New process may rescue styrenics industry

To the rescue?

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Toluene Alkylation with Methanol to form Styrene Monomer

The styrenics market has been suffering poor profitability for many years. But now a cheaper manufacturing process has been developed that could help rescue the sector

Peter Taffe/London

THE STYRENE monomer (SM) market is mature, with average global growth rates of only 3-3.5%/year, a figure not much above the economy’s growth. But it is a large market, with world demand more than 25m tonnes/year, supplying feedstock for many important polymers and elastomers.

However, styrene's largest derivative, polystyrene (PS), has seen torrid times recently with its own market shrinking. This has been due mainly to high prices of benzene and styrene, and consequently PS, resulting in users switching to other polymers and materials. As a result, margins in the styrenics chain have been woefully thin, and even nonexistent. So when a new process that is claimed to substantially reduce capital and operating costs comes along, it seems nearly too good to be true.

A process that appears to meet these claims is under development by the Livingston, New Jersey, US-based process research organization Exelus. Called the ExSyM process, it employs toluene and methanol feedstocks to reduce operating costs while the one-step process with relatively mild operating conditions leads to lower capital costs. If pilot plant testing and commercial demonstration prove successful, then relief could be on the way for the styrenics industry.

"The time is right to make a shift to a new styrene technology," says Mitrajit Mukherjee, president of Exelus. "The economic driver is the lower cost of toluene and methanol compared to benzene and ethylene in conventional technology."

Conventional styrene technology has been in use for some 70 years. It is based on a two-step process. First, benzene is alkylated with ethylene over a solid acid catalyst to make ethylbenzene (EB). In the next step, the EB is mixed with high-temperature steam near to 900°C (1,652°F) and passed over an iron oxide catalyst at a temperature in excess of 600°C. The catalyst dehydrogenates the EB to styrene.

A problem with the conventional process is that it consumes a large amount of energy in the second EB dehydrogenation step. The reaction is thermodynamically limited and highly endothermic, resulting in a significant input of energy.

Most developments in EB and styrene technologies in recent years have centered on process optimization, catalyst upgrades and equipment improvements. However, major improvements in process performance are unlikely, and achieving a competitive advantage is difficult, says Mukherjee.

A more recent problem for conventional styrene manufacturers has been the high price of feedstocks. In particular, benzene prices in the past couple of years have been volatile and have reached record highs, making life difficult for styrene producers.

Styrene can also be manufactured as a coproduct with propylene oxide (PO) by the PO/SM process. In this process, EB is oxidized to its hydroperoxide, which is next reacted with propylene to produce PO and methyl benzyl alcohol. The latter product is then dehydrated to styrene.

An alternative styrene route is the side-chain alkylation of toluene, with methanol to yield styrene, hydrogen and water. Researchers have been attempting to develop this route for the past 30 years, but it has been difficult to devise a catalyst with the yield and selectivity to make a commercially viable process, explains Mukherjee.
One problem was that the methanol decomposed easily to hydrogen and carbon monoxide, leading to a low selectivity. In addition, the hydrogen could convert the styrene to EB, leading to low styrene yields. This by-product formation also made the styrene purification difficult. As a result, the maximum styrene yield achieved was 10%.

Past efforts to improve yields have concentrated on catalyst improvements only, says Mukherjee. "The breakthrough to the higher selectivity of styrene has been achieved through a combination of catalyst science, reaction engineering and process design," he adds.

The catalyst is a modified zeolite material containing basic active sites in a highly optimized pore structure. The active sites selectively adsorb toluene over methanol to limit methanol decomposition. The pore structure facilitates diffusion and residence time of the reactants to enhance toluene alkylation.

Improvements to the reactor design have also concentrated on reducing methanol decomposition and enhancing conversion. Process enhancements have aimed to increase the SM/EB ratio of the product and maintain energy efficiency.

As a result, Mukherjee claims that combined styrene and EB selectivity of more than 90% has been achieved at high methanol conversion with a SM/EB distribution of 85/15%. This gives a total styrene yield in excess of 60%, based on methanol.

On a production scale, the EB produced could be sold to a conventional styrene producer or dehydrogenated on-site to increase styrene yields. The hydrogen coproduct is easily recovered and burned to provide much of the energy required to operate the process.

These breakthroughs have allowed for the development of a simple, fixed-bed process, says Mukherjee. The reaction occurs at around 400-425°C at atmospheric pressure and there is no need to generate large amounts of steam, leading to claimed energy savings of up to 40%, compared with the conventional route.

The milder reaction conditions and the elimination of the EB dehydrogenation unit are claimed to reduce capital costs significantly.

Mukherjee calculates that the investment costs for a 250,000 tonne/year styrene plant, based on the ExSyM process, would be $63m (€42.4m), compared with $125m for a conventional unit. Using long-term average prices of $750/tonne for benzene, $820/tonne for ethylene, $580/tonne for toluene and $315/tonne for methanol, variable operating costs could be reduced by $200/tonne.

A feature of the ExSyM process is that it is configured to resemble a conventional styrene plant, enabling existing units to be retrofitted. Mukherjee claims that revamping a 250,000 tonne/year plant with the new process could cost in the region of $10m-15m, giving a quick payback time.

The new process also reduces the amount of greenhouse gas emissions, in particular methane and carbon dioxide. This has enabled the research by Exelus to be partly funded by grants from the US Department of Energy and the New Jersey Commission on Science & Technology.

The next step in the commercialization of the process is for pilot plant testing to prove the long-term stability of the catalyst. The pilot plant consists of a 1m tall reactor to mimic the length of the conventional radial flow styrene reactor and will use industrial-grade toluene and methanol. The unit is being started up in the first quarter of 2008, with the aim to demonstrate catalyst stability of 1,000 hours.

If successful, the next step would be demonstration on a commercial scale. Mukherjee reveals that the plan is to convert an existing 250,000 tonne/year line at a large styrene complex to the new process. He adds that the process should be ready to license by the end of 2008.

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