PERP Program – New Report Alert

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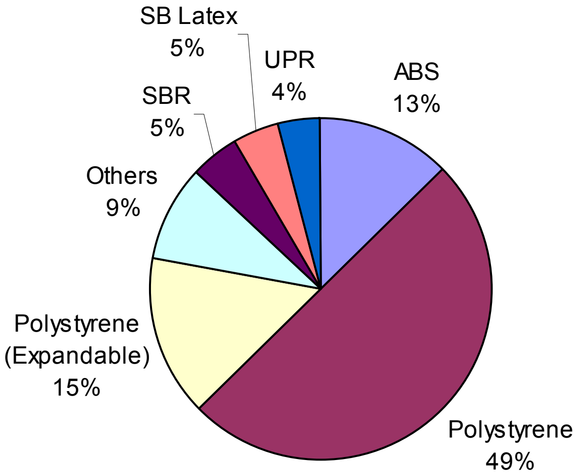
Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Styrene/Ethylbenzene (03/04-8)***.

Introduction

The global consumption for styrene in 2004 is estimated at nearly 24 million metric tons. The largest use for styrene is as a monomer for polystyrene. General purpose, high impact, and expandable polystyrene compose about 64 percent of the total demand for styrene. ABS is the next largest end-use for styrene at 13 percent of overall demand.

Global Styrene Demand Pattern, 2004



Supply/demand balances and capacity listings for the United States, Western Europe, and Japan are provided in the report. Demand and capacity forecasts for South Korea, Taiwan, and China are also presented. A global supply/demand balance for styrene is also provided. Capacity growth is expected to outpace consumption, leading to a drop in operating rates by 2010.

Most developments in ethylbenzene (EB) and styrene technologies in recent years have centered on process optimization, catalyst upgrades and equipment improvements that have led the way for large- scale capacities and enhanced project economics. A decade ago, typical capacities for single-train grassroots ethylbenzene/styrene plants averaged 200,000 metric tons per year. Today, unit capacities greater than 700,000 metric tons per year are being considered and built.

The major licensors of liquid-phase ethylbenzene technologies are: ABB Lummus Global (Lummus) with its EBOne process, and Badger 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, distillation features, and the specific operating conditions throughout the processes. Lummus' CDTECH EB reactive distillation process is available for utilizing dilute ethylene feed as a means of reducing feedstock costs.

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.

The propylene oxide co-product process is a mature technology, which represents an important source of styrene. Recent developments in propylene oxide "only" technologies may influence styrene sourcing in the future.

Technology

Ethylbenzene (EB) is made by alkylation of benzene with ethylene in the presence of aluminum chloride or zeolite catalyst. The polyethylbenzenes produced by successive alkylations can be transalkylated (transfer of ethyl groups) with benzene to produce additional ethylbenzene.

Aluminum chloride catalyst is used only in a liquid phase process, whereas zeolite catalyst may be used in either liquid or vapor phase processes. Variations include the use of dilute ethylene and a catalytic distillation approach where liquid phase alkylation and product separation take place simultaneously.

Ethylbenzene is dehydrogenated to styrene and hydrogen over a catalyst in the presence of steam. Rapid quenching of reaction products is necessary to minimize byproduct formation. Ethylbenzene dehydrogenation catalysts consist primarily of ferric oxide with potassium oxide as a promoter. Generally, 99.9 percent purity reduces all impurities to sufficiently low levels for most applications. Higher purities can be attained, when required, by simply providing sufficient trays and reflux in the final purification column.

The vast majority of ethylbenzene dehydrogenation units perform the reaction adiabatically in a series of two reactors with indirect heat addition between stages. Typically, heat is supplied in a shell-and-tube exchanger by superheated steam. A typical current design employs a molar steam-to-oil ratio of 6 and utilizes a reheat exchanger constructed of 304 stainless steel. Designs at lower steam-to-oil ratios can result in significant energy savings. However, these designs require that the reheat exchanger be constructed of Incoloy 800H material because of the higher steam temperatures required to supply the needed reaction heat. In addition to a somewhat higher cost, the high alloy 800H material requires careful post weld heat treatment. This can be a troublesome maintenance issue when performing repairs in the field.

To overcome the high temperatures required for ultra low steam-to-oil operation, Badger now offers a direct heating method that features patented know-how developed and supplied by Shell Oil. This patented technology, termed Flameless Distributed Combustion (FDC), is now being incorporated into the ATOFINA/Badger process for heating of styrene reactor feed streams. The Badger technology is based on using an axial flow heat exchanger concept that provides heat to the process via FDC heating tubes. In this manner, heat is added “directly” to the process, completely independent of reaction steam and thus the term Direct Heating Technology. With Direct Heating, catalyst and thermodynamic limitations govern the minimum steam-to-oil ratio instead of exchanger and piping metallurgy considerations.

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 POSM process 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. While the process technology for POSM is mature, incremental improvements continue to be made. However, the major issue for the POSM approach is the fact that styrene is made in about a 2.4 times excess over propylene oxide. Thus, the POSM route puts the users of this technology in the styrene business whether they want to be or not; and it is likely that in most cases, they would rather not have to deal with the ups and downs of the commodity styrene market. This concern has prompted Sumitomo Chemical to develop and commercialize a “co-product free” route to PO. Lyondell and Sumitomo have developed a partnership to develop this technology further. Other co-product free routes to PO are also under development by BASF, Dow, Degussa, Nippon Shokubai, Lyondell and Shell. Successful development of these new technologies will have significant impact on the cost structure of the styrene business in the future.

The report also includes discussion of recent developments including direct heating technology, the dehydrogenation of hydrocarbons using carbon dioxide, and the use of extractive distillation for styrene recovery from pyrolysis gasoline. A survey of key patents published since January 2000 includes, in addition to the dehydrogenation using carbon dioxide, alkylation catalyst improvements; dehydrogenation catalyst improvements; novel dehydrogenation reactor designs; catalysts for oxidative dehydrogenation; and others.

For completeness, alternate technologies based on methanol alkylation of toluene and butadiene dimerization/dehydrogenation are mentioned, although these technologies have not been commercialized and no recent work in this area is evident. The report also includes a discussion of Snamprogetti’s new scheme for producing styrene from benzene and ethane.

Economics

Ethylbenzene

A comparison of the three ethylbenzene processes considered shows that the reactive-distillation process feeding dilute ethylene from an FCC unit offers the most favorable economics. The zeolite-catalyzed process represents the state of the art for most situations. The aluminum chloridecatalyzed process may still be able to compete on the basis of a depreciated capital base in existing plants, but plants using it are problematical due to the relatively high investment and concerns about spent catalyst disposal. There is about 22 percent variation between the production cost plus ROCE estimates for the three processes.

Styrene

An economic comparison of the styrene processes is presented. One approach to PO/SM economics is to consider the propylene oxide to be a by-product and assign a credit based on its market price. This introduces a variation in the calculated styrene cost in response to market price gyrations in propylene oxide. Under some market scenarios, the by-product approach will yield lower styrene costs than obtained from conventional ethylbenzene dehydrogenation. Other market conditions can produce a contrary result.

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