa
Piazza Boldrini, 1
20097 San Donato Milanese (MI) - Italy
Ph. 0039 02 520.1

info@versalis.eni.com
versalis.eni.com

Responsible Care

SINCERT

Licensing:
Piazza Boldrini, 1
20097 San Donato Milanese (MI) - Italy
Ph. 0039 02 520.42931 - fax 0039 02 520.42286

info.licensing@versalis.eni.com

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