STYRENE

1. Introduction

Styrene [100-42-5] (phenylethene, vinylbenzene, phenylethylene, styrol, cinnamene), $C_6H_5CH{=}CH_2$, is the simplest and by far the most important member of a series of aromatic monomers. Also known commercially as styrene monomer (SM), styrene is produced in large quantities for polymerization. It is a versatile monomer extensively used for the manufacture of plastics, including crystalline polystyrene, rubber-modified impact polystyrene, expandable polystyrene, acrylonitrile–butadiene–styrene copolymer (ABS), styrene–acrylonitrile resins (SAN), styrene–butadiene latex, styrene–butadiene rubber (qv) (SBR), and unsaturated polyester resins (see Acrylonitrile polymers, survey and styrene-acrylonitrile (san); Styrene plastics).

Styrene was first isolated in the nineteenth century from the distillation of storax, a natural balsam. Although it was known to polymerize, no commercial applications were attempted for many years because the polymers were brittle and readily cracked. The development of dehydrogenation processes by I. G. Farben in Germany and Dow Chemical in the United States during the 1930s was the first step toward the modern styrene technology. Several plants were built in Germany before World War II to produce styrene, primarily for making synthetic rubber. It also became a material of strategic importance in the United States when the supply of nature rubber from South Asia was cut off from the Allied countries's access, and large-scale plants were built. After the war the demand for styrene monomer continued to grow, but its main use has shifted from synthetic rubber to polystyrene. Polystyrene (PS) accounts for 65% of the total styrene demand. The production of styrene in the United States was 2.0 million metric tons in 1970, which increased to 3.2×10^6 t in 1980 and 5.8×10^6 t in 2004. Rapid growth has also been seen in Western Europe and Japan and, since the 1980s in the Pacific Rim. Many factors contribute to its growth: it is a liquid that can be handled easily and safely, it can be polymerized and copolymerized under a variety of conditions by common methods of plastics technology to a large number of polymers of different properties and applications, polystyrene is easy to extrude and mold and is one of the least expensive thermoplastics volumetrically, the raw materials benzene and ethylene are produced in very large quantities in refineries and can be supplied to styrene plants through pipelines, and the manufacturing technologies are efficient and plants can be built on a large scale to produce styrene at low cost.

Two process routes are used commercially for the manufacture of styrene: dehydrogenation and coproduction with propylene oxide. Both routes use ethylbenzene as the intermediate; ethylbenzene is made from benzene and ethylene. The manufacture of styrene via ethylbenzene consumes more than 50% of the commercial benzene in the world. The great majority of the ethylbenzene and styrene plants are based on licensed technologies which are available at rather modest licensing fees. Styrene is a commodity chemical traded in large volumes domestically and internationally. The product specifications are largely dictated by the market. The minimum purity is usually 99.8%, which can be easily met in a well-operated plant of modern design. Some producers choose to have their plants designed to produce high purity styrene at a small incremental investment to gain marketing advantages and in anticipation of its future demand. Production of 99.95% styrene could become routine as a result of recent advances in manufacturing technology.

The commodity nature of the product and the easy access to the licensed processes enable new producers, particularly in developing countries, to enter the global styrene merchant market with little experience in styrene technology. Access to ethylene, which cannot be easily transported by means other than pipelines, is a key factor in considering new styrene facilities. Timing, or luck, is even more important because the supply and demand of styrene are seldom in balance and the price fluctuates broadly and rapidly as a result.

2. Properties

Styrene is a colorless liquid with an aromatic odor. Important physical properties of styrene are shown in Table 1 (1). Styrene is infinitely soluble in acetone, carbon tetrachloride, benzene, ether, *n*-heptane, and ethanol. Nearly all of the commercial styrene is consumed in polymerization and copolymerization processes. Common methods in plastics technology such as mass, suspension, solution, and emulsion polymerization can be used to manufacture polystyrene and styrene copolymers with different physical characteristics, but processes relating to the first two methods account for most of the styrene polymers currently being manufactured (2–8). Polymerization generally takes place by free-radical reactions initiated thermally or catalytically. Polymerization occurs slowly even at ambient temperatures. It can be retarded by inhibitors.

Styrene undergoes many reactions of an unsaturated compound, such as addition, and of an aromatic compound, such as substitution (2,8). It reacts with various oxidizing agents to form styrene oxide, benzaldehyde, benzoic acid, and other oxygenated compounds. It reacts with benzene on an acidic catalyst to form diphenylethane. Further dehydrogenation of styrene to phenylacetylene is unfavorable even at the high temperature of 600°C, but a concentration of about 50 ppm of phenylacetylene is usually seen in the commercial styrene product.

3. Ethylbenzene Manufacture

Styrene is manufactured from ethylbenzene. Ethylbenzene [100-41-4] is produced by alkylation of benzene with ethylene, except for a very small fraction that is recovered from mixed C_8 aromatics by superfractionation. Ethylbenzene and styrene units are almost always installed together with matching capacities because nearly all of the ethylbenzene produced commercially is converted to styrene. Alkylation is exothermic and dehydrogenation is endothermic. In a typical ethylbenzene–styrene complex, energy economy is realized by advantageously integrating the energy flows of the two units. A plant intended to produce ethylbenzene exclusively or mostly for the merchant market is also not considered viable because the merchant market is small and sporadic.

The reaction of benzene and ethylene takes place on acidic catalysts and

$$C_6H_6 + CH_2{=}CH_2 \rightleftharpoons C_6H_5CH_2CH_3$$

can be carried out either in the liquid or vapor phase. Benzene in excess of the stoichiometric ratio to ethylene is used. The forward reaction is highly favored thermodynamically; the equilibrium conversion of ethylene is nearly complete. Alkylation does not stop at monoethylbenzene. Part of the ethylbenzene is further alkylated to diethylbenzenes, triethylbenzenes, tetraethylbenzenes, etc, collectively referred to as polyethylbenzenes (PEB). A high benzene-to-ethylene ratio in the feed mixture gives a low polyethylbenzenes-to-ethylbenzene ratio in the reaction product, but requires larger equipment and more energy consumption to recover the additional unreacted benzene by distillation for recycle to the reactor. The quantity of polyalkylbenzenes formed relative to ethylbenzene is also affected by the catalyst and reaction conditions. The polyethylbenzenes are recovered by distillation and transalkylated with benzene to produce additional ethylbenzene. For example, the transalkylation of diethylbenzene proceeds as follows:

$$CH_3CH_2C_6H_4CH_2CH_3 + C_6H_6 \rightleftharpoons 2\,C_6H_5CH_2CH_3$$

The transalkylation reaction is essentially isothermal and is reversible. A high ratio of benzene to polyethylbenzene favors the transalkylation reaction to the right and retards the disproportionation reaction to the left. Although alkylation and transalkylation can be carried out in the same reactor, as has been practiced in some processes, higher ethylbenzene yield and purity are achieved with a separate alkylator and transalkylator, operating under different conditions optimized for the respective reactions.

A number of side reactions occur in both the alkylator and the transalkylator, including oligomerization, cracking, dehydrogenation, isomerization, alkylation of alkanes by ethylene, alkylation of toluene by ethylene, alkylation of benzene by higher olefins, etc. The reactor effluent can be shown by high sensitivity chromatography to contain a large number of aromatic and nonaromatic by-products, most of them in parts per million or less. Isomerization causes formation of xylenes. Oligomerization is the first step in the formation of most of the by-products and is the side reaction that is most harmful to the yield and quality of the product and the stability of the catalyst. Some of the oligomers boil close to ethylbenzene and remain as nonaromatic impurities in the product. Other oligomers react further to form cumene, *n*-propylbenzene, butylbenzenes, and other higher alkylbenzenes. These alkylbenzenes either become impurities in the product or are recycled with the polyethylbenzene stream to the transalkylator. Depending on the process used, the alkylbenzenes that cannot be transalkylated to ethylbenzene are either decomposed or converted to heavies on repeated recycle. The heavies, consisting of diphenyl compounds and heavy aromatics and nonaromatics, are rejected from the process as residue, which is usually used as fuel. Control of side reactions and by-products is the most important consideration in the development of catalysts and processes for ethylbenzene production.

The benzene feedstock contains C_6 nonaromatics, ranging from 50 to 2000 ppm, depending on the source of supply. The C_6 nonaromatics do not directly contaminate the product because their boiling points are typically 40–60°C lower than that of ethylbenzene. However, part of these nonaromatics are alkylated by ethylene in certain processes to form higher nonaromatics, which may contaminate the product. The nonaromatics may also be cracked in the reactors, and the resulting components react with benzene to form various alkylbenzenes, such as cumene, which may also contaminate the product. The only aromatic impurity in a significant concentration in the typical benzene feedstock is toluene, ranging from 50 to 1000 ppm. It reacts with ethylene to form ethyltoluene in the alkylator; ethyltoluene is converted back to toluene in the transalkylator. Toluene is distilled together with ethylbenzene and becomes a product impurity that is innocuous downstream in the dehydrogenation process. However, any ethyltoluene that is not separated from ethylbenzene contaminates the styrene product as ethyltoluene and vinyltoluene.

The ethylene feedstock used in most plants is of high purity and contains 200–2000 ppm of ethane as the only significant impurity. Ethane is inert in the reactor and is rejected from the plant in the vent gas for use as fuel. Dilute gas streams, such as treated fluid-catalytic cracking (FCC) off-gas from refineries with ethylene concentrations as low as 10%, have also been used as the ethylene feedstock. The refinery FCC off-gas, which is otherwise used as fuel, can be an attractive source of ethylene even with the added costs of the treatments needed to remove undesirable impurities such as acetylene and higher olefins. Its use for ethylbenzene production, however, is limited by the quantity available. Only large refineries are capable of delivering sufficient FCC off-gas to support an ethylbenzene–styrene plant of an economical scale.

Commercial ethylbenzene is manufactured almost exclusively for captive use to produce styrene; only a small fraction is traded (9). The specifications of merchant ethylbenzene are usually negotiated between the seller and the buyer. An assay as low as 99% can be acceptable, provided that most of the impurities are benzene, which is strictly a distillation consideration, and toluene, which is largely dependent on the benzene feedstock. They are usually inconsequential in the dehydrogenation of ethylbenzene which makes far more benzene and toluene by side reactions. However, they must not be excessive, because the distillation train in the styrene unit is designed to accept specified quantities of benzene and toluene. Other possible impurities in ethylbenzene are nonaromatics in the C_7–C_{10} range and aromatics in the C_8–C_{10} range. Their nature and quantities depend on the feedstocks, the process used, and the design and operation of the plant. The C_7–C_{10} nonaromatics originate, in some processes, from oligomerization of ethylene and alkylation of the C_6 nonaromatics contained in benzene. The C_8–C_{10} aromatics impurities include xylenes, cumene, *n*-propylbenzene, ethyltoluenes, and butylbenzenes.

Diethylbenzenes are not considered by-products of the ethylbenzene process because they are recycled and transalkylated to ethylbenzene. Nonetheless, their concentrations in the ethylbenzene product must be minimized. Diethylbenzenes are converted in the dehydrogenation reactor to divinylbenzenes, which are exceedingly reactive, forming cross-linked polymers and causing polymer buildup in pipes, columns, and tanks. In severe cases, a styrene plant can be forced to shut down to clean out the polymers. The diethylbenzene content in the ethylbenzene product is generally specified to be 10 ppm maximum, largely because more accurate analytical instruments have become readily available only in recent years. The new plants are designed to limit this content to ≤ 1 ppm, which is not difficult to achieve by distillation because the relative volatility of ethylbenzene and diethylbenzenes is very high. Chlorides are poisons to the dehydrogenation catalyst. This fact rarely poses a problem in the manufacturing process, but possible contamination in storage and shipping must be prevented.

Most of the ethylbenzene plants built before 1980 are based on use of aluminum chloride catalysts. Aluminum chloride is an effective alkylation catalyst but is corrosive; its use as the catalyst requires glass-lined, brick-lined, or Hastelloy reactors, and thus results in high capital costs for the reactor section. The necessity of washing and neutralizing the reactor effluent to remove the spent catalyst adds to the complexity of both the plant itself and its operation. It also creates an aqueous waste that is environmentally objectionable and becoming increasingly difficult to dispose of. The corrosivity also increases plant downtime and maintenance cost. Many older plants based on aluminum chloride are still in operation. The newer plants are based on zeolite catalysts.

3.1. Zeolite-Based Alkylation. Zeolites have the obvious advantages of being noncorrosive and environmentally benign. They have been extensively researched as catalysts for ethylbenzene synthesis. Earlier efforts were unsuccessful because the catalysts did not have sufficient selectivity and activity and were susceptible to rapid coke formation and deactivation.

The Mobil-Badger vapor-phase ethylbenzene process was the first zeolite-based process to achieve commercial success. It is based on a synthetic zeolite catalyst, ZSM-5, developed and optimized by Mobil Oil Corporation for the synthesis of ethylbenzene (10–19) (see MOLECULAR SIEVES). It has the desirable characteristics of high activity, low oligomerization, and low coke formation. The catalyst is regenerable by controlled burning of the coke deposited on the catalyst.

Since its first commercialization, the Mobil-Badger process has undergone several important improvements. The Third Generation Technology extends the catalyst cycle length between regenerations to two years and eliminates the spare reactor in the earlier generations. It achieves a yield of greater than 99.5% and reduces the xylene, which is the only significant impurity in the Mobil-Badger product, by more than 50%. Oligomerization is negligible in this process and the product does not contain nonaromatics. A unique feature of this process is its ability to decompose nonaromatics to light gases and remove them in the vent gas, thus avoiding the need to purge part of the recycled benzene to remove the nonaromatics. This process is also unique in its ability to remove higher alkylbenzenes such as cumene by dealkylation and to recover the benzene value. A high nonaromatics content in the benzene feedstock and a high propylene content in the ethylene feedstock have little effect on the yield and purity of the product.

A simplified flow diagram of the Mobil-Badger vapor-phase process is shown in Figure 1.

A liquid-phase process based on an ultraselective Y (USY)-type zeolite catalyst developed by Unocal in the 1980s (20,21). This process is now called the Lummus-UOP process. The flow scheme of this liquid-phase process, shown schematically in Figure 2, is similar to the Mobil-Badger vapor-phase process. The differences are primarily in the catalysts, reaction conditions, reactor sizes, yields, and product specifications. To maximize the productivity of the catalyst in the Unocal process, the reactors operate at close to the critical temperatures of the reaction mixtures, ie, up to 270°C, and at pressures sufficient to maintain the reaction mixtures in the liquid state, ie, approximately 3.79 MPa (550 psig).

A two-phase process developed by CDTech in the 1980s (21,22) was claimed to be applicable to dilute ethylene feed as well as polymer-grade ethylene feed. The alkylation reaction is carried out in a catalytic distillation column with the liquid and vapor in countercurrent flow. The catalyst is packaged into bales, which are usually fiber glass containers having a cylindrical shape. The bales are arranged in the column to provide separate paths for the liquid to move downward by gravity and for the vapor to move upward by pressure. The complexity of the reactor and the use of baled catalyst, which does not flow freely, complicate the loading, unloading, and regeneration of the catalyst.

All of the processes described above require more benzene recycle than the aluminum chloride-based processes. Retrofitting an existing aluminum chloride-based plant to a zeolite-based plant requires not only replacement of the reaction section but also additional investment in the distillation train.

A newer alkylation technology named EBMax was developed by Mobil Oil Corporation and Raytheon Engineers & Constructors and commercialized in Japan in late 1995 at Chiba Styrene Monomer Company, in a unit originally based on the Lummus-UOP liquid-phase process. The EBMax technology is based on a Mobil zeolite catalyst called MCM-22. MCM-22 overcomes the oligomerization problem that plagues other liquid-phase alkylation processes. Because the catalyst is highly active for alkylation but inactive for oligomerization and cracking, it permits operation at low benzene-to-ethylene ratios, while achieving the highest yield and product purity among the ethylbenzene processes (23).

3.2. Aluminum Chloride-Based Alkylation. The earlier alkylation processes were variations of the Friedel-Craft reaction on an aluminum chloride catalyst complex in a liquid-phase reactor (24), including those developed by Dow Chemical, BASF, Monsanto, and Union Carbide in cooperation with Badger. The Union Carbide-Badger process was the one most widely used during the 1960s and 1970s, with 20 plants built worldwide.

An improved aluminum chloride-based process was developed by Monsanto (25) in the 1970s. Using a presynthesized aluminum chloride complex and operating the reactor at higher temperature and pressure, the catalyst inventory is reduced to below its solubility in the reaction mixture. The reactants and the catalyst complex are mixed in the reactor to form a homogeneous liquid. The transalkylation of polyethylbenzenes is carried out separately. These improvements result in a higher yield. The higher reactor temperature permits recovery of the heat of reaction as useful steam. The reduced inventory of the catalyst, however, also reduces its capacity to resist deactivation by water and other poisons. A simplified flow diagram of the homogeneous alkylation process is shown in Figure 3.

3.3. Other Technologies.

Ethylbenzene can be recovered from mixed C_8 aromatics by superfractionation. This technology was first practiced by Cosden Oil & Chemical Company in 1957 (Big Spring, Texas), based on a design developed jointly with The Badger Company. Several superfractionation plants were built in the United States, Europe, and Japan around 1960. The quantity that can be recovered is limited by the supply of mixed C_8 aromatics and by the low ethylbenzene content (ca 20%). High capital and energy costs resulting from the small boiling-point difference of 1.8°C between ethylbenzene and *para*-xylene and low product purity are some other factors. A process for recovery of ethylbenzene from C_8 aromatic streams by selective adsorption called EBEX was developed by UOP in the 1970s.

Production of ethylbenzene from butadiene has been investigated by many researchers. It consists of two steps: cyclodimerization of 1,3-butadiene to 4-vinylcyclohexene and dehydrogenation of the vinylcyclohexene to ethylbenzene.

4. Styrene Manufacture

Styrene manufacture by dehydrogenation of ethylbenzene is simple in concept and has the virtue of being a single-product technology, an important consideration for a product of such enormous volume. This route is used for nearly 90% of the worldwide styrene production. The rest is obtained from the coproduction of propylene oxide (PO) and styrene (SM). The PO–SM route is complex and capital-intensive in comparison to dehydrogenation of ethylbenzene, but it still can be very attractive. However, its use is limited by the mismatch between the demands for styrene and propylene oxides (qv). The global demand for propylene oxide is only 2/10 of that of styrene by weight, while the ratio of propylene oxide to styrene from the PO–SM route is more than 4:10. The propylene oxide from PO–SM must also compete with that obtained from other routes. Consequently, the propylene oxide market dictates the PO–SM capacity that can be profitably installed, and the larger-volume styrene is thus reduced to the status of a by-product. As such, this styrene can be priced elastically and profitably at the same time. The PO–SM operators are thus the envy of the styrene industry when propylene oxide is in demand. However, the styrene production in the PO–SM plant cannot be increased alone to take advantage of a rising styrene market, and viewed in this light their position becomes less enviable. The PO–SM processes, unlike some of the dehydrogenation processes, are not available for licensing.

4.1. Dehydrogenation.

The dehydrogenation of ethylbenzene to styrene takes

$$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2$$

place on a promoted iron oxide–potassium oxide catalyst in a fixed-bed reactor at the 550–680°C temperature range in the presence of steam. The reaction is limited by thermodynamic equilibrium. Low pressure favors the forward reaction, as is to be expected from the stoichiometric relation that one mole of reactant dissociates into two moles of products. Earlier dehydrogenation reactors were designed for operation above atmospheric pressure, at about 138 kPa (20 psia), so that a compressor would not be required to remove hydrogen from the condensed reactor effluent. Since the 1970s, vacuum design has become standard because the benefits of high conversion and selectivity achievable and low dilution steam required at low pressure outweigh the cost of the compressor. Pressures of 41 kPa (6 psia) or lower at the reactor outlet have been designed. Dehydrogenation is an endothermic reaction. The reaction rate is highly temperature-dependent. High temperature favors dehydrogenation both kinetically and thermodynamically but also increases by-products from side reactions and decreases the styrene selectivity.

The main by-products in the dehydrogenation reactor are toluene and benzene. The formation of toluene accounts for the biggest yield loss, ie, approximately 2% of the styrene produced when a high selectivity catalyst is used. Toluene is formed mostly from styrene by catalytic reactions such as the following:

$$C_6H_5CH{=}CH_2 + 2\,H_2 \rightarrow C_6H_5CH_3 + CH_4$$

$$C_6H_5CH{=}CH_2 \rightarrow C_6H_5CH_3 + C$$

The formation of benzene accounts for a yield loss of up to 1% of the styrene produced, mostly the result of thermal decomposition of ethylbenzene and styrene. Other by-products include carbon dioxide, methane, ethylene, phenylacetylene, α-methylstyrene, allylbenzene, vinyltoluenes, xylenes, cumene, *n*-propylbenzene, ethyltoluenes, butylbenzenes, and heavy aromatics. Although they are rather insignificant in terms of the related yield losses, these compounds can affect the cost of purification and the quality of the styrene product. The alkylbenzene and alkenylbenzene by-products are formed by free-radical and catalytic reactions from ethylbenzene and styrene. With the exception of phenylacetylene, these compounds may also originate from impurities in the ethylbenzene feedstock. Phenylacetylene is formed from dehydrogenation of styrene thermally and catalytically. It is largely temperature-dependent but is also affected by catalyst formulation. Its concentration relative to styrene increases typically from 50 ppm at the start-of-run of a high selectivity catalyst to over 100 ppm at the end-of-run as the temperature is raised to compensate for the declining activity of the catalyst. Phenylacetylene is undesirable in certain styrene uses, such as SBR, because of its propensity to cross-link with styrene and to terminate free-radical reactions during polymerization. If necessary, it can be reduced to parts per million in the styrene product by hydrogenation on a noble metal catalyst under mild conditions. Technologies such as Fina-Badger's PAR technology are available for this treatment. Among the aromatic by-products, α-methylstyrene has the highest concentration in crude styrene. It is partially separated from styrene by distillation and removed in the residue stream.

A small fraction of the hydrocarbons decompose and deposit on the catalyst as carbon. Although the effect is minute in terms of yield losses, this carbon can still significantly reduce the activity of the catalyst. The carbon is formed from cracking of alkyl groups on the aromatic ring and of nonaromatics present in certain ethylbenzene feedstocks. It can be removed by the water gas reaction, which is catalyzed by potassium compounds in the catalyst. Steam, which is

$$C + 2\,H_2O \rightarrow CO_2 + 2\,H_2$$

co-fed with ethylbenzene to the reactor, serves three purposes: as an energy carrier, it supplies the endothermic heat of reaction; as a diluent, it shifts the equilibrium toward the formation of styrene; and as a reactant in the water gas reaction, it retards and limits carbon deposition on the catalyst. However, as important as steam is in the dehydrogenation reactor, its use must be minimized for economic reasons. The steam-to-hydrocarbon ratio, or SHR, is an important consideration in the selection of catalysts and processes.

Dehydrogenation catalysts usually contain 40–90% Fe_2O_3, 5–30% K_2O, and promoters such as chromium, cerium, molybdenum, calcium, and magnesium oxides. As raw material costs for styrene production increased rapidly during the 1970s, the need for development of high selectivity catalysts became urgent. The earlier catalysts of this type suffer from poor mechanical integrity and low activity. The high selectivity catalysts generally require higher reaction temperature to effect the same ethylbenzene conversion. The higher temperature imposes additional demands on the equipment metallurgy, and increases the formation of phenylacetylene. During the 1980s, the mechanical integrity of the high selectivity catalyst was greatly improved. The catalyst manufacturers have also had considerable success in increasing the activity while preserving the selectivity.

An important property of the dehydrogenation catalyst is its steam stability, which refers to the ability of the catalyst to sustain the desired ethylbenzene conversion under a given set of operating conditions, ie, pressure, temperature, and especially steam-to-hydrocarbon ratio (SHR). Steam instability is characterized by accelerated decrease in the ethylbenzene conversion as a result of rapid carbon deposition on the catalyst when the SHR is too low. Most catalysts require a minimum SHR in the 8–10 range. Since the steam-to-hydrocarbon ratio has a large impact on the energy efficiency of a styrene plant, the search for a high selectivity catalyst that is stable at a low ratio has been a topic of intensive research efforts. One developed catalyst has been shown to be stable at a SHR of 7 or lower while retaining a high selectivity in pilot-plant operations.

The quantity of catalyst used for a given plant capacity is related to the liquid hourly space velocity (LHSV), ie, the volume of liquid hydrocarbon feed per hour per volume of catalyst. To determine the optimal LHSV for a given design, several factors are considered: ethylene conversion, styrene selectivity, temperature, pressure, pressure drop, SHR, and catalyst life and cost. In most cases, the LHSV is in the range of 0.4–0.5 h/L. It corresponds to a large quantity of catalyst, approximately $120\,m^3$ or 120–160 t depending on the density of the catalyst, for a plant of 300,000 t/yr capacity.

All of the dehydrogenation catalysts deteriorate, or age, in use, causing the ethylbenzene conversion to decrease with time. This phenomenon is intrinsic in the catalytic reaction, though the aging rate may also be affected by poisons and impurities in the feed. The iron oxide–potassium oxide catalyst is susceptible to poisoning by chlorides, but this is a rare occurrence in commercial plants, particularly when the ethylbenzene feedstock comes from a zeolite-based process. In most cases catalyst aging is caused by carbon deposition on the catalyst, chemical decomposition of the active ingredient in the catalyst, and mechanical disintegration of catalyst particles. In commercial practice, the reaction temperature is increased to compensate for the decrease in the activity of the catalyst and to maintain the desired conversion. This procedure continues until the temperature reaches the limit allowed by the mechanical design of the reactor system or when the styrene selectively is deemed too low to be economical. The useful lives of dehydrogenation catalysts vary from one to four years, and in most cases 18–24 months, depending on the nature of the catalyst, the design and operation of the reactor system, and the quality of the feedstock. Catalyst is a significant cost in the production of styrene owing to the large quantity required. There is considerable incentive to extend the useful life of the catalyst. Even more important than savings in catalyst cost is the reduction in downtime and increase in production that result from an extended catalyst life. Carbon deposition can be reversed to a large degree by steaming the catalyst, but the effect is only short-term; frequent steaming is not deemed to be economical. Steaming is ineffective for extending catalyst life because it does not prevent chemical decomposition of the catalyst. A method of preventing decomposition and disintegration of the dehydrogenation catalysts called Catalyst Stabilization Technology (CST) was invented in 1995 at Weymouth Laboratory of Raytheon Engineers and Constructors (26).

Dehydrogenation is carried out either isothermally or adiabatically. In principle, isothermal dehydrogenation has the duel advantage of avoiding a very high temperature at the reactor inlet and maintaining a sufficiently high temperature at the reactor outlet. In practice, these advantages are negated by formidable heat-transfer problems. First, to facilitate heat transfer from an external source to provide the reaction heat, expensive tubular reactors are used. Second, the reaction temperature exceeds the stable temperatures of the molten salts commonly used as heat-transfer media in tubular reactors. Flue gas is used, but its heat capacity and heat-transfer rate are low, requiring a large number of tubes and multiple reactor trains for large plants. Isothermal processes are practiced in Europe and in Japan. An isothermal reactor system that uses a molten salt mixture of sodium, lithium, and potassium carbonates as the heating medium was offered for licensing by Lurgi, Montedison, and Denggendarfer. A demonstration unit was built in 1985, but no commercial units have been built.

In an adiabatic reactor, the endothermic heat of reaction is supplied by the preheated steam that is mixed with ethylbenzene upstream of the reactor. As the reaction progresses, the temperature decreases. To obtain a high conversion of ethylbenzene to styrene, usually two, and occasionally three, reactors are used in series with a reheater between the reactors to raise the temperature of the reaction mixture. The reactors are fixed bed in design with the catalyst confined between two concentric screens in each reactor, which is cylindrical and vertical. The reaction mixture flows radially from the inner screen through the catalyst and outside screen. The radial design provides a large flow area and minimizes the pressure drop through the catalyst in an economical way. Large plants with a single train capable of producing more than 500,000 t/yr of styrene are in operation.

Other than the reactor system, the distillation column that separates the unconverted ethylbenzene from the crude styrene is the most important and expensive equipment in a styrene plant. It is expensive because the relative volatility between ethylbenzene and styrene is small, requiring a large number of distillation stages and a high reflux ratio. Its design must also take into consideration that styrene polymerizes in the liquid phase even at the ambient temperature and the rate of polymerization increases rapidly with the temperature and the concentration. In addition to reducing the styrene yield, polymerization could cause operating difficulties. Therefore, the distillation is carried out at a high vacuum to keep the temperature low, and inhibitors are used to retard polymerization. Many efforts have been made to minimize the pressure drop in the distillation column, and thus to reduce the temperatures in the stripping section and in the reboiler. The Linde sieve tray (27), developed in the 1960s, succeeded in reducing the pressure drop, decreasing the liquid holdup, and increasing the tray efficiency. Another significant advancement in the styrene distillation technology was introduced in the 1980s by the development of structural packings (28). This results in further reduction of pressure drop and increases of separation efficiency and throughput.

To minimize yield losses and to prevent equipment fouling by polymer formation, which may lead to a reduced production rate and plant shutdown, polymerization inhibitors are used in the distillation train, product storage, and more recently in vent gas compressors. Inhibitor usage is a significant cost in the production of styrene. Sulfur was used extensively as polymerization inhibitor until the mid-1970s. It is effective but the residue leaving the distillation train is contaminated with sulfur and is not environmentally acceptable as fuel. Newer inhibitors, mostly nitrogen-containing organic compounds such as dinitrophenol and dinitrocresol, have been developed to replace sulfur. They are more expensive and some are highly toxic, but it is acceptable to use the residue containing inhibitors of this type as fuel. The styrene product also needs inhibitor to retard polymerization in storage and shipping. The most commonly used inhibitor for this service is 4-*tert*-butylcatechol (TBC), which is colorless, usually in 10–15 ppm concentration. The term inhibitor is used in the styrene industry often indiscriminately to denote substances ranging from true inhibitor to retarder. True inhibitors prevent the initiation of polymerization by reacting rapidly with free radicals; retarders reduce the rate of polymerization. New inhibitor systems that are claimed to be capable of dramatically reducing polymer formation have been developed.

The qualities of the styrene product and toluene by-product depend primarily on three factors: the impurities in the ethylbenzene feedstock, the catalyst used, and the design and operation of the dehydrogenation and distillation units. Other than benzene and toluene, the presence of which is usually inconsequential, possible impurities in ethylbenzene are C_7–C_{10} nonaromatics and C_8–C_{10} aromatics. Parts of the nonaromatics are cracked and dehydrogenated. The C_7 and some of the C_8 nonaromatics remain in the toluene stream as alkane and alkene impurities and decrease its by-product value. These impurities are also reported to be the likely cause of color problems in the toluene by-product

(29). The remaining nonaromatics remain in the styrene product. Among the C_8 aromatics, *m*- and *p*-xylene can be recycled to extinction; *o*-xylene remains in the styrene product. The C_9–C_{10} aromatics include cumene, *n*-propylbenzene, ethyltoluenes, butylbenzenes, etc. They pass through the dehydrogenation reactor partly unchanged and partly converted to their corresponding dehydrogenated compounds. For example, cumene is partially converted to α-methylstyrene. Part of these aromatic and dehydrogenated compounds remain in the styrene product.

The development of the high selectivity catalyst is the most important advancement in the styrene manufacturing technology during the quarter century prior to the mid-1990s. Other important improvements include better design of the reactor system to assure uniform composition, temperature, and distribution of the reaction mixture, to minimize thermal reactions, and to prevent localized catalyst aging; low reactor pressure to enhance styrene selectivity and catalyst stability; efficient heat exchange systems to reduce the energy cost; structural packings to reduce the pressure drops in distillation columns; polymerization inhibitors that are more effective and less environmentally objectionable; use of high purity ethylbenzene feedstock to increase the purity of the styrene product; and improved design of the recovery and purification system to minimize polymer formation and styrene loss to the residue.

A modern adiabatic dehydrogenation unit with two reactors and an interreactor reheater, operating with a high selectivity catalyst and at a pressure of 41 kPa (6 psia) at the second reactor outlet, can give a styrene selectivity as high as 97% at an ethylbenzene conversion of 60–70%. The choice of a desired conversion is a matter of economic optimization. A low conversion gives a high selectivity but increases energy consumption; a high conversion decreases the energy cost but increases the raw material cost.

Most of the styrene plants in operation or under construction in the world are based on one of two adiabatic processes: the Fina-Badger process licensed by Badger Technology Division of Raytheon Engineers & Constructors and the Monsanto process licensed by ABB Lummus Crest. Dow Chemical, a primary styrene producer, uses its own adiabatic process. These processes are similar to one another in principle, but differ in details. In selecting a process, the licensee usually considers the capital cost, yield, product quality, energy efficiency, inhibitor consumption, plant reliability, operating flexibility, and other factors that are of significance to the project. The details are important. For example, operating reliability and flexibility have proved to be crucial to the profitability of a plant because the supply and demand of styrene are seldom in balance.

Figure 4 illustrates a typical dehydrogenation unit. Fresh and recycled ethylbenzene are combined and mixed with steam, then heat-exchanged with the reactor effluent. The vapor mixture of ethylbenzene and steam is raised to the desired reaction temperature by mixing with more steam that has been superheated to 800°C or higher in a fired heater. This mixture is fed to the reactors, two or three stages in series with interstage reheaters. The reactor effluent goes through heat exchangers to preheat the ethylbenzene–steam feed mixture and to generate steam for use in the distillation train. The condensed reactor effluent is separated in the settling drum into vent gas (mostly hydrogen), process water, and organic phase. The vent gas is removed by a compressor for use as fuel or for hydrogen recovery. The process water is stripped of organics and reused. The organic phase with polymerization inhibitor added is pumped to the distillation train. In an optional energy recovery scheme offered in conjunction with the Fina-Badger process, after the high level energy in the reactor effluent is recovered, the latent heat is recovered by using the condensing reactor effluent to vaporize a ethylbenzene–water azeotrope, which is then compressed and used as the reactor feed. This option is highly energy efficient but requires an incremental investment. It has been used in the Far East.

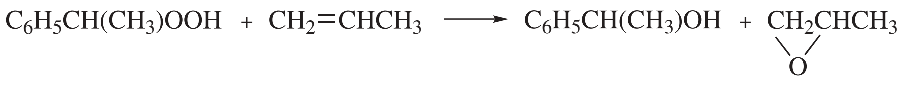
Figure 5 illustrates a typical distillation train in a styrene plant. Benzene and toluene by-products are recovered in the overhead of the benzene–toluene column. The bottoms from the benzene–toluene column are distilled in the ethylbenzene recycle column, where the separation of ethylbenzene and styrene is effected. The ethylbenzene, containing up to 3% styrene, is taken overhead and recycled to the dehydrogenation section. The bottoms, which contain styrene, by-products heavier than styrene, polymers, inhibitor, and up to 1000 ppm ethylbenzene, are pumped to the styrene finishing column. The overhead product from this column is purified styrene. The bottoms are further processed in a residue-finishing system to recover additional styrene from the residue, which consists of heavy by-products, polymers, and inhibitor. The residue is used as fuel. The residue-finishing system can be a flash evaporator or a small distillation column. This distillation sequence is used in the Fina-Badger process and the Dow process.

In the Monsanto process (now called Lummus-UOP Classic process, as distinct from the SMART process to be described later), ethylbenzene, together with benzene and toluene, is separated from styrene in the first column. The overhead condensate from this column then goes to the benzene–toluene column and is redistilled to recover the benzene–toluene fraction in the overhead and ethylbenzene in the bottoms. It has been argued that energy is wasted in this scheme by distilling the benzene–toluene fraction twice, once together with ethylbenzene and once away from ethylbenzene. Actually, this extra energy consumption, which can be computed, is small. It has also been argued that less polymer is formed in having the styrene bypass the benzene–toluene column. Actually, any possible reduction of polymerization resulting from this arrangement, which has never been substantiated, is insignificant because polymerization of the styrene in solution with ethylbenzene through a small benzene–toluene column is negligible in comparison with polymerization of the high concentration styrene in the much larger ethylbenzene–styrene distillation column. Moreover, the higher vapor and liquid loadings required by having to distill benzene and toluene together with ethylbenzene may slightly increase styrene polymerization. In any case, these effects are insignificantly small and every process owner continues to use its own design very likely for historical reasons. An optional scheme to utilize the latent heat of the ethylbenzene vapor in the column overhead to vaporize an ethylbenzene–water azeotrope for use as reactor feed is offered in conjunction with the Monsanto process. This scheme recovers less energy than the Fina-Badger scheme but does not require a compressor. However, the condensing temperature of the ethylbenzene vapor must be raised by having the ethylbenzene–styrene column operate at higher temperatures. The inhibitor usage and polymer formation increase substantially because the rate of polymerization increases rapidly with the temperature. Consequently, the quantity and viscosity of the residue are high. A wipe-film evaporator is then used downstream of the styrene finishing column to minimize yield losses. This scheme has also been used in the Far East. It has been reported that the increased polymerization has caused difficult operating problems and reduced operating flexibility. The economics of the optional energy recovery schemes are marginal at best in most situations insofar as the energy savings are negated by the incremental investment, extra inhibitor usage and yield losses, and reduced operating flexibility. Neither of them is used by the producers in the United States.

The benzene–toluene fraction is further fractionated in a small column, not shown in Figure 5, to recover benzene for recycle to the alkylation unit and toluene for sale. This toluene can be converted to benzene by hydrodealkylation but the high selectivity catalyst has reduced the formation of toluene in the dehydrogenation reactor to the point where the cost of installing a hydrodealkylation unit is difficult to justify even in a large styrene plant.

4.2. PO–SM Coproduction. The coproduction of propylene oxide and styrene (30–39) includes three reaction steps: (*1*) oxidation of ethylbenzene to ethylbenzene hydroperoxide, (*2*) epoxidation of ethylbenzene hydroperoxide with propylene to form α-phenylethanol and propylene oxide, and (*3*) dehydration of α-phenylethanol to styrene.

$$C_6H_5CH_2CH_3 + O_2 \rightarrow C_6H_5CH(CH_3)OOH$$



$$C_6H_5CH(CH_3)OOH + CH_2{=}CHCH_3 \longrightarrow C_6H_5CH(CH_3)OH + \underset{\diagdown O \diagup}{CH_2CHCH_3}$$

$$C_6H_5CH(CH_3)OH \rightarrow C_6H_5CH{=}CH_2 + H_2O$$

The oxidation step is similar to the oxidation of cumene to cumene hydroperoxide that was developed earlier and is widely used in the production of phenol and acetone. It is carried out with air bubbling through the liquid reaction mixture in a series of reactors with decreasing temperatures from 150 to 130°C, approximately. The epoxidation of ethylbenzene hydroperoxide to α-phenylethanol and propylene oxide is the key development in the process. It is carried out in the liquid phase at 100–130°C and catalyzed by a soluble molybdenum naphthenate catalyst, also in a series of reactors with interreactor coolers. The dehydration of α-phenylethanol to styrene takes place over an acidic catalyst at about 225°C. A commercial plant (40–42) was commissioned in Spain in 1973 by Halcon International in a joint venture with Enpetrol based on these reactions, in a process that became known as the Oxirane process, owned by Oxirane Corporation, a joint venture of ARCO and Halcon International. Oxirane Corporation merged into ARCO in 1980 and this process is now generally known as the ARCO process.

The recovery and purification facilities in these processes are also complex. One reason is that oxygenated by-products are made in the reactors. Oxygenates, particularly aldehydes, are known to hinder polymerization of styrene and to cause color instability. Elaborate purification is required to remove the oxygenates. The styrene assay becomes very high as a result, but its quality as a monomer relative to the styrene produced by the dehydrogenation technology has been a matter of differing opinion among polymer producers.

4.3. Other Technologies. As important as dehydrogenation of ethylbenzene is in the production of styrene, it suffers from two theoretical disadvantages: it is endothermic and is limited by thermodynamic equilibrium. The endothermicity requires heat input at high temperature, which is difficult. The thermodynamic limitation necessitates the separation of the unreacted ethylbenzene from styrene, which are close-boiling compounds. The obvious solution is to effect the reaction oxidatively:

$$C_6H_5CH_2CH_3 + 1/2\,O_2 \rightarrow C_6H_5CH{=}CH_2 + H_2O$$

Oxidative dehydrogenation is exothermic and is irreversible for all practical purposes. It could greatly reduce the cost of styrene production. The theoretical elegance and the potential benefit of the concept are so seductive that it has been a topic of extensive research and development since the 1940s not only in the petrochemical industry but also in universities. Molecular oxygen as well as various oxygen carriers, such as sulfur trioxide and ferric oxide, have been used as oxidants in fixed-bed and fluid-bed reactors. These research efforts have not resulted in commercial processes mainly because the selectivity to styrene is too low, in comparison with the dehydrogenation technology, to be economical.

A similar but somewhat less ambitious approach is to carry out dehydrogenation of ethylbenzene and oxidation of the hydrogen product alternately in separate reactors containing different catalysts:

Dehydrogenation $C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2$

Oxidation $H_2 + 1/2\,O_2 \rightarrow H_2O$

The oxidation reactor replaces the reheater in the adiabatic dehydrogenation technology. The oxidation of hydrogen not only reheats the reaction mixture from a dehydrogenation reactor but also shifts the reaction equilibrium, thus allowing a higher conversion of ethylbenzene in the following dehydrogenation reactor. An ethylbenzene conversion of greater than 80% is claimed to be obtainable with three dehydrogenation reactors and two oxidation reactors. Such an oxidative reheat technology using a palladium catalyst in the oxidation reactor was developed by UOP (42) and implemented in a demonstration-scale unit at Mitsubishi Chemical in Japan. It was offered for licensing as a new styrene process in the mid-1980s under the trade name of StyroPlus. It has not attained commercial acceptance, probably because of the high cost of the palladium catalyst and the necessity of diluting the oxygen with steam prior to its injection into the reaction mixture. There are also concerns about the safety of the oxygen mixing step, potential damage to the dehydrogenation catalyst by oxygen, and the possibility of contaminating the styrene product with oxygenates. It is now called oxidative reheat technology and offered as a way of increasing existing plant capacity. It is also called SMART (styrene monomer advanced reactor technology) in combination with the Monsanto dehydrogenation process licensed by ABB Lummus Crest (42–46).

A three-step process involving the oxidation of acetophenone, hydrogenation of the ketone to α-phenylethanol, and dehydration of the alcohol to styrene was practiced commercially by Union Carbide (47) until the early 1960s. Other technologies considered during the infancy of the styrene industry include side-chain chlorination of ethylbenzene followed by dehydrochlorination or followed by hydrolysis and dehydration.

Technologies for producing styrene from alternative raw materials have also been seriously investigated. Toluene is priced lower than benzene historically and its use as a starting raw material in lieu of benzene received much attention during the 1970s. Side-chain alkylation of toluene with methanol or formaldehyde was studied by Monsanto and others (48,49). Monsanto and others (50–53) also undertook programs to develop oxidative coupling of toluene to stilbene, followed by disproportionation of stilbene with ethylene to form styrene:

$$2\,C_6H_5CH_3 + O_2 \rightarrow C_6H_5CH{=}CHC_6H_5 + 2\,H_2O$$

$$C_6H_5CH{=}CHC_6H_5 + CH_2{=}CH_2 \rightarrow 2\,C_6H_5CH{=}CH_2$$

This route uses toluene in lieu of benzene and cuts the ethylene consumption in half in comparison with the commercial alkylation–dehydrogenation technology via ethylbenzene. It affords a potential cost savings of 20% in raw materials. It would also avoid the costly separation of ethylbenzene and styrene. In actuality, however, these toluene-based technologies suffer from low yields which negate the potential advantages. They were not brought to the commercial stage, and the research programs were discontinued in the early 1980s. A technology for cracking diphenylethane to styrene and benzene originally developed by Nippon Petrochemicals is reported to have been used to reclaim the diphenylethane contained in the residue from a ethylbenzene plant based on the Unocal alkylation process. Recovery of styrene from various petroleum streams, such as pyrolysis gasoline, has been considered but is deemed uneconomical.

Production of styrene from butadiene has also been extensively investigated. Dow announced licensing a process involving cyclodimerization of 1,3-butadiene to 4-vinylcyclohexene, followed by oxidative dehydrogenation of the vinylcyclohexene to styrene (53,54). The cyclodimerization step takes place in

$$2\,C_4H_6 \rightarrow C_6H_9CH{=}CH_2$$

the liquid phase at about 100°C and 2.76 MPa (400 psig) over a copper–zeolite catalyst. The vinylcyclohexene is converted to styrene by oxidative dehydrogenation with molecular oxygen diluted with steam in the vapor phase at about 400°C

$$C_6H_9CH{=}CH_2 + O_2 \rightarrow C_6H_5CH{=}CH_2 + 2\,H_2O$$

and 138 kPa (20 psig) on a mixed metal oxide catalyst. A three-step process from butadiene to styrene has also been extensively investigated (55–57). The first step also involves cyclodimerization of butadiene to vinylcyclohexene, using an iron dinitrosyl chloride–zinc catalyst complex which is very active and selective. The reaction is carried out in tetrahydrofuran solvent at about 75°C and 0.52 MPa (75 psig). The second step involves dehydrogenation of vinylcyclohexene to ethylbenzene in the vapor phase at 400°C and 0.69 MPa (100 psig) or

$$C_6H_9CH{=}CH_2 \rightarrow C_6H_5CH_2CH_3 + H_2$$

higher pressure on a noblemetal catalyst. The third step is the conventional dehydrogenation of ethylbenzene to styrene. Interest in the butadiene route is prompted by the projection of a worldwide surplus of butadiene as a by-product of ethylene plants.

5. Economic Aspects

Table 2 lists the North American producers of styrene and their capacities. Commercial production is from dehydrogenation of ethylbenzene obtained by the alkylation of benzene with ethylene. Lyondell's process produces propylene oxide with styrene as co-product.

Styrene markets follow the economy. Consumption of styrene for polystyrene and co-polymer production has shown considerable maturity in the last 10 years. Consumption fell with the recession of 2000–2001, but it is now rebounding. The market is strained by a run up in energy and raw materials costs. Demand in the U.S. is expected at 4.7×10^3 t in 2007. Growth is expected at the rate of 2%/yr through 2007 (59).

World demand was expected to reach 26×10^6 t in 2006. The fastest growing demand will be in South America, Eastern Europe and the Middle East. World styrene demand grew at an average rate of 4.0% during 1996–2001 to nearly 21×10^6 t. Most of this demand (61%) went into the production of polystyrene. It is expected that demand in Asian countries (excluding Japan) will grow faster than the world rate. South America, Eastern Europe, and the Middle East will grow at the rate of 8.4% through 2006. China and Taiwan are expected to be the significant importers of styrene in the next few years.

6. Specifications and Analysis

Styrene specifications are largely dictated by the market. There is no formal agreement in the industry. Specifications for a typical polymerization-grade styrene product are shown in Table 3. The typical assay increased from 99.6% to 99.8% during the 1980s. As of 1996, an assay of 99.8% is still generally accepted. Newer plants in the United States are designed for 99.90% purity and in some cases as high as 99.95%. Some producers choose to have their plants designed to produce high purity styrene at a small incremental investment to gain marketing advantages and in anticipation of its future demand.

The advance in alkylation technology enables the production of ultrahigh purity ethylbenzene at a low cost. With this ethylbenzene as the intermediate, a dehydrogenation unit of the present design will be able to produce styrene of 99.95% purity routinely. It may prompt a new standard in the styrene industry.

Methods for the analysis of styrene monomer are also shown in Table 3. The freezing point measurement was the standard method for the determination of styrene assay until the 1970s, but it has been largely replaced by gas chromatography. Modern gas chromatography gives a great amount of detail on the impurities and is accurate to parts per million or lower; styrene assay is determined by difference. However, certain impurities and properties are not amenable to chromatographic analysis. Color is measured spectrophotometrically and registered on the APHA or the platinum–cobalt scale. The TBC (4-*tert*-butylcatechol, the inhibitor) is extracted with aqueous sodium hydroxide and the resulting reddish quinone is measured photometrically. The polymer content is precipitated by addition of methanol to the monomer and the resulting mixture is measured with a turbidity meter. Other possible impurities, such as chlorides, sulfur, aldehydes (expressed as benzaldehyde), and peroxides (expressed as hydrogen peroxide) are measured by the methods commonly used in the chemical industry, also listed in Table 3.

7. Health and Safety Factors

Styrene is mildly toxic, flammable, and can be made to polymerize violently under certain conditions. However, handled according to proper procedures, it is a relatively safe organic chemical. Styrene vapor has an odor threshold of 50–150 ppm (60,61).

Styrene is listed in the U.S. Toxic Substance Control Act (TSCA) Inventory of Chemicals. It is confirmed as a carcinogen. The recommended exposure limits are OSHA PEL 50 ppm, ACGIH TLV 20 ppm (62). For higher concentrations, NIOSH/MSHA-approved respiratory protection devices should be used. For skin protection, use of protective garments and gloves of Viton, Nitrile, or PVA construction should be made. The acute effects of overexposure to styrene are shown in Table 4 (63).

Styrene liquid is inflammable and has sufficient vapor pressure at slightly elevated temperatures to form explosive mixtures with air, as shown in Figure 6. Uninhibited styrene polymerizes slowly at room temperature, and the polymerization rate increases with the temperature. Styrene polymerization is exothermic and this can cause the reaction to run awry. Polymerization can be inhibited by the presence of 10 ppm or more of TBC. Oxygen is necessary for effective action of the inhibitor (64). It is recommended that air be added periodically to the storage vessels, which are blanketed with an inert gas. Properly inhibited and attended, styrene can be stored for an extended period of time. In climates where the average daily temperature in excess of 27°C is common, refrigeration of bulk storage is recommended (65). Copper and copper alloys should not be used in the handling or storage of styrene, because copper can dissolve in styrene to cause discoloration and interferes with polymerization.

8. Uses

Commercial styrene is used almost entirely for the manufacture of polymers. Polystyrene accounts for 61% of the worldwide demand for styrene. The rest is for manufacture of copolymers: ABS/SAN, 14%; SBR and SBR latex, 10%; UPR, 5%; others, 11% (59).

8.1. Polystyrene (PS). Packaging applications are the main use for PS. Food containers, and disposable tableware; toys; furniture, appliances, television cabinets, and sports goods; and electrical and electronic parts are the remaining markets. For some of these applications, PS is modified by blending or graft polymerization with SBR to form impact polystyrene, which is less sensitive to breakage. Expandable polystyrene is widely used in construction for thermal insulation.

8.2. Acrylonitrile–Butadiene–Styrene Copolymer (ABS). Uses for ABS are in sewer pipes, vehicle parts, appliance parts, business machine casings, sports goods, luggage, and toys.

8.3. Styrene–Butadiene Latex. SB latex is used in paper coatings, carpet backing, paper adhesives, cement additives, and latex paint.

8.4. Styrene–Butadiene Rubber (SBR). This elastomer is used primarily in tires, vehicle parts, industrial hose and belting, and consumer goods.

8.5. Unsaturated Polyester Resins (UPR). The principal uses are in putty, coatings, and adhesives. Glass-reinforced UPR is used for marine construction, and vehicle materials, as well as for electrical parts.

9. Derivatives

A large number of compounds related to styrene have been reported in the literature. Those having the vinyl group $CH_2{=}CH-$ attached to the aromatic ring are referred to as styrenic monomers. Several of them have been used for manufacturing small-volume specialty polymers. The specialty styrenic monomers that are manufactured in commercial quantities are vinyltoluene, *para*-methylstyrene, α-methylstyrene, and divinylbenzene. In addition, 4-*tert*-butylstyrene [1746-23-2] (TBS) is a specialty monomer that is superior to vinyltoluene and *para*-methylstyrene in many applications. It is manufactured by Amoco in a complex process and its use has been limited by its high price. Other styrenic monomers produced in small quantities include chlorostyrene and vinylbenzene chloride.

With the exception of α-methylstyrene, which is a by-product of the phenol–acetone process, these specialty monomers are more difficult and expensive to manufacture than styrene. Their more complex molecular structures give rise to the formation of more types and greater quantities of by-products in chemical reactions, and the yields are low in comparison with styrene synthesis. As a result, the recovery and purification facilities are more complex. The high boiling points of these monomers require that distillation be carried out at high temperatures, which would cause high yield losses to polymerization, or at low pressures, which would increase the investment and operating costs. These difficulties, together with the lack of economy in large-scale production, keep the cost of these monomers high and limit their uses.

9.1. Vinyltoluene. This is a specialty monomer with properties similar to those of styrene (66). It was originally developed to compete with styrene when benzene was in short supply after World War II. It is more difficult to manufacture than styrene. With the development of new technologies for producing benzene from petroleum, notably catalytic reforming and naphtha cracking, styrene retained its lead position and became a large-volume monomer. Vinyltoluene [25013-15-4] has continued to be produced for special applications. Its copolymers are more heat-resistant than the corresponding styrene copolymers. The increased solubility in aliphatic solvents and the faster reaction rates resulting from the added methyl group make vinyltoluene better suited than styrene as a specialty monomer for paint, varnish, and polyester applications.

Vinyltoluene (VT) is a mixture of *meta*- and *para*-vinyltoluenes, typically in the ratio of 60:40. This isomer ratio results from the ratio of the corresponding ethyltoluenes in thermodynamic equilibrium. Physical properties and chemical analysis of a typical vinyltoluene product are shown in Tables 5 and 6, respectively.

Ethyltoluene is manufactured by aluminum chloride-catalyzed alkylation similar to that used for ethylbenzene production. All three isomers are formed. A typical analysis of the reactor effluent is shown in Table 7. After the unconverted toluene and light by-products are removed, the mixture of ethyltoluene isomers and polyethyltoluenes is fractionated to recover the meta and para isomers (bp 161.3 and 162.0°C, respectively) as the overhead product, which typically contains 0.2% or less ortho isomer (bp 165.1°C). This isomer separation is difficult but essential because *o*-ethyltoluene undergoes ring closure to form indan and indene in the subsequent dehydrogenation process. These compounds are even more difficult to remove from vinyltoluene, and their presence in the monomer results in inferior polymers. The *o*-ethyltoluene and polyethyltoluenes are recovered and recycled to the reactor for isomerization and transalkylation to produce more ethyltoluenes. Fina uses a zeolite-catalyzed vapor-phase alkylation process to produce ethyltoluenes.

The dehydrogenation of the mixture of *m*- and *p*-ethyltoluenes is similar to that of ethylbenzene, but more dilution steam is required to prevent rapid coking on the catalyst. The recovery and purification of vinyltoluene monomer is considerably more difficult than for styrene owing to the high boiling point and high rate of thermal polymerization of the former and the complexity of the reactor effluent, which contains a large number of by-products. Pressures as low as 2.7 kPa (20 mm Hg) are used to keep distillation temperatures low even in the presence of polymerization inhibitor. The finished vinyltoluene monomer typically has an assay of 99.6%.

9.2. para-Methylstyrene. PMS is the para isomer of vinyltoluene in high purity. It is probably the only compound that has the potential to compete against styrene in the large commodity market as a styrenic monomer. *p*-Methylstyrene [627-97-9] has an apparent raw material cost advantage over styrene, and the characteristics of its polymers and copolymers are superior to those of the corresponding styrene polymers and copolymers in some important aspects. PMS is made by alkylation of toluene with ethylene to *p*-ethyltoluene, followed by dehydrogenation of *p*-ethyltoluene. Stoichiometrically, it takes 78 t of toluene and 24 t of ethylene to make 100 t of PMS, whereas it takes 75 t of benzene and 25 t of ethylene to make 100 t of styrene. Toluene is priced lower than benzene by weight, and ethylene is more expensive than both. The use of toluene in lieu of benzene and the lower ethylene requirement together give PMS a potential savings of 10–20%. It has an additional cost advantage of 4% as a monomer resulting from poly-PMS having a lower density than polystyrene, as polymers are usually sold (and used) by volume rather than by weight.

The most difficult problem in manufacturing PMS is in the synthesis of the *p*-ethyltoluene precursor in high purity. A conventional alkylation process makes all three isomers, and isolation of the para isomer from this mixture by distillation or any other technique would be prohibitively expensive. The manufacture of PMS as a large-volume monomer became feasible with the development by Mobil of a ZSM-5 catalyst which is selective to the para isomer in alkylation (67). It attracted much attention in the styrene industry in the early 1980s. PMS was billed as "high-tech styrene" and forecasts were made of its gradually replacing styrene as the dominant styrenic monomer. This did not happen for several reasons. Aside from the isomer selectivity, the production of PMS is more difficult than that of styrene with higher investment, lower yield, and higher energy consumption in both the alkylation and dehydrogenation steps. In reality, the production cost advantage is far less than the apparent raw material cost savings. Moreover, the markets for both the monomer and its polymers must be developed on a large scale for it to compete on the basis of both quality and price. This requires a large investment, which would involve considerable risk in view of the well-established position of styrene monomer in the plastics industry. It was deemed to be too risky, and the expectation of PMS becoming a large-volume monomer faded.

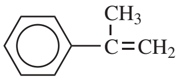
9.3. Divinylbenzene. This is a specialty monomer used primarily to make cross-linked polystyrene resins. Pure divinylbenzene (DVB) monomer is highly reactive polymerically and is impractical to produce and store. Commercial DVB monomer (65–68) is generally manufactured and supplied as mixtures of *m*- and *p*-divinylbenzenes and ethylvinylbenzenes. DVB products are designated by commercial grades in accordance with the divinylbenzene content. Physical properties of DVB-22 and DVB-55 are shown in Table 8. Typical analyses of DVB-22 and DVB-55 are shown in Table 9. Divinylbenzene [1321-74-0] is readily polymerized to give brittle insoluble polymers even at ambient temperatures. The product is heavily inhibited with TBC and sulfur to minimize polymerization and oxidation.

Small quantities of DVB copolymerized with styrene yield polymers which have the appearance of polystyrene but possess higher heat distortion temperatures, greater hardness, and slightly better impact and tensile strengths. The increased resistance to thermal distortion allows the plastics to be machined more easily and to have broader use in electrical insulation applications. Beads of styrene–divinylbenzene resins made by suspension polymerization are used as the basis of ion-exchange resins. (The ionic sites are formed afterward by substitution on the aromatic rings.) The cross-links resulting from divinylbenzene help stabilize the bead structure and minimize swelling. The largest use of DVB is in ion-exchange resins for domestic and industrial water softening.

Ion-exchange resins are also used as solid acid catalysts for certain reactions, such as esterification.

Divinylbenzene is manufactured by dehydrogenation of diethylbenzene, which is an internal product in the alkylation plant for ethylbenzene production. This internal product is normally transalkylated to produce more ethylbenzene. A stream of the diethylbenzene can be diverted for divinylbenzene production. The technology for dehydrogenation of diethylbenzene is similar to that for dehydrogenation of ethylbenzene. The presence of two ethyl groups on the aromatic ring, however, greatly increases the number of possible products and by-products. Light by-products include benzene, toluene, xylene, ethylbenzene, styrene, ethyltoluene, and vinyltoluene. *Meta*- and *para*-diethylbenzenes are converted to their corresponding ethylvinylbenzenes and divinylbenzenes. The unconverted diethylbenzenes and part of the ethylvinylbenzenes are removed together with the light by-products and, after further fractionation, recycled to the reactor. *ortho*-Ethylbenzene [135-01-3] is dehydrogenated and cyclized to naphthalene, which is removed together with other heavy by-products as the residue from the product, which is a mixture of divinylbenzenes and ethylvinylbenzenes. This last distillation is carried out at a very low pressure of 1.33–2 kPa (10–15 mm Hg) absolute and in the presence of inhibitors to keep the temperature low and to prevent polymerization. Further isolation of the product components is neither necessary nor desirable. For most commercial applications, divinylbenzene is used in low concentrations as a cross-linking agent. Ethylvinylbenzene itself is a monomer much like vinyltoluene and is easily incorporated into polymers of styrene.

9.4. α-Methylstyrene. This compound is not a styrenic monomer in the strict sense. The methyl substitution on the side chain, rather than the aromatic ring, moderates its reactivity in polymerization. It is used as a specialty monomer in ABS resins, coatings, polyester resins, and hot-melt adhesives. As a copolymer in ABS and polystyrene, it increases the heat-distortion resistance of the product. In coatings and resins, it moderates reaction rates and improves clarity. Physical properties of α-methylstyrene [98-83-9] are shown in Table 10.



Production of α-methylstyrene (AMS) from cumene by dehydrogenation was practiced commercially by Dow until 1977. It is now produced as a by-product in the production of phenol and acetone from cumene. Cumene is manufactured by alkylation of benzene with propylene. In the phenol–acetone process, cumene is oxidized in the liquid phase thermally to cumene hydroperoxide. The hydroperoxide is split into phenol and acetone by a cleavage reaction catalyzed by sulfur dioxide. Up to 2% of the cumene is converted to α-methylstyrene. Phenol and acetone are large-volume chemicals and the supply of the by-product α-methylstyrene is well in excess of its demand. Producers are forced to hydrogenate it back to cumene for recycle to the phenol–acetone plant.

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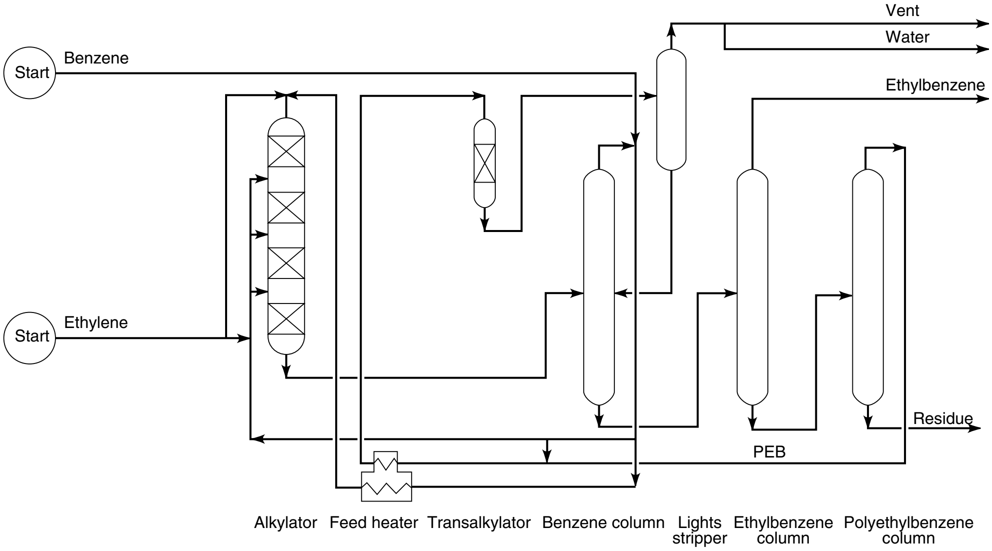

Fig. 1. Mobil-Badger vapor-phase ethylbenzene process where PEB = polyethylbenzene.

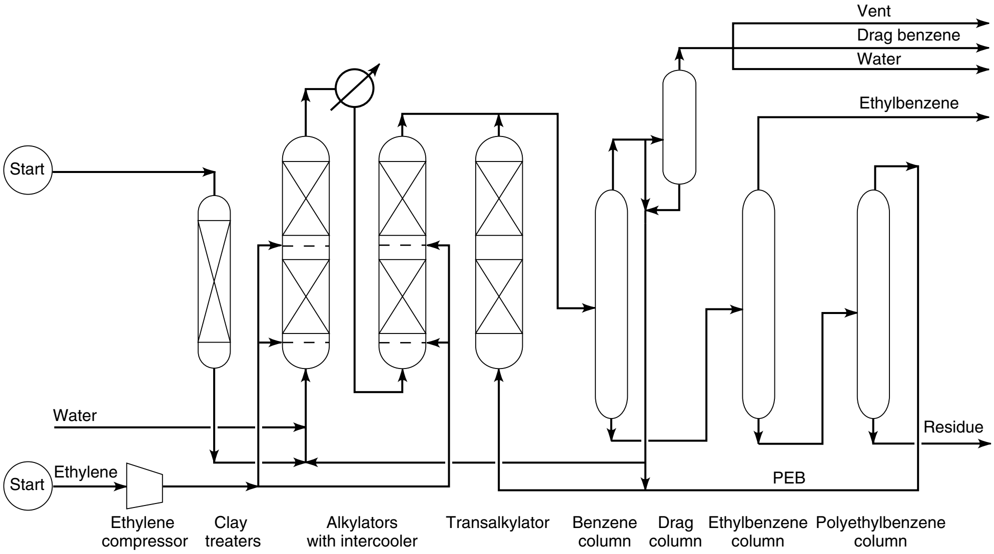

Fig. 2. Lummus–Unocal–UOP liquid-phase ethylbenzene process where PEB = polyethylbenzene.

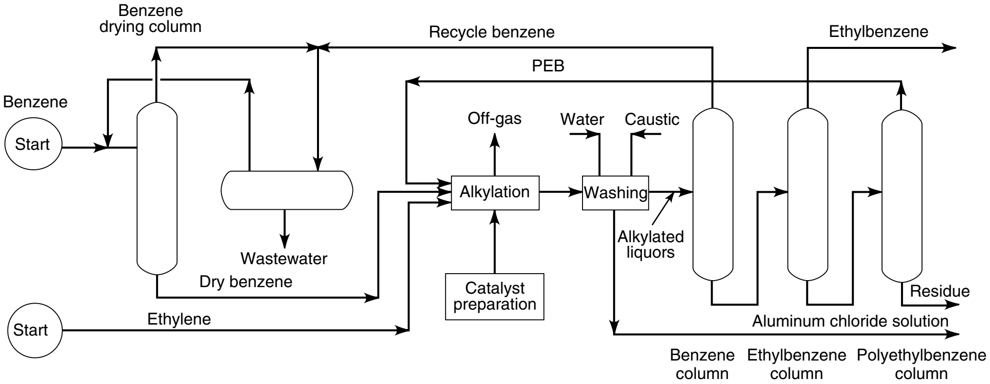

Fig. 3. Monsanto ethylbenzene process. Courtesy of *Hydrocarbon Processing*.

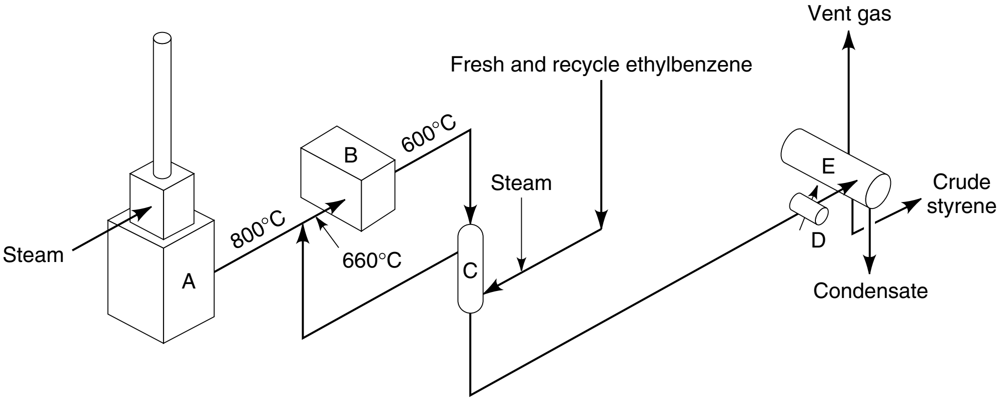

Fig. 4. Manufacture of styrene by adiabatic dehydrogenation of ethylbenzene: A, steam superheater; B, reactor section; C, feed–effluent exchanger; D, condenser; and E, settling drum. Courtesy of The Badger Company, Inc.

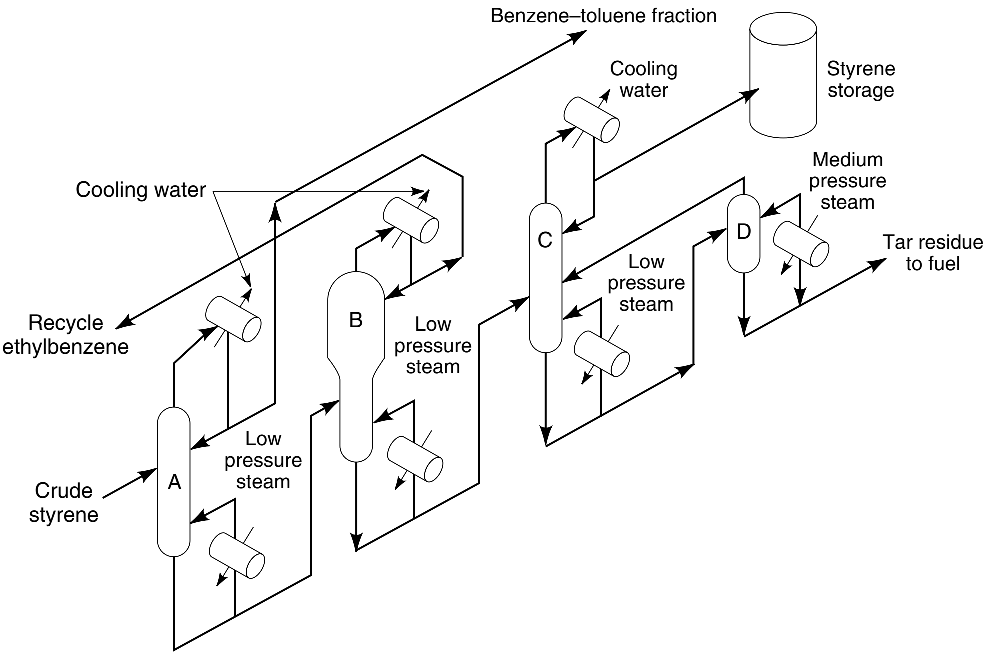

Fig. 5. Purification of styrene in the dehydrogenation reactor effluent in the FinaBadger styrene process: A, benzene–toluene column; B, ethylbenzene recycle column; C, styrene finishing column; and D, residue finishing. Courtesy of The Badger Company, Inc.

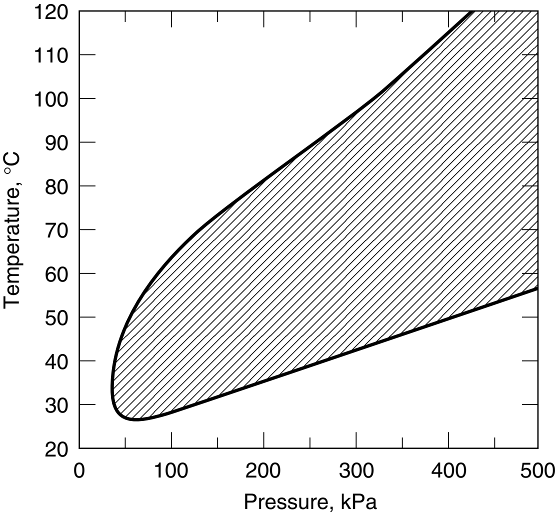

Fig. 6. Approximate explosive limits of styrene monomer vapor in equilibrium with liquid styrene in air, where ▨ represents the explosive region. To convert kPa to mm Hg, multiply by 7.5. Courtesy of the Dow Chemical Company.

Table 1. **Physical Properties of Styrene Monomer**[a]

Property			Value		
boiling point at 101.3 kPa = 1 atm, °C			145.0		
freezing point, °C			−30.6		
flash point (fire point), °C					
Tag open-cup			34.4 (34.4)		
Cleveland open-cup			31.4 (34.4)		
autoignition temperature, °C			490.0		
explosive limits in air, %			1.1–6.1		
vapor pressure, kPa, Antoine equation[b]			$\log_{10} P = 6.08201 - \frac{1445.58}{209.43 + t°\mathrm{C}}$		
critical pressure, P_c, MPa[c]			3.81		
critical temperature, t_c, °C			369.0		
critical volume, V_c, cm^3/g			3.55		
refractive index, $n^{20}{}_D$			1.5467		
	at 0°C	20°C	60°C	100°C	140°C
viscosity, mPa·s(=cP)	1.040	0.763	0.470	0.326	0.243
surface tension, mN/m (= dyn/cm)	31.80	30.86	29.01	27.15	25.30
density, g/cm^3[d]	0.9237	0.9059	0.8702	0.8346	
specific heat (liquid), J/(g·K)[e]	1.636	1.690	1.811	1.983	2.238
specific heat (vapor) at 25°C, C_p, J/(g·K)[e]			1.179		
latent heat of vaporization, ΔH_v, J/g[e]					
at 25°C			428.44		
145°C			354.34		
heat of combustion (gas at constant pressure) at 25°C, ΔH_c, kJ/mol[e]			4262.78		
heat of formation (liquid) at 25°C, ΔH_f, kJ/mol[e]			147.36		
heat of polymerization, kJ/mol[e]			74.48		
Q value			1.0		
e value			−0.8		
volumetric shrinkage upon polymerization, vol %			17.0		
cubical coefficient of expansion, $°C^{-1}$					
at 20°C			9.710×10^{-4}		
40°C			9.902×10^{-4}		
solubility (at 25°C), wt %					
monomer in H_2O			0.032		
H_2O in monomer			0.070		

[a] Ref. 1.

[b] To convert from $\log_{10} P_{kPa}$ to $\log_{10} P_{mmHg}$, add 0.8751 to the constant.

[c] To convert MPa to psi, multiply by 145.

[d] Density at 150°C is 0.7900 g/cm^3.

[e] To convert J to cal, divide by 4.184.

Table 2. **North American Producers of Styrene and Their Capacities, 2004**[a]

Producer	Location	Capacity, $\times 10^3$ t
United States		
BP	Texas City, Tex.	453
Chevron Philips Chemical	St. James, La.	952
Cos-Mar	Carville, La.	906
Dow Chemical	Freeport, Tex.	680
Lyondell Chemical	Channelview, Tex.	1246
Nova Chemicals	Bayport, Tex.	589
Sterling Chemicals	Texas City, Tex.	770
Westlake Styrene	Lake Charles, La.	159
Total U.S.		*5756*
Canada		
Nova	Sarnia, Ontario	431
Shell Canada	Scotford, Alberta	453
Total Canada		*884*
Mexico		
Petroleos, Mexicanos	Pemex	150
Grand Total		*6790*

[a] Ref. 59.

Table 3. **Specifications for Typical Polymerization-Grade Styrene Monomer Product**

Parameter	Specification[a]	Test method
purity	99.80[b]	chromatography
hydrocarbon impurities	2000	chromatography
color	10[c]	ASTM D1209
polymer	10	ASTM D2121
aldehydes (as benzaldehyde)	50	ASTM D2119
peroxides (as hydrogen peroxide)	30	ASTM D2340
TBC[d] (inhibitor)	10–50	ASTM D2120
chlorides (as chlorine)	1	ASTM D4929
sulfur	1	ASTM D2747

[a] Value shown is in ppm by wt max, unless otherwise specified.
[b] Wt % min.
[c] Pt–Co scale, max.
[d] 4-*tert*-Butylcatechol.

Table 4. **Acute Effects of Overexposure to Styrene**[a]

Area affected	Effect
eye	slight to moderate irritation
skin	slight irritation; repeated exposure may produce severe irritation including blistering
inhalation	may cause headache, nausea, dizziness, muscle weakness; produces central nervous system depression; irritates nose, throat, and lungs
ingestion	may cause nausea, headache, dizziness, muscle weakness; produces central nervous system depression, and diarrhea; may be aspirated into lungs if swallowed, resulting in pulmonary edema and chemical pneumonitis

[a] Ref. 63.

Table 5. **Physical Properties of a 60:40 Mixture of *m*- and *p*-Vinyltoluene**[a]

Property	Value
molecular weight	118.17
refractive index, n^{20}_{D}	1.5422
viscosity at 20°C, mPa·s(=cP)	0.837
surface tension at 20°C, mN/m (= dyn/cm)	31.66
density at 20°C, g/cm^3	0.8973
boiling point at 101.3 kPa (=1 atm), °C	172
freezing point, °C	−77
flash point (Cleveland open-cup), °C	60
fire point (Cleveland open-cup), °C	68.3
autoignition temperature, °C	575
explosive limits, % in air	1.9–6.1
vapor pressure, kPa[b]	
at 20°C	0.15
60°C	1.76
160°C	74.66
critical pressure, P_c, MPa[c]	4.19
critical temperature, t_c, °C	382
critical volume, V_c, mL/g	3.33
critical density, d_c, g/mL	0.30
specific heat of vapor, C_p, at 25°C, J/(g·K)[d]	1.2284
latent heat of vaporization, ΔH_v, J/g[d]	
at 25°C	426.10
boiling point	349.24
heat of combustion (ΔH_c), kJ/mol,[d] gas at constant pressure at 25°C	4816.54
heat of formation (ΔH_f), kJ/mol,[d] liquid at 25°C	115.48
heat of polymerization, kJ/mol[d]	$+66.9 \pm 0.2$
Q value	0.95
e value	−0.89
shrinkage upon polymerization, vol %	12.6
cubical coefficient of expansion at 20°C	9.361×10^{-4}
solubility, wt % in H_2O at 25°C	0.0089
H_2O in monomer at 25°C	0.47
solvent compatibility[e]	

[a] Ref. 1.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] To convert MPa to psi, multiply by 145.

[d] To convert J to cal, divide by 4.184.

[e] Infinitely soluble in acetone, carbon tetrachloride, benzene, diethyl ether, *n*-heptane, and ethanol.

Table 6. **Chemical Analysis of Commercial Vinyltoluene**[a]

Assay	ppm[b]
purity	99.6[c]
polymer	none
phenylacetylene	58
aldehydes as CHO	10
peroxides as H_2O_2	5
chlorides as Cl	5
TBC	12
m-vinyltoluene	60[c]
p-vinyltoluene	40[c]

[a] Ref. 1.

[b] Unless otherwise indicated.

[c] Percent.

Table 7. **Composition of Unrefined Product Obtained in the Manufacture of Ethyltoluene**

Compound	Wt %
benzene and lights	0.2
toluene	48.3
ethylbenzene and xylenes	1.2
p-ethyltoluene	11.9
m-ethyltoluene	19.3
o-ethyltoluene	3.8
polyethyltoluenes and other by-products	14.4
tar	0.9

Table 8. **Physical Properties of Two Divinylbenzene Mixtures**[a]

	Value	
Property	DVB-22[b]	DVB-55[b]
molecular weight	130.08	130.18
refractive index, $n^{25}{}_{\mathrm{D}}$	1.5326	1.5585
viscosity at 25°C, mPa·s(=cP)	0.883	1.007
surface tension at 25°C, mN/m (= dyn/cm)	30.55	32.10
density at 20°C, g/cm^3	0.8979	0.9126
boiling point, °C	180[c]	195[c]
freezing point, °C		−45
flash point (Cleveland open-cup), °C	57	74
fire point (Cleveland open-cup), °C	57	74
explosive limits, % in air	1.1–6.2	≥1.1[d]
critical pressure, P_c, MPa[e]	2.45[c]	2.45[c]
critical temperature, t_c, °C	348[c]	369[c]
latent heat of vaporization, ΔH_v, at boiling point, J/g[f]	320.49	350.62
solubility at 25°C, % in H_2O	0.0065	0.0052
H_2O in monomer at 25°C	0.051	0.054
solvent compatibility[g]		

[a] Ref.1 .

[b] Dow Chemical Co.'s designations for 22 and 55% divinylbenzene, respectively.

[c] Calculated.

[d] Could not be measured at 130°C.

[e] To convert MPa to psi, multiply by 145.

[f] To convert J to cal, divide by 4.184.

[g] Both types are infinitely soluble in acetone, carbon tetrachloride, benzene, and ethanol.

Table 9. **Chemical Analysis of Two Divinylbenzene Mixtures**[a]

	Value	
Assay	DVB-22	DVB-55
polymer, ppm	100	100
aldehydes as CHO, ppm	40	40
peroxides as H_2O_2, ppm	5	5
sulfur as S, ppm	20	230
TBC, ppm	1000	1000
total unsaturation[b]	83.3	149.4
divinylbenzene, %		
meta	17.1	36.4
para	8.2	18.6
total	25.3	55.0
ethylvinyltoluene, %		
meta	23.1	25.0
para	10.0	13.0

[a] Ref. 1.

[b] As ethylvinylbenzene.

Table 10. **Physical Properties of α-Methylstyrene**[a]

Property	Value
molecular weight	118.18
refractive index, $n^{20}{}_{D}$	1.53864
viscosity at 20°C, mPa·s(=cP)	0.940
surface tension at 20°C, mN/m (= dyn/cm)	32.40
density at 20°C, g/cm^3	0.9106
boiling point, °C	165
freezing point, °C	−23.2
flash point (Cleveland open-cup), °C	57.8
fire point (Cleveland open-cup), °C	57.8
explosive limits, % in air	0.7−3.4
vapor pressure, kPa[b]	
at 20°C	0.253
60°C	2.400
100°C	13.066
160°C	88.660
critical pressure, P_c, MPa[c]	4.36
critical temperature, t_c, °C	384
critical volume, V_c, mL/g	3.26
critical density, d_c, g/mL	0.29
specific heat of liquid, J/(g·K)[d]	
at 40°C	2.0460
100°C	2.1757
specific heat of vapor at 25°C, J/(g·K)[d]	1.2357
latent heat of vaporization, ΔH_v, J/g[d]	
at 25°C	404.55
boiling point	326.35
heat of combustion, ΔH_c, gas at constant pressure at 25°C, kJ/mol[d]	4863.73
heat of formation, ΔH_f, liquid at 25°C, kJ/mol[d]	112.97
heat of polymerization, kJ/mol[d]	39.75
Q value	0.76
e value	−1.17
cubical coefficient of expansion at 20°C	9.774×10^{-4}
solubility in H_2O at 25°C	0.056
H_2O in monomer at 25°C	0.010
solvent compatibility[e]	

[a] Ref. 1.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] To convert MPa to psi, multiply by 145.

[d] To convert J to cal, divide by 4.184.

[e] Infinitely soluble in acetone, carbon tetrachloride, benzene, diethyl ether, *n*-heptane, and ethanol.