



## New Process for Producing Styrene Cuts Costs, Saves Energy, and Reduces Greenhouse Gas Emissions

With support from the U.S. Department of Energy's (DOE) Small Business Innovation Research (SBIR) program, Exelus Inc. has developed the Exelus Styrene Monomer (ExSyM) process, which uses novel catalytic technology to maximize styrene monomer (SM) production using toluene and methanol feedstocks. The ExSyM process requires less capital investment, operates at lower temperatures, uses less energy, and produces fewer greenhouse gas (GHG) emissions than conventional SM production methods.

### Challenge

SM, a colorless oily liquid, is a valuable, large-volume commodity chemical used in making polystyrene plastics, protective coatings, polyesters, and resins, and as a chemical intermediate. Global production of styrene in 2010 was 25 million metric tons (27.5 million U.S. tons), of which approximately 4 million metric tons (4.4 million U.S. tons) originated in the U.S. The global market is valued at approximately \$32.5 billion<sup>1</sup> and is forecast to grow an average of 3.6% per year. However, the conventional process for producing SM consumes tremendous amounts of energy—up to ten times as much as the production of similar chemicals—and is a major contributor to emissions of GHGs such as methane and carbon dioxide.

Conventional SM production methods—in use for more than 70 years—usually require a two-step process. The first step involves the alkylation<sup>2</sup> of ethylene with benzene over an acid catalyst to form ethylbenzene (EB). The second step combines EB with high-temperature steam (near 900°C), then dehydrogenates the EB over an iron oxide catalyst under vacuum at temperatures in excess of 600°C. The cost of production is elevated by the high-priced feedstocks and the severity and endothermicity of the second step. Attempts to reduce the energy consumption in this two-step process, through measures such as process optimization and catalyst upgrades, have not had a significant impact. A single-step SM production method was investigated using a side chain alkylation reaction of toluene with methanol; however, reaction complications limited the SM yields. Many past efforts to improve SM yields in the toluene-methanol approach have primarily concentrated on conventional catalyst improvements.

### Innovating Solutions

To overcome reaction limitations, Exelus Inc., with support from the DOE's SBIR program and the New Jersey Commission on Science & Technology, has been able to make significant strides in developing an innovative new process known as ExSyM. This process uses the toluene-methanol approach and employs a proprietary, engineered solid catalyst in a one-step reaction that enables the production of SM under relatively mild operating conditions with reaction temperatures around 400°C. Results thus far show dramatic improvement in SM product selectivity (the ratio of the desired product quantity to the total quantity of products) of around 80%. The process has been tested in bench-scale reactors, with the catalyst showing no signs of deactivation in long-term stability tests. As a retrofit for existing plants, the ExSyM process has great potential as a cost-effective alternative to conventional SM production methods.

In addition to its novel catalyst, ExSyM incorporates reactor design improvements and process innovations that reduce the decomposition of methanol, minimize the formation of EB, and improve energy efficiency. At production scale, any EB by-product produced via the ExSyM process could be separated and sold to a conventional SM producer, or dehydrogenated on-site to boost the overall SM yield. Hydrogen by-product could also be burned to produce steam to help heat product distillation columns. The single-step ExSyM method eliminates the energy-intensive dehydrogenation step, allowing for significant energy use reduction and concomitant cost savings and lower GHG emissions.

<sup>1</sup> A current value of styrene is \$1300/metric ton.

<sup>2</sup> Alkylation is the transfer of an alkyl group of chemical compounds from one molecule to another.



**Styrofoam cups are one of many products made from styrene monomer.**

### Commercializing ExSyM

In 2010, Exelus was selected to receive funding under DOE's SBIR Phase III Xlerator program. With this support, Exelus aims to advance the commercialization of ExSyM technology by constructing and operating a pilot-scale testing unit that meets industry-standard specifications for capacity and design. With lower feedstock and capital costs, ExSyM is an exciting new pathway for SM production.

**Exelus Inc.** (Livingston, NJ), established in 2000, develops and licenses “Cleaner-by-Design” chemical technologies to produce a vast array of products and materials used in consumer goods, transportation, and food processing. Currently, the company's principal process technologies are:

**ExSact** – a refining technology that overcomes the environmental concerns, safety hazards and rising costs associated with conventional liquid acid technologies

**ExSyM** – energy efficient, low cost SM production technology

**BTG** – efficient, cost-effective conversion of biomass to clean, high-octane, gasoline-compatible fuel

<http://www.exelusinc.com/>

A case study from the DOE/EERE SBIR Program portfolio, providing competitive grants for scientific excellence and technological innovation to advance critical American priorities and build a strong national economy – one small business at a time.

# New Process Chemistry for Producing Styrene Monomer Saves Energy, Reduces Emissions

The cost reduction realized with the implementation of the new SM production process could increase global competitiveness of U.S. SM manufacturers, thereby saving jobs and increasing exports.

## SBIR Impacts

### Projected Benefits of ExSyM vs. Conventional Styrene Monomer Production<sup>3</sup>

	Conventional SM Production	→	ExSyM
<b>Energy</b>	<ul style="list-style-type: none"><li>• Second-step dehydrogenation required</li><li>• Operation temperature &gt;600°C; steam ~900°C</li><li>• Vacuum operation requires large compressor</li></ul>		<ul style="list-style-type: none"><li>• Energy-intensive dehydrogenation step is eliminated</li><li>• Reaction temperatures between 400-425°C</li><li>• 50% less endothermic</li><li>• Energy savings up to 40%</li></ul>
<b>Environmental</b>	<ul style="list-style-type: none"><li>• Large contributor to GHG emissions such as methane and CO<sub>2</sub></li></ul>		<ul style="list-style-type: none"><li>• Lower GHG emissions by 40%</li><li>• Possible recovery and reuse of up to 50% of hydrogen byproduct for use as an energy supply, thereby reducing carbon emissions</li><li>• Replaces carcinogenic benzene feed with toluene, which is much less toxic</li></ul>
<b>Economic</b>	<ul style="list-style-type: none"><li>• Higher feedstock costs of ethylene (\$1100/metric ton) and benzene (\$940/metric ton)<sup>4</sup></li><li>• Investment cost to build a 250,000 metric ton/year plant: \$125 million</li></ul>		<ul style="list-style-type: none"><li>• Reduced feedstock costs of toluene (\$650/metric ton) and methanol (\$350/metric ton) result in operating cost savings of \$250/ton of styrene<sup>4</sup></li><li>• Investment cost to build a 250,000 metric ton/year plant: \$63 million (ExSyM retrofit: \$10-15 million)</li></ul>

## Innovation

The ExSyM system is configured to resemble conventional SM process units to facilitate retrofitting of existing plants. ExSyM replaces the more expensive feedstocks of benzene and ethylene with toluene and methanol in a more cost-effective, energy efficient one-step route for SM production. Characteristics of the novel proprietary catalyst that facilitates the required reaction include:

- the ability to be used in standard fixed-bed reactors
- 'active sites' that selectively adsorb toluene to limit methanol decomposition
- highly-structured pores optimize diffusion and residence time of reactants and products

## Company Success

DOE support has been an integral part of the success achieved by Exelus Inc. and their 'Engineered Catalysts' (EnCats) technology platform, a unique class of reactive systems that aim to blur the line of distinction between a catalyst and reactor by incorporating many characteristics that one associates with a reactor within the catalyst structure.

EnCats facilitate the development of, next-generation, clean process technologies. As a part of the EnCats family, ExSyM represents a breakthrough in industrial catalysis as a low cost SM production technology based on new process chemistry, with its potential highlighted in trade journals such as *Chemical & Engineering News*, *Chemical Engineering Magazine*, and *ICIS Chemical Business*.

From Phase I development to its most recent Phase III Xlerator award for pilot-scale testing and further manufacturing scale-up, SBIR support has been essential to Exelus Inc. in developing its promising new ExSyM technology.

*Exelus Inc. has grown from three employees when founded in 2000 to 18 employees in 2011, with projected 2012 revenue of \$2.5 million.*

<sup>3</sup> ExSyM projections provided by Exelus Inc. based on bench-scale test results.

<sup>4</sup> ICIS Price Reports.

For additional information, please contact:

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