Proprietary process technology

ETHYLBENZENE

WITH PBE-1/2 ZEOLITE BASED PROPRIETARY CATALYST

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 Ethylbenzene technology

Versalis is in the position to offer an up-to-date and flexible Ethylbenzene production technology, based on the proprietary zeolite-based catalysts PBE-1 for alkylation and PBE-2 for transalkylation stages. Technology is reliable and proven at industrial scale with an Ethylbenzene grass root plant of 650 KTA capacity, successfully started up in 2009 to feed a Styrene downstream plant. Points of strength of Versalis technology are the high selectivity and excellent stability of PBE-1 and PBE-2 zeolite based catalysts, along with high design capabilities, always oriented to reliability, safety and great attention to details, based also on Versalis industrial experience as EB producer.

Key features of Versalis EB production technology are:

- proprietary, non-corrosive and extremely tolerant to poison PBE-1/2 zeolite based catalyst;
- ultra high product purity (typical value 99.98%);
- 100% ethylene conversion and overall 99.7% yield throughout the whole run length;
- negligible amount of xylenes by-produced (less than 10 ppm);
- simple and safe operation;
- all carbon steel construction and no critical proprietary equipment that have to be supplied by the licensor;
- low investment and plant maintenance costs;
- environmentally friendly proprietary zeolite catalyst. Easy catalyst handling and spent catalyst disposal;
- stable catalyst; continuous run-length between regenerations from 2 to 7 years;
- extended catalyst life (up to 5 reaction/regeneration cycles without performance deterioration);
- efficient and reliable fresh benzene treatment to protect the catalyst from nitrogen contaminants;
- low environmental impact;
- no acid waste stream and minimal fugitive emissions.

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

Research & development

Starting in the beginning of the 90s, a huge number of different zeolite catalysts have been tested, covering a wide range of process operating conditions, for both alkylation and transalkylation reactions.
Experimental activities have led to the choice of zeolite catalysts tailored for each section and to the definition of relevant best process scheme and operating conditions.
A great effort also has been made in investigating catalysts deactivation due to the different possible poisons and to set up suitable pre-treatment sections, to avoid sudden losses of activity.
For all these purposes, several laboratory scale pilot plants have been used, together with a large pilot plant (500 kg/h flow rate), all of them still in operation.
The first industrial PBE catalyst drop in case started operations in 2001.

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 extensively applied to the design of key equipment such as reactors, their internals and main heat exchangers.

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.

PBE type catalysts

PBE type catalysts show very high selectivity for alkylation and transalkylation and, above all, a very high stability, at the highest level among common zeolite based catalysts. More particularly, the preparation procedures allow optimal values for extrazeolite porosity and degree of interconnectivity, which results in very high catalyst stability, with very low ethylene oligomerisation and deactivation due to coke deposition. Versalis has also developed and experienced, for its PBE catalysts, industrial scale production and regeneration. Up to now, hundreds of tons of PBE catalyst have been produced and loaded in industrial reactors since 1996.

Wastes and emissions

The process produces no liquid wastes or vapour emissions with the exception of oily water and vacuum pumps vents.
Spent catalyst can be regenerated several times and at the end of its lifetime can be disposed in a normal landfill. The plant can be provided with a vent recovery network, for continuous and non-continuous vents, to be sent to a combustor in order to lower all the plant emissions to a practically negligible amount.

Industrial applications

The first industrial Ethylbenzene plant was a PBE type catalyst drop in case which started the operations in 2001; a second grass-root Ethylbenzene unit of 650 kt/y has been licensed by and started-up in 2009.

Product quality

Ethylbenzene	99.98% wt
Di-ethylbenzene	< 5 ppm wt max
Xylenes	almost nil

Main process parameters

Material Balance	**MT per MT EB**
Benzene	0.738
Ethylene	0.265

Utilities Consumption	**per MT EB**
Net steam Consumption(1)	– 0.3 MT

(1) As a Balance between HP Steam Import and LP Steam Export.
All Steam Export can be consumed in the Downstream Styrene Plant.

Process description

The fresh benzene feeds a pre-treatment section, where a guard bed is used to remove harmful impurities (catalyst poisons). Then, treated benzene enters in the distillation section where is pumped to the reaction sections with recycled benzene.

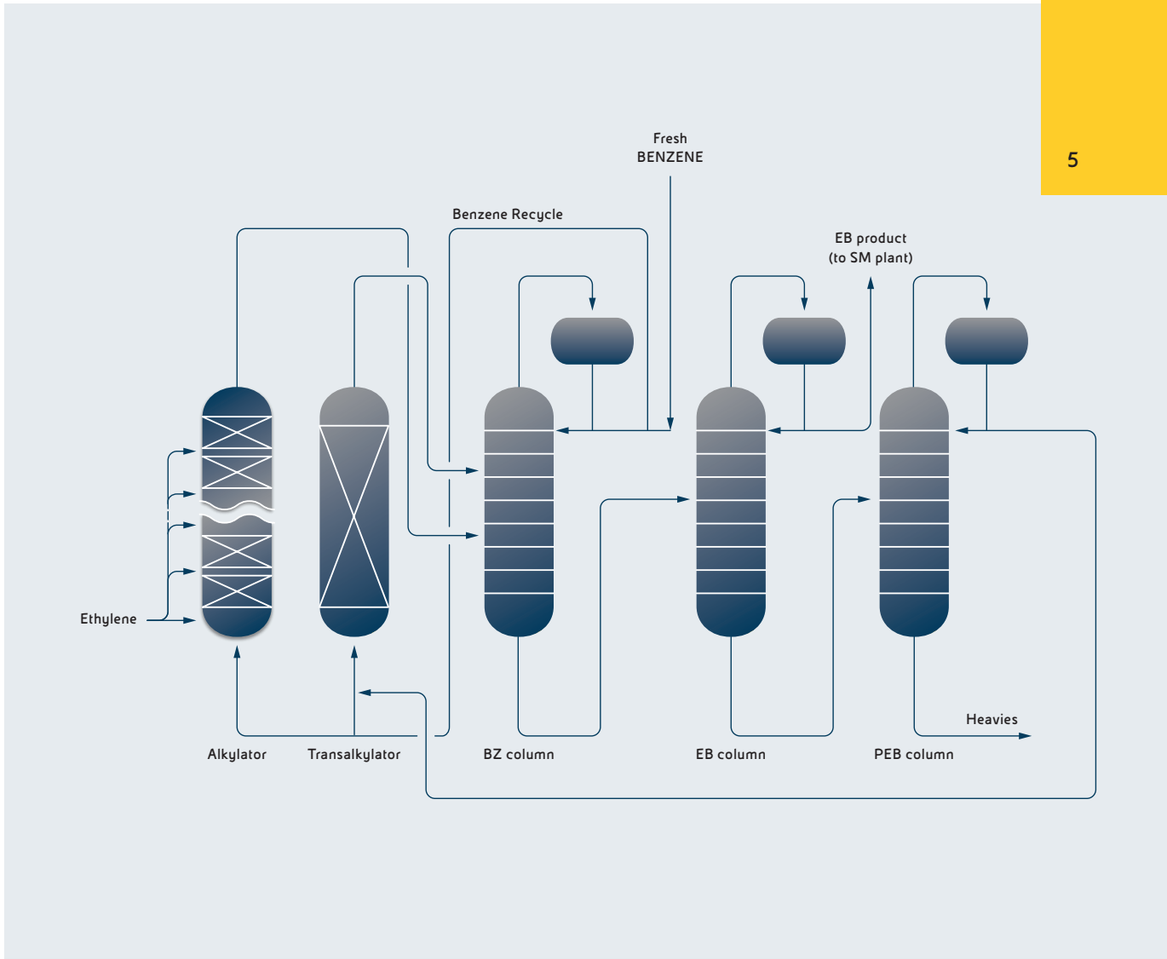
In the alkylation section, the reaction of ethylene with benzene takes place in liquid phase in one or more fixed bed reactors with multibed arrangement. Due to reaction exotermicity, external intra-bed refrigerators are required, with complete heat recovery. The alkylation effluent, which consists mainly of unconverted benzene, ethylbenzene, diethylbenzene and other by products feeds the distillation section.

In the transalkylation section, the diethylbenzene produced in the alkylation and separated in the distillation section reacts with excess benzene to produce additional EB. The benzene/diethyl benzene mixture is first preheated and then sent to a dedicated fixed bed reactor, where the isothermal reaction takes place in liquid phase.
The transalkylation effluent, which consists mainly of ethylbenzene, unreacted benzene and diethyl benzenes, and by-products such as diphenilethanes, feeds the distillation section.

The distillation consists of a 3 columns train. From the first one, the benzene is removed from the top to be recycled back to reaction sections. From the top of the second column is separated pure EB. In the third column, operated under vacuum, is carried out the separation of heavier by-products. Transalkylable polyethyl benzenes (mainly diethylbenzene) are removed from the top of the column, while high boiling by-products (Flux oil) are extracted from the bottom.

Fig. 1

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

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

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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