PERP Program – Styrene from Ethane and Benzene
New Report Alert
January 2007

Nexant’s ChemSystems Process Evaluation/Research Planning program has published a new report, *Styrene from Ethane and Benzene (05/06S3)*. To view the table of contents or order this report, please click on the link below:
http://www.chemsystems.com/search/docs/toc/0506S3_toc.pdf

Introduction
There are two routes to produce styrene currently used in industry. One of them is the dehydrogenation of ethylbenzene to styrene in the presence of an iron catalyst which is used in 90 percent of commercial production facilities. Styrene can be also be produced by what is known as POSM co-production, where propylene oxide (PO) and styrene (SM) are made simultaneously. For this evaluation, the former is compared to a new route being investigated by Dow and Snamprogetti.

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. They have recently each been awarded patents in this area. 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.

The conventional method of preparing styrene has several disadvantages:

- The steam crackers needed to produce the ethylene are high cost items from both a capital investment and operating standpoint.
- Since transportation of ethylene is expensive, the styrene production facility must be located at the site of the steam cracker or at worst have access to an ethylene pipeline.
- The ethylene needed for the alkylation step is required to be essentially pure, otherwise undesirable alkylated products are produced in the reactor and the catalyst life reduced.
- The cost of ethylene is not only high but relatively volatile compared to ethane

Employing dilute ethylene from Fluid Cat Cracker (FCC) operations has similar disadvantages.

The new route from ethane is expected to enable significant cost savings and provide greater flexibility with respect to plant location. Dow has been operating an ethane to styrene process
development unit (PDU) with feed rates in the range of 500 kg/h since 2002. According to Snamprogetti, commercialization is expected by the end of the decade.

This report discusses Dow patent U.S. 7,002,052 (February 21, 2006) whereby ethylene is produced from the dehydrogenation of ethane and, in fact, combines the dehydrogenation of ethane and ethylbenzene in one reactor. In addition, this novel process integrates the processes of preparing ethylene, ethylbenzene and styrene. An additional and economically important advantage in the Dow process is the recovery of commercial grade hydrogen as a by-product.

**Ethane Dehydrogenation**

In general, the most important factors that influence the economic viability of chemical processes are conversion per pass and selectivity to the desired product. Both impact on feedstock consumption and recycles, which in turn, impact on energy consumption and capital investment and associated variable and fixed costs. It can be demonstrated for paraffin dehydrogenation that, for a given operating pressure, selectivity to a desired olefin declines with increasing conversion, usually facilitated by temperature elevation. Optimum operating conditions, therefore, become a compromise of feedstock consumption, capital investment and operating costs.

The thermodynamic equilibrium between paraffins and olefins is strongly dependent on temperature and pressure. Thus, for any set of chosen operating conditions, there will always be a limit to paraffin conversion. In principle, the longer the carbon chain, the more facile the dehydrogenation reaction.

The thermodynamic equilibria take no account of undesirable side reactions and unwanted by-products. These reactions fall into two main categories, namely thermal cracking of paraffins and olefins to light gases and the oligomerization of olefins and subsequent hydrogen loss to form coke. Coke and heavy material will, of course, gradually impair the efficiency of any catalyst, thus the need for regeneration. The actual kinetics associated with various process designs are extremely complex and difficult to model. Variations in temperature and pressure occur within reactor systems, especially if they have a cyclic nature, and impact on reaction rates and equilibria enormously. It must be noted, however, that in general increasing reaction temperature for a given pressure will accelerate the rate of thermal cracking to a greater extent than dehydrogenation. This factor in combination with chemical thermodynamics underpins the process design philosophies for light paraffin dehydrogenation.

The preferred catalyst for the dehydrogenation reactor is based on gallium and platinum supported on alumina in the delta or theta phase, or in a mixture of delta plus theta phases, or theta plus alpha
phase, or delta plus theta plus alpha phases, modified with silica and having a surface area preferably less than about 100 m\(^2\)/g (as determined by the BET (Brunauer, Emmett, Teller) method).

The Dow patent claims a conversion of ethane of 10 weight percent and selectivity to ethylene of 90 weight percent at essentially atmospheric pressure and 600°C (1,112°F). The low conversion of ethane leads to high ethane traffic throughout the plant. The preferred operating conditions are a temperature between 530 and 680°C (986 and 1,256°F) and a pressure between 0.3 atmospheres (4.4 psia, 30 kPa) and 1.5 atmospheres (22.1 psia, 150 kPa). A fluidized bed dehydrogenation reactor was used with a total gas hourly space velocity (GHSV) of between 150 and 300 h\(^{-1}\). The patent notes that other reactor designs are just as suitable (i.e., fixed bed or transport bed).

**Ethylbenzene via Alkylation**

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.

Higher ethylated benzenes also participate. The heat of the transalkylation reaction is essentially zero, and the reaction is effectively isothermal.

A small amount of ethylene oligomerization occurs to form butenes and higher olefins. In addition, some propylene and butenes are made by high temperature cracking of non-aromatic components (such as cyclohexane) contained in the benzene feedstock. Any propylene that may be present reacts with benzene to form isopropylbenzene (cumene). Small amounts of xylenes are formed in the alkylation reactor from the isomerization of ethylbenzene; similar reactions also produce toluene.

Oligomers create high boiling alkylaromatics (by alkylation of benzene), which lead to an increased yield loss of benzene in the form of residue. The presence of oligomers also accelerates the coking of the alkylation catalyst.

Of greater significance is the fate of the nonaromatic species, notably cyclohexane, which enter in trace amounts with the benzene feed. These species are close boiling with benzene and are not easily removed by distillation. If nonaromatics are allowed to accumulate to high enough levels,
they may undergo some alkylation to C₉ impurities that contaminate the EB product. Ultimately, C₉ impurities may also contribute to coking of the styrene dehydrogenation catalyst and contaminate the styrene monomer (SM) product.

The volatility of cumene is between ethylbenzene and polyethylbenzenes (PEB). Cumene deleteriously affects styrene quality, because it cannot be separated from styrene. Some cumene dehydrogenates in the styrene reactors to alpha-methyl styrene (AMS), a portion of which also will enter the styrene product.

Butylbenzene and amylbenzene accumulation in the system should also be avoided, which is easier in vapor phase systems. These compounds ultimately form alkyl diphenyl compounds, the main components of ethylbenzene residue.

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.

**Styrene via Dehydrogenation**

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.

Reaction temperatures are high, between 550°C and 630°C (1,022°F and 1,166°F), and rapid quenching of reaction products is necessary to minimize byproduct formation. As for kinetics, the reaction temperature is usually above 580°C (1,076°F); however, since both styrene and ethylbenzene will crack above 610°C (1,130°F), the reactor must operate in a fairly narrow temperature band. Conversion per pass is typically 60-70 percent, and selectivity to styrene is 93-96 percent.

Ethylbenzene dehydrogenation catalysts typically consist primarily of ferric oxide with potassium oxide as a promoter. Other metal oxides have been employed as supplemental promoters, including oxides of chromium, cerium, tin, calcium, molybdenum, magnesium, titanium, and others.
For the analysis in this report, the dehydrogenation reaction is carried out in the gaseous phase operating in a fluidized bed catalytic reactor. The catalyst for the dehydrogenation reaction is based on gallium and platinum supported on alumina in the delta or theta phase, or in a mixture of delta plus theta phases, or theta plus alpha phases, or delta plus theta plus alpha phases modified with silica and having a surface area less than about 100 m²/g (as determined by the BET method). The preferred catalyst comprises:

- From 0.2 to 3.8 weight percent gallium oxide (Ga₂O₃)
- From 3 to 80 wppm platinum
- From 0.1 to 3 weight percent of an alkaline and/or alkaline-earth oxide (e.g., potassium oxide)
- From 0.8 to 3 weight percent silica
- The balance being alumina

The above mentioned catalyst can be used as such or diluted with an inert material (e.g., alpha-alumina) at a concentration of the inert product of between 0 and 50 weight percent.

**Process Description**

The Dow patent 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. The process design used in the report is based on Example 2 illustrated in the Dow patent. The novelty of this invention is the integrated process of preparing the styrene using ethane and benzene as raw starting materials. Essentially pure chemical grade hydrogen is produced as a co-product and energy is recovered from the process for use within the unit process operations.

For this evaluation the dehydrogenation reactions of ethane and ethylbenzene are carried out in a fluidized bed reactor operating at slightly above atmospheric pressure (e.g., 5 psig) and 600°C (1,112°F). Per the Dow patent, a total gas hourly space velocity of 300 h⁻¹ is assumed. The reactor feed consists of fresh ethane, recycled ethylbenzene from both the ethylbenzene column and the alkylation unit, and recycle ethane from both the C₂ splitter and the alkylation unit. The molar ratio of ethylene to ethane is 0.25:1. The dehydrogenation catalyst comprises gallium oxide (2.33 weight percent), potassium oxide (0.4 weight percent), platinum (75 wppm), silica (1.56 weight percent), and the balance to 100 percent being alumina. The conversion of ethane is assumed to be 10 weight percent and the selectivity to ethylene is assumed to be 90 weight percent. The conversion of ethylbenzene is assumed to be 55 weight percent and the selectivity to styrene is assumed to be 92 weight percent.
The design employed continuously removes the catalyst plus any inert material from the reactor to a regenerator to be regenerated in the presence of a regeneration gas comprising oxygen and optionally, a gaseous fuel (e.g., methane, ethane, refinery fuel gas, etc.). Generally, an excess of oxygen is employed above the stoichiometric ratio required for complete combustion of the gaseous fuel to carbon dioxide and water. The regenerator operates at slightly above atmospheric pressure and a temperature between 600 and 700°C (1,112 and 1,292°F).

The alkylation feed is comprised of benzene (both fresh and recycled) and a stream from the dehydrogenation unit rich in ethylene. The alkylation reactor is operated in the vapor phase using a zeolite ZSM catalyst at 400°C (752°F) and 369 psig (2,545 kPa). The total feed weight hourly space velocity is 130 h⁻¹. Essentially, all the ethylene is assumed to be reacted in the alkylation reactor. The benzene conversion is assumed to be 22 percent and the selectivity to ethylbenzene is assumed to be 92 mole percent. The total selectivity to ethylbenzene and polyethylbenzene is assumed to be 98.8 percent.

**Economic Analysis**

The economics of the production of styrene have been developed for a 650 thousand metric ton per year (1,433 million pounds per year) plant on the USGC for the first quarter of 2006. The conventional route to styrene, ethylene plus benzene to form ethylbenzene and then dehydrogenation to styrene, is compared to the proposed Dow ethane/benzene-based styrene process.

The purchased equipment cost for a 650 kta plant employing Dow’s process for producing styrene from ethane and benzene has been estimated using the Aspen Icarus Process Evaluator.

The cost of production of the Dow process to produce styrene via ethane and benzene is compared with the conventional route. Two cases for the Dow process are presented – chemical value and fuel value for by-product hydrogen. On a net raw material basis, we find that the Dow process has an advantage as compared to the conventional route, largely stemming from the low cost of ethane in relation to ethylene (even with an increase in unit consumption owing to the lower selectivity and slightly higher molecular weight of ethane versus ethylene). On a cash cost basis, the feedstock cost advantage is mitigated due to the larger utility requirement of the Dow process and the higher fixed costs.

**Commercial Analysis**

The global consumption of styrene is estimated to be 25 million metric tons in 2006. Figure 1 shows the global distribution of styrene consumption by product. By far polystyrene (PS) is the largest consumer of styrene, followed by expandable polystyrene (EPS) and acrylonitrile butadiene styrene.
(ABS). It is estimated that growth over the next 5 years will be led by EPS and ABS. Almost 50 percent of the styrene consumed is within the Asia/Pacific region.

The global capacity for styrene is 28.7 million metric tons per year. The global distribution of the styrene production facilities is shown in Figure 2. The Asia/Pacific region has the largest percentage of styrene production facilities (43 percent) followed by Europe (25 percent) and North America (25 percent). Eighty percent of the capacity is based on benzene alkylation technology. The other twenty percent is based on POSM technology, where propylene oxide is produced as a by-product.

Supply, demand and trade forecasts are also provided in the report for the United States, Western Europe, and Asia Pacific.

Figure 1
Global Styrene Consumption, 2006

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Figure 2
Global Styrene Capacity, 2006

North America 25%
South America 2%
Europe 25%
Middle East 5%
Asia/Pacific 43%