



Styrene/Ethylbenzene

Process Technology (including New Developments such as Exelus' ExSyM Process via Methanol and Toluene), Production Costs, and Regional Supply/Demand Forecasts are discussed.

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Report Abstract

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INTRODUCTION

In recent years, technological developments in the ethylbenzene (EB) and styrene area have focused on process optimization, catalyst upgrades, and equipment improvements. The major licensors of EB technologies include: Lummus Technology with its $EBOne^{TM}$ process and Badger Licensing LLC with its ExxonMobil/Badger EB Max process. These processes are generally quite similar, the main distinguishing factors being the catalysts used in the alkylation and transalkylation reactions and the specific operating conditions throughout the processes.

Lummus offers the CDTECH $EB^{\text{®}}$ technology, which combines catalytic reaction and distillation in a single operation. This technology can utilize dilute ethylene, such as ethylene in fluid catalytic cracker (FCC) offgas streams, as a means of reducing feedstock costs. A liquid phase alkylation system is typically used in the EBMax technology. However, for more dilute streams, the alkylation reactor operates under partial liquid phase conditions.

Aluminum-chloride catalyzed alkylation remains in use in numerous existing plants where suitable means of disposing of spent catalyst are available. However, this disposal can represent a cost disadvantage in addition to those, which follow from these plants typically being older and smaller than state-of-the-art zeolite-catalyzed EB plants.

Dehydrogenation of EB to styrene is a mature technology with continuing refinement of catalysts and reactor designs in an attempt to increase EB conversion without losing selectivity to styrene. Flameless Distributed Combustion (FDC) developed and supplied by Shell Oil is being incorporated into the TOTAL/Badger process for heating of reactor feed streams. This technique provides continuous heat input to the endothermic reaction and permits operation at lower temperatures. Heat transfer is primarily by convection, as opposed to conduction as in conventional heat exchangers.

The Lummus/UOP SMART oxidative dehydrogenation process is used primarily for revamp projects where capacity increase at nominal capital cost is desired. In this approach, heat needed for the dehydrogenation reaction is generated by controlled combustion of hydrogen. By removing hydrogen from the reaction mixture, the reaction equilibrium is shifted towards higher EB conversion.

The propylene oxide co-product process is a mature technology, which represents an important source of styrene. Most propylene oxide is now made by co-product routes (styrene or tertiary-butyl alcohol) rather than the environmentally disadvantaged chlorohydrin route. Although propylene oxide demand controls the siting and capacity of these co-product plants, the primary output is styrene by a weight ratio of 2.4 to 1.

Snamprogetti S.p.A. and Dow are jointly developing a process for the production of styrene monomer from ethane and benzene. Ethane, along with ethylbenzene from the alkylation unit, is fed to a dehydrogenation reactor with a catalyst capable of simultaneously producing styrene and ethylene. The dehydrogenation reactor effluent is cooled and separated and the ethylene stream is recycled to the alkylation unit. The catalyst suitable for this type of reaction is composed of gallium, platinum and potassium on alumina modified with silica.

Recent technological developments from Exelus revolve around a new route to styrene using methanol and toluene. This new route to styrene may influence the market in the future using different feedstocks and reaction conditions that could significantly affect the production economics of styrene. Exelus' ExSyM process for making styrene via methanol and toluene is discussed.

Updated economics are compared for commercial EB and styrene processes. Sensitivity analyses show the effect of variations in economic parameters such as feed prices, capacities, etc.

Supply and demand estimates are presented for the United States, Western Europe, Japan, and East Asia.

COMMERCIAL TECHNOLOGY

Ethylbenzene

Ethylbenzene (EB) is made by alkylation of benzene with ethylene in the presence of aluminum chloride or zeolite catalyst.



Successive alkylations occur, producing diethylbenzene (DEB) and higher ethylated benzenes:



Zeolite catalysis removes the need for aqueous catalyst residue disposal. Other coupling reactions occur to a minor extent, yielding materials such as butylbenzene, diphenyl ethane, and higher boiling compounds. All the alkylation reactions are highly exothermic.

The polyethylbenzenes produced by successive alkylations can be transalkylated (transfer of ethyl groups) with benzene to produce additional ethylbenzene. These reactions are slower than alkylation and limited in extent by equilibrium. The following reaction is typical:





Liquid Phase Alkylation with Zeolite Catalysts

- The Lummus/UOP EBOneTM process for ethylbenzene is a liquid phase alkylation process using proprietary zeolite alkylation and transalkylation catalysts supplied by UOP. A simplified process flow sheet and process description, including typical feed and product specifications, are given in the report.
- ExxonMobil/Badger EB Max Process is presently available for license. The EBMax technology can accept both polymer grade ethylene and dilute ethylene feed streams. The ethylbenzene unit has three subsystems: alkylation, transalkylation, and distillation. A simplified process flowsheet and process description are given in the report.

Alkylation via Catalytic Distillation

FCC Plant and Propylene Recovery: A typical propylene recovery unit for an FCC plant is shown schematically, as well as a schematic representation of the process to remove olefins from FCC offgas to low levels.

CDTECH EB[®]: key features of the process, as well as process description and flow diagram are given in the report.

Aluminum Chloride Liquid Phase Alkylation: The process sequence, including diagram and description, for the manufacture of ethylbenzene from ethylene or benzene using an aluminum chloride catalyst is given.

Styrene

Conventional Ethylbenzene Dehydrogenation Process

Ethylbenzene is dehydrogenated to styrene and hydrogen over a catalyst in the presence of steam:



Toluene and benzene are formed as byproducts. The overall reaction is endothermic, and heat is supplied by steam in adiabatic reactors or by external firing in tubular isothermal reactors.

The apparent simplicity of the chemistry, however, conceals the more complex situation experienced in practice. The reaction is favored by low pressures and is generally conducted under partial vacuum.

■ Lummus/UOP CLASSIC SMTM Process: Process flow diagrams and description of the Lummus/UOP CLASSIC SMTM styrene process is given. This is Lummus' standard offering for new plants. Its SMARTTM process, involving oxidative reheat technology, is generally applied only in revamp projects.



- TOTAL/Badger Styrene Process: TOTAL and Badger have been jointly developing and licensing styrene monomer technology since the early 1960s. This long-term association has resulted in the development of six unique generations of technology. The combination of TOTAL's operations know-how and Badger's engineering expertise has resulted in a steady improvement in both variable operating cost and plant reliability. This process is discussed in the report, as well as a process flow diagram of the Badger dehydrogenation reaction system.
- Lummus/UOP SMARTTM SM Process: An alternative approach in styrene technology is the combination of oxidative reheat technology and adiabatic dehydrogenation technology as the Lummus/UOP SMARTTM SM process. The special reactor design uses two different catalysts to achieve what is, in effect, oxidative dehydrogenation. The Lummus/UOP SMARTTM system is shown schematically as well as discussed further in the report.

Propylene Oxide/Styrene Monomer (POSM) Co-product Process

The hydroperoxidation technology for the production of styrene features co-production of propylene oxide and styrene via an ethylbenzene hydroperoxide intermediate. The hydroperoxide, made by direct air oxidation of ethylbenzene, is subsequently converted to an alcohol in the epoxidation reaction with propylene. The alcohol is then dehydrated to styrene.

• Schematic flow diagrams of the LyondellBasell process for producing propylene oxide by ethylbenzene hydroperoxide are given along with a process description.

DEVELOPING TECHNOLOGIES

Styrene via Benzene and Ethane

Snamprogetti S.p.A. (the engineering and main contracting company of Italy's Eni) and Dow are jointly developing a process for the production of styrene monomer from ethane and benzene. Ethane, along with ethylbenzene from the alkylation unit, is fed to a dehydrogenation reactor with a catalyst capable of simultaneously producing styrene and ethylene. The dehydrogenation reactor effluent is cooled and separated and the ethylene stream is recycled to the alkylation unit. The process attempts to overcome previous shortcomings in the development of processes employing ethane to produce styrene. These include inefficient recovery of aromatics, production of high levels of heavies and tars, and inefficient separation of hydrogen and ethane. A basic block flow diagram of the process is shown below.





Process descriptions and process flow diagrams are detailed in the report.

Styrene via Methanol and Toluene

The ability to successfully synthesize styrene on a commercial scale from toluene and methanol would very likely have a significant impact on the styrene market. This has long been realized and for that reason there has been a long history of attempts to develop such a process.

A small company called Exelus Inc. is developing a process based on this chemical route to making styrene, i.e., using the side-chain alkylation of toluene with methanol. This is made possible by a particular catalyst which allows for the side-chain alkylation of toluene to take place when reacted with methanol.

Exelus claims to have invented a new catalytic technology that allows for a breakthrough selectivity of 80 percent at full methanol conversion. If the claims of high selectivities are borne out in Exelus' pilot test, the cost of styrene production could be significantly reduced.

- A literature review and the lesson learned from the review with respect to insights on the developing Exelus process are discussed in the report
- Process description based on information provided by Exelus combined with Nexant *ChemSystems* judgment is given in the report, including a pertinent process flow diagram.

Patent Survey

A survey of key patents published since the last PERP report on this subject detailing assignee, patent number, publication date, and title is provided.

ECONOMIC ANALYSIS

Cost of production estimates for the production of **ethylbenzene** by the following processes have been carried out:

- Ethylbenzene via a liquid-phase zeolite-catalyzed process
- Reactive distillation process for ethylbenzene from dilute ethylene feedstock
- Liquid-phase alkylation catalyzed by aluminum chloride

Cost of production estimates for the production of **styrene** by the following commercial and developing process routes have been carried out:

- Catalytic dehydrogenation of ethylbenzene to styrene
- Production of styrene with propylene oxide as co-product

Cost of production estimates have been carried out with different valuations of byproduct credit for propylene oxide, i.e., production via the chlorohydrin route with and without integrated chlor-alkali plant, and valued at export price. The relationship between propylene oxide co-product value and styrene cost is also illustrated

- Speculative Dow ethane/benzene route to styrene
- Speculative ExSyM process-to styrene using methanol and toluene

COMMERCIAL ANALYSIS

In response to overcapacity, styrenics producers are continuing to restructure, and close less competitive plants in order to boost and restore profitability. The figure below shows U.S. consumption of styrene by derivative. Overall, styrene consumption in the United States is expected to grow through 2015.



The report discusses consumption and supply in the United States, Western Europe, Japan, South Korea, Taiwan, and China.

For each region/nation, supply, demand and trade data are given

Tables giving specific plant capacity by company and location for the various regions (United States, Western Europe, Japan, South Korea, Taiwan, China) are listed





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