

MANUFACTURING PROCESSES AND SELECTION¹

Many different techniques has been investigated for the manufacture of styrene monomer. Of these, the following methods have been used or seriously considered for commercial production:

1. dehydrogenation of ethyl benzene;
2. oxidation of ethyl benzene to ethyl benzene hydro peroxide, which reacts with propylene oxide, after which the alcohol is dehydrated to styrene
3. oxidative conversion of ethyl benzene to ∞ -phenyl ethanol via acetophenon and subsequent dehydration of alcohol
4. side-chain chlorination of ethyl benzene followed by dechlorination
5. side-chain chlorination of ethyl benzene ,hydrolysis to the corresponding alcohols, followed by dehydration
6. Pyrolysis of petroleum recovery from various petroleum processes.

The first two methods are only two commercially utilized routes to styrene production. Method 3 was practiced by Union-Carbide Corporation but later was replaced with a dehydrogenation process. Method 4 & 5, involving chlorine, have generally been suffered from high cost of the raw materials and from the chlorinated contaminants in the monomer. Manufacture of styrene directly from petroleum streams is difficult and costly.

The two commercially important routes to styrene are based on ethyl benzene production by alkylation of benzene and ethylene .Research programs aimed at replacing expensive benzene and ethylene feed stocks with less costly alternatives have been carried out by a number of companies.

PROCESS DESCRIPTION¹

OXIDATION PROCESS

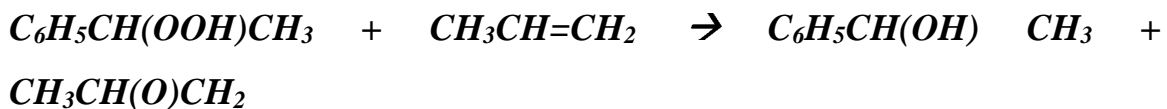
One of the most notable oxidation processes is Halcon international's process to produce styrene from propylene oxide. In this technique, ethyl benzene is oxidized to hydro peroxide as follows:



The reaction takes place in the liquid phase with air bubbling through the liquid, and no catalyst is required. However, since hydro peroxides are unstable compounds, exposure to high temperature must be minimized to reduce the rate of decomposition. Fewer by-products are formed from the decomposition if the reaction temperature is gradually reduced during the course of reaction, i.e., from 135-160⁰C during the first half of reaction to 125-155⁰C during the second half.

The reaction is more selective to the production of by-product acids, when it is carried out at constant temperature than when the temperature is gradually reduced. In practice, the temperature is reduced by means of a series of reactors, each of which is maintained at a progressively lower temperature. The pressure required for the reaction is not critical; 800-1500 kPa is sufficient to maintain the reactants at liquid phase.

Reaction is given below:



Catalysts for this reaction are compounds of metals, e.g. molybdenum, tungsten, vanadium. The epoxidation reaction generally proceeds at 100-130⁰C in the liquid phase under self-generated pressures. The conversion of ethyl benzene hydro peroxide is nearly complete, and selectivity of the reaction in producing propylene oxide is

greater than 70%. The alcohol can be dehydrated to styrene or it is reduced to ethyl benzene for recycle if styrene is not desired.

Montoro, a Spanish joint venture between Oxirane and Enpetrol, first commercializes the process in 1973. The plant had an annual capacity of 7.5×10^4 ton of styrene and 3×10^4 ton of propylene oxide. The Oxirane plant in Channelview, Texas, set up in 1977 had a capacity of 2.25×10^5 ton annual production.

DEHYDROGENATION OF ETHYL-BENZENE

REACTION:



Several licensed processes are available for the conversion of ethyl-benzene to styrene. Although all such processes share the catalytic dehydrogenation of ethyl benzene to styrene in the presence of steam, there are two distinct approaches to the reaction section design: the adiabatic process and the isothermal process. As the dehydrogenation reaction is endothermic, requiring 1.26-1.33 MJ/kg of ethyl benzene converted at 25⁰C, heat must be supplied. In the adiabatic process, steam superheated to 800-950⁰C is mixed with preheated ethyl benzene (EB) feed prior to exposure to the catalyst. The isothermal process takes place in PFR and reaction heat is provided by indirect heat exchange between the process fluid and a suitable heat transfer medium, e.g., flue gas (BASF technology).

For a given dehydrogenation catalyst, the catalyst life, the molar conversion of ethyl benzene, and the molar selectivity of ethyl benzene to styrene are effected by reactor operating pressure, molar steam to hydrocarbon ratio, reactor operating temp. and reactor liquid hourly space velocity (LHSV). For all catalysts, there is a compromise between activity, otherwise EB conversion, and styrene selectivity.

Because the dehydrogenation reaction produces 2 moles of products otherwise styrene & Hydrogen, for every mole of reactant, i.e., EB, the desired reaction course can be enhanced by adding steam to the reactor system to reduce the styrene partial pressure in the reactor and /or by reducing the reactor operating pressure.

As these increase conversion or other refinements and approaches equilibrium, the rate of the main reaction slows down but the rates of undesired side reactions do not. Adiabatic operating pressures were generally about 138 kPa with molar steam to hydrocarbon ratio above 14:1. For the isothermal reactor designs, it is maintained at 6-8:1.

Since the reaction is endothermic with increase in temperature, conversion also increases. However, an upper limit to reactor temp; when temp are increased above 610⁰C, thermal cracking of EB & styrene occurs, since in isothermal process the temp maintained at 580-610⁰C across the catalyst bed, where in adiabatic reactor the feed mixture generally introduced at 660-610⁰C. Decreasing the residence time in the adiabatic process reduces the potential selectivity over isothermal process.

As for LHSV, molar conversion of EB is an inverse function of this parameter since higher velocities mean lower residence time. This in turn reduces molar conversion. For adiabatic reactors designed LHSVs of .4-.6 m³/hr EB per cubic meter of catalyst. Within this range, a 60-70% molar conversion of EB and a 90-95% molar selectivity of EB to styrene can be achieved with commercially available dehydrogenation. It is believed that similar results are obtained with the isothermal process.

The main difference between the isothermal and adiabatic processes is in the way the endothermic reaction heat is supplied. In principle, the isothermal reactor is designed like a shell& tube H.E.: a fixed bed dehydrogenation catalyst and reactant gas is on the tube side, & a suitable heat transfer medium is on the shell side. The diameter of the self-contained reactor tubes are 10-20 cm and the lengths are 2.4-3.7m. All commercial catalysts are formulated around an iron oxide base inherent to this ferric compound is the reduction to lower oxides at the dehydrogenation reaction temperature. The most widely used additives are chromic oxide as the stabilizer and

potassium oxide as the coke retardants. Thus, the catalyst is self-regenerative, there by allowing such residues to built up to an equilibrium level.

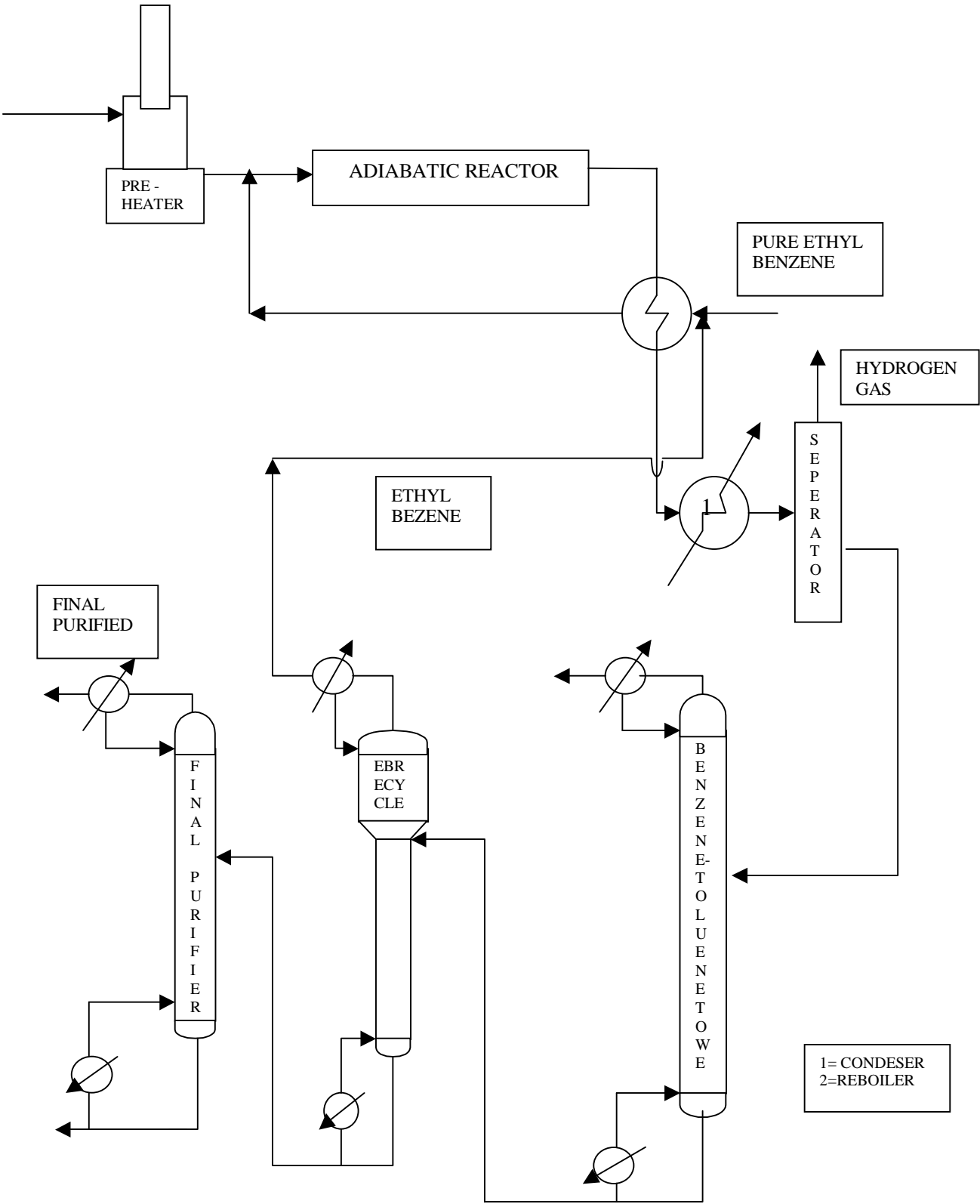
One difference between licensed adiabatic technologies is in the configuration of the dehydrogenation reactor, e.g., instead of a radial-flow reactor, a fixed-bed axial reactor may be employed. Another difference in technologies is in the reactor feed heat exchanger section. Instead of only steam passing through a fired heater, all of the EB and vaporization/dilution is combined with the mixture is raised to the reaction temp in a fired heater. Although similar in concept, the process involves heating the steam and EB in separate coils of a fired heater. As temperatures well above 850 °C may be encountered with both processes, the potential for thermal cracking of EB is increased. Therefore, the residence time in heater should be minimized.

PURIFICATION

To obtain the desired product, crude styrene effluent from the reaction section must be fractionated and undesirable by-products are removed. To minimize the polymerization of vinyl aromatic compounds, low temp vacuum distillation of the crude styrene is necessary. Further reduction in polymerization is obtained by employing inhibitors. Inhibitors were used as extensively polymerization reductant. The main nonsulfur inhibitors are nitrogen-substituted aromatics, e.g., nitro-phenols. The most commonly used commercial inhibitor for this service 4-tert-butylcetahol. The entire purification section is composed of three vacuum fractionators in series. In the first column benzene& toluene impurities are been separated from the crude styrene. The next column is EB recycle column, here unreacted EB been recovered and fed back to the reactor. The separation of EB from styrene is difficult because they have a very close boiling point. High efficiency, low-pressure distillation column are used. However, extensive effort is being made to commercialize the use of packing for this purpose. Such approach offers significant reduction in pressure drop.

The bottom stream from the EB recycle stream is been fed to the final styrene purification column. The feed stream to the final purification column contains EB at a concentration of 1000 ppm. High purity product of styrene is obtained as the distillate and send to storage.

FLOW SHEET OF THE STYRENE PLANT



HEALTH AND SAFETY¹

Styrene is mildly toxic and inflammable, and it can polymerize violently under specific conditions. However, none of the hazards associated with styrene is severe, and it is considered a relatively safe organic chemical when handled according to appropriate safeguards.

Styrene has an odor threshold of .05-.15 ppmv. Both liquid and vapor irritate the eye and respiratory system, and high vapor concentration results in depression of central nervous system.

Irritation of eye and respiratory tract occurs at 400-500 ppmv, but does not result in permanent injury. Test animals for one hr serious systematic effects can tolerate concentration up to 2500 ppmv. Exposure for 30-40 min to a conc. of 10000 ppmv may be fatal.

Styrene is low in oral toxicity. Contact with eyes is painful, but results in transient damage. Short term contact with skin, do not cause irritation; however prolonged contact may cause swelling, blistering. However, styrene as it is commonly stored and transported contains TBC, which is skin sensitizer. Styrene monomer is flammable and can form explosive mixture with air at atmospheric ambient condition. It is generally suggested to store & handle styrene below or at atmospheric temp.

Polymerization of styrene is an exothermic reaction and proceeds slowly at room temperature. Thus, there is potential for a runaway polymerization reaction, which may result in an accelerating evolution of styrene vapor that may cause fire or rupture in the confining vessel. The polymerization reaction is generally prevented by adding TBC inhibitor.

Effective inhibition of polymerization by TBC occurs in presence of dissolved oxygen, and so storage in an atmosphere-permeable tank is preferred, where inert gas blanketing of the stored material is to be done. Periodic air addition is recommended to maintain the presence of dissolved oxygen.

For the areas, where, average temperature is over 27° C, additional refrigeration is required.

MEASURES:

- The efficiency of the, condenser should must be properly justified, so that there be minimum loss of styrene in the atmosphere.
- The reactor is generally made adiabatic, and the reaction is endothermic. The heat of reaction is generally supplied by adding steam at 800° C. This steam is then condensed and separated as an aqueous solution, saturated with different organic chemical. To maintain the proper industrial economy, this condensate must be treated and recycled back at maximum possible limit.
- The heavy end from the final column, contain styrene polymers and some styrene derivatives, which have good economical values. However, disposal of this heavy end causes problem. So by adopting proper separation method it is desired to separate those components of high economical values.
- In order to prevent the chance polymerization, final treatments are generally carried out under reduced temperature and low pressure.