Recent Advances in Ethylbenzene/Styrene Technologies

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eni.com
### versalis EB/SM Expertise

#### Over 50 years of EB/SM production experience
- Over 25 years of EB/SM designing experience
- Over 20 years of zeolite based catalysts experience

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
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<tbody>
<tr>
<td>2007</td>
<td>On 2007, a new styrene recovery section (owner versalis - styrene recovery from un-reacted liquid condensate recycled back from polystyrene plants) designed by versalis has been successfully started up.</td>
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<td>2010</td>
<td>On 2010, a new 600,000 MTPA EB/SM plant designed by versalis (owner PPC-Iran) has been successfully started-up.</td>
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<td>2011</td>
<td>On 2011, a revamping of a EB/SM splitter (owner versalis - SM plant 1) designed by versalis has been successfully started-up.</td>
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<tr>
<td>2012</td>
<td>On 2012, versalis has designed a new improved reactor/ reheater (owner versalis - 2nd and 3rd reactors SM plant 2, start-up Q4 2013)</td>
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- 8 production lines were started up in the 60s using Monsanto technology (shut-down in 1972)
- 1 production line (SM plant 1 205,000 MTPA - old technology operating above ATM pressure) was started up in 1972 using Badger technology
- SM plant 1 has been retrofitted in 1985 and revamped in 1996 by versalis engineering team (versalis technology operating under vacuum conditions with 2 adiabatic reactors). The plant is still in operation with a nominal capacity of 420,000 MTPA
- SM plant 2 has been designed and started up in 1992 by versalis engineering team (versalis technology operating under vacuum conditions with 3 adiabatic reactors). The plant is still in operation with a nominal capacity of 190,000 MTPA
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.
versalis EB technology highlights

- Superior PBE-1/PBE-2 catalysts
  - High activity and extremely tolerant to poisons (run lengths of 7+ years)
- Excellent yield up to 99.7 % wt
- High product purity of up to 99.98 wt%
- Minimum investment
  - simple flow-sheet
  - mild process conditions
  - all carbon steel construction
- Superior energy recovery fully integrated with SM plant
- Good operability and stable performance throughout entire operation
EB Process Scheme
PBE catalysts advantages

**Extra-zeolite Porosity**
- Proprietary forming procedure gives high extra-zeolite porosity
- Allows optimal diffusion of reactants/products through catalyst particle
- Leads to low, non-detectable catalyst deactivation rate

**High mechanical strength**
- Catalyst is exceptionally sturdy, both mechanically and chemically
- Negligible fines produced during loading and unloading
- Low and constant pressure drop
- Maintains structure over life of catalyst and regenerations

**Superior stability/durability**
- Tolerates oxygenates/alcohol
- Tolerates diolefins – no adverse impact on catalyst stability but forms undesirable side products
- No guard beds or dryers needed to remove saturated water or oxygenates or alcohols
PBE catalysts extra zeolite porosity

Proprietary zeolite-based catalyst forming procedure

Conventional zeolite-based catalyst forming procedure
versalis is in the position to offer an up-to-date and flexible SM production technology, based on state of the art adiabatic multiple stages dehydrogenation reaction using commercially available catalysts
versalis SM technology highlights

- Unique and patented solutions for EB/steam mixing
- Unique and patented solutions for dehydrogenated mixture condensation
- High product purity of up to 99.95 wt%
- High catalyst run length up to 36 months
- High plant reliability up to 99% on-stream factor
- Extensive lab testing and proprietary simulation model for assessing retarders and inhibitors performances in the distillation section
- Long experience not only as licensor but as styrene plant owner
SM Process Scheme
Recent Advances in Styrene Reaction section

- EB/steam near ideal mixing is required in order to assure homogeneous steam to oil ratio conditions through-out the catalyst bed leading to high catalyst performance

- Versalis solution: An innovative ultra-low pressure drop EB/steam mixing device came on stream on 2008 with excellent results
Recent Advances in Styrene Condensation section

- Minimize fouling issues in the condensation section is crucial in order to assure the lowest pressure profile in the reaction section throughout the entire catalyst life cycle.
- versalis solution: An innovative main condenser design industrially proven for “self-cleaning” operation with almost zero pressure drop over 3 years run.
Design options available with versalis technology

- Hydrogen rich gas stream can be either exported for chemical usage or internally recycle back as fuel to steam superheater
  - versalis has a proprietary technology for hydrogen rich gas purification proven to reach the most stringent requirements (CO, CO₂, S) for commercially available hydrogenation catalysts.

- Benzene/Toluene mixture can be either exported to an aromatic plant or separated and the recovered benzene recycles back to the ethylbenzene plant
  - versalis has a patented system for the treatment of benzene by-product stream proven to reach the requirements for PBE catalysts

- For special applications, a dedicated selective hydrogenation section can be implemented to get an ultra low PA content (<10 ppm wt)
  - versalis can offer a PA selective removal section based on a commercially available catalyst proven on a versalis bench scale pilot plant.
Summary

- Versalis can offer an unrivalled EB/SM technology in terms of product quality, production cost, reliability and industrial proven experience.

- Versalis PBE catalyst family offers excellent alkylation performances due to the proprietary forming procedure leading to an exceptionally high extra-zeolite porosity.

- Versalis patented devices for ultra-low pressure drop mixing and “self-cleaning” condensing are industrially proven solutions, now available for licensing, able to further reduce operating plant cost.