Styrene

Proprietary
process technology

eni polimeri europa

POLIMERI EUROPA PRODUCTION TECHNOLOGIES FOR LICENSING

Licensing

Proprietary process technologies

Phenol and derivatives
PBE-1 Zeolite catalyst based Cumene *
Phenol, Acetone, Alphamethylstyrene *
Isopropyl Alcohol Acetone hydrogenation *
Isopropyl Alcohol to Cumene *
PBE-1 Zeolite catalyst
TS-1 Titanium silicalite catalyst based Ammoximation

DMC and derivatives
Dimethylcarbonate
via Carbon Monoxide and Methanol *
Dimethylcarbonate / Diphenylcarbonate *

Polyethylene
LDPE
HDPE
EVA

Styrenics
PBE-1 and PBE-2 Zeolite catalyst based Ethylbenzene
Styrene monomer
GPPS
HIPS
EPS
ABS continuous mass polymerization
SAN

Elastomers
e-SBR
s-SBR
SBS / SB / LCBR
Polybutadiene

Proprietary catalyst technologies

Titanium silicalite
PBE-1 Zeolite
PBE-2 Zeolite

* Co-licensing in cooperation with Lummus Technology

Polimeri Europa

Polimeri Europa – the petrochemical company of Eni – manages the production and marketing of Basic Chemicals, Polyethylene, Elastomers and Styrenics.

With its 17 production sites throughout Europe and a widespread sales network, Polimeri Europa can present itself to the intermediates, thermoplastic resins and elastomers market as a sound and comprehensive supplier whose key strength is its integration. From raw materials to production plants, from research laboratories to technology, through to the interface with the market which can turn to a single source with the certainty of finding solutions to its requirements not only in terms of products, but also in terms of assistance and service. Thanks to the definition of the e-commerce and the logistic portal express, Polimeri Europa can offer to its customers the opportunity to use their tailored made e-shopping and logistics.
Saving time and money.

On the basis of its first hand experience, Polimeri Europa can also license its proprietary production technologies aiming to satisfy the even more specific customers needs.

Polimeri Europa's commitment to quality, improvement and innovation continues, as does its pledge to promote sustainable growth with regard to the community and the environment.

NOW AVAILABLE

Introduction to Polimeri Europa Styrene process

Styrene is one of the most important basic chemicals.
In the late fifties, Polimeri Europa started the production of styrene in Mantova (Italy). Driven by its Research Centre in Mantova, in the second half of the seventies the company began the development of a proprietary technology, by improving process and key equipment of existing units. The final result of this effort was the design of a new styrene production unit, that went on stream in early nineties, in Mantova.

In the present competitive styrene market, small differences in raw materials and utilities specific consumption can heavily influence the profit. For this reason it is very important to take into account any possible aspect that can affect the choice of process parameters of a new unit, to find the most optimised design, specifically tailored for site condition and customer’s needs.
Taking advantage of its long experience on both design and manufacturing of styrene plants, Polimeri Europa is now in a position to offer a competitive styrene technology.

Low ethylbenzene consumption, high conversion/yield, low energy consumption, long catalyst life, plant reliability, low maintenance cost is a multi function with an optimum to be defined as a compromise, case by case, in relation with site conditions and customer’s needs.

With this aim, Polimeri Europa can provide appropriate solutions thanks to:

Research and Operation

Polimeri Europa background and expertise in styrene technology comes from manufacturing experience and constant lab & pilot plant testing on dehydrogenation catalysts and polymerisation inhibitors/retarders.

Process design

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

Accuracy in this field is really important, because it affects plant reliability.
Thermal and mechanical analysis (including FEA) are applied to minimise temperature gradients, reach smooth discontinuity in wall thickness, improve stress distribution.
Very important is also the hot zone lay-out, where mutual relevant position of reactors and exchangers is settled in order to minimise residence time at high temperature in interconnecting pipelines, taking care either of pressure drop and piping elasticity.

TECHNICAL DATA

Product purity and material balance

Styrene quality
Styrene

Styrene plant material balance
Raw materials
Ethylbenzene

Process parameters

Styrene plant
Steam/Oil
Continuous run length
Conversion

99.9% wt min
MT per MT Styrene
1.055

1.4
3 years min
72% min

Process economics and product purity

A styrene plant, operating with three reactor stages, has a typical set of process parameters as reported; the consumption of utilities (electric power, steam and fuel gas) is typically related to adopted scheme, depending on customer needs.
A 500 kt/y ISBL Styrene unit has an estimated investment cost of 120 million Euro (NWE basis).

Industrial applications

Two styrene plants, based on proprietary technology, are on stream in Italy: a 430 kt/y, 2 reaction stages, with feed/effluent heat recovery and a 190 kt/y, 3 reaction stages, with medium pressure superheated steam generation, to drive off gas compressor.
A styrene unit of 600 kt/y, licensed in Iran by Polimeri Europa, will start up at the end of 2005.

Process description

Reaction (hot zone)

The gas phase ethylbenzene dehydrogenation occours in two or three reactors (depending on the overall balance of different economical aspects) used in series with an interstage re-heater. The heat is provided by superheated steam, that, at the end of the cycle, will enter in the first reactor together with ethylbenzene. Steam has other two positive effects on the catalyst:

- decreases the amount of coke or coke precursors, formed by parallel cracking reactions of ethylbenzene, by steam-reforming reactions;
- avoid catalyst over-reduction and deactivation, by controlling the oxidation state of iron; steam, that has oxidant proprieties, balances the high reduction capacity of hydrogen at high concentration and temperature.

The main reaction by-products are toluene and benzene; carbon dioxide is also an important by-product which comes from the steam reforming reaction with the coke settled on the catalyst. Due to high operative temperature a small amount of heavy components are formed.

Condensation (cold zone)

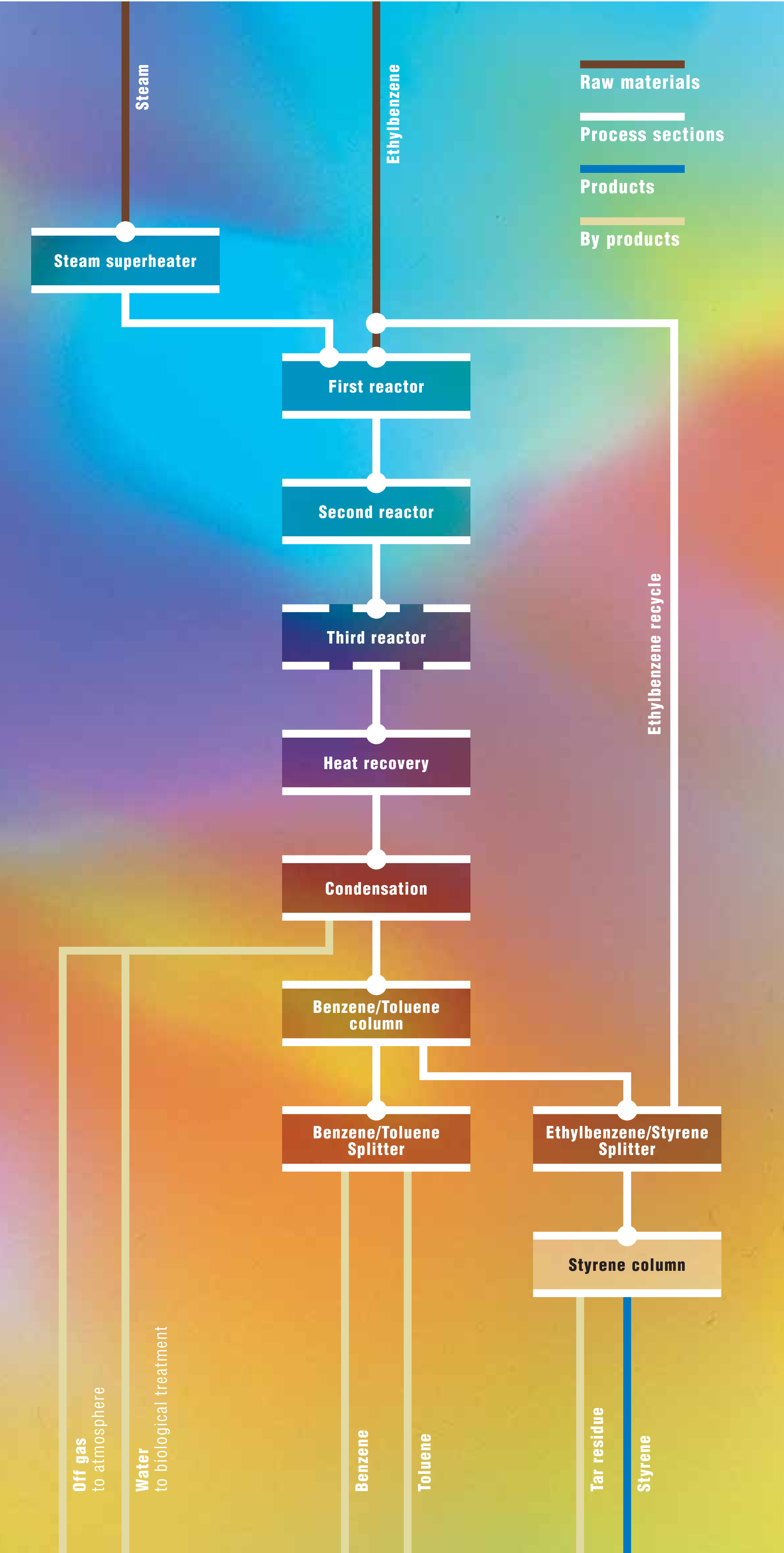
The reaction effluent, after heat recovery, is sent to the following section, where organic and steam are condensed and separated from off gases (hydrogen, carbon dioxide, methane, ethylene, etc).
Off gas is removed by a compressor that assures the sub-atmospheric pressure in the reactors. Water is purified and normally reused, whereas organic phase is sent to distillation section.
With reference to such scheme, Polimeri Europa 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 feeds another column where benzene and toluene are separated. Ethylbenzene, styrene and heavies feed another column, where ethylbenzene is separated from styrene in vacuum conditions. This is a quite difficult separation because the normal boiling points of ethylbenzene and styrene differ by only 9°C. Ethylbenzene, with some residual styrene (normally no more than 2%), is recovered as overhead and recycled to the dehydrogenation section. 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-butyl-catechol (TBC) is added, to prevent the polymerisation 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 polymerisation. This is a very critical design feature, because the formation of polymer, in the distillation section, can have a negative impact not only in raw material consumption, but also in the maintenance cost and mainly in plant reliability. 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.

Polimeri Europa 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. Polimeri Europa has also developed a simulation program suitable to optimise inhibitor/retarder dosage against polymer formation prediction.



Raw materials
Process sections
Products
By products
Steam
Ethylbenzene
Steam superheater
First reactor
Second reactor
Third reactor
Heat recovery
Condensation
Benzene/Toluene column
Benzene/Toluene Splitter
Ethylbenzene/Styrene Splitter
Styrene column
Ethylbenzene recycle
Off gas to atmosphere
Water to biological treatment
Benzene
Toluene
Tar residue
Styrene

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Responsible Care

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07/2009