

## VARIOUS COMMERCIAL PROCESS

### PRODUCTION

Currently, the primary source of ethyl benzene is the alkylation of benzene with ethylene. The only other source, the superfractionation of mixed C<sub>8</sub> aromatic streams, supplies only a small portion of the ethyl benzene produced. Two distinct types of ethylbenzene alkylation processes are currently used commercially: liquid-phase alkylation and vapor-phase alkylation.

### PRODUCTION BY LIQUID PHASE ALKYLATION:

Liquid phase aluminum chloride processes have been the dominant source of ethylbenzene since the 1930s. Several companies have developed variations of this technology. Processes currently in use include those of Dow chemical, BASF, shell chemical, Monsanto, *societe chimique des cahrbonnages*, and union carbide/ badger. The Monsanto process is currently the most modern commercially licensed aluminum chloride alkylation technology.

Alkylation of benzene with in the presence of an aluminum chloride catalyst complex is exothermic ( $\Delta H = -114$  kJ/mol); the reaction is very fast and produces almost stoichiometric yields of ethylbenzene. In addition to AlCl<sub>3</sub>, a wide range of Lewis acid catalysts, including AlBr<sub>3</sub>, FeCl<sub>3</sub>, and BF<sub>3</sub>, have been used. Aluminum chloride processes generally use ethyl chloride or hydrogen chloride as a catalyst promoter. These halide promoters reduce the amount of AlCl<sub>3</sub> required. The reaction mechanism has been studied in detail [5].

**Alkylation:** In the conventional AlCl<sub>3</sub> process (see Fig 1), three phases are present in the reactor. Aromatic liquid, ethylene gas, and a liquid catalyst complex phase (a reddish-brown material called red oil). A mixture of catalyst complex, dry benzene, and recycled polyalkylbenzenes is continuously fed to the reactor and agitated to disperse the catalyst complex phase in the aromatic phase. Ethylene and the catalyst promoter are injected into the reaction mixture through spargers, and essentially 100% of the ethylene is converted. Low ethylene: Benzene ratios are used to give optimum overall yield of ethylbenzene. Commercial plants typically operate at ethylene: because molar ratios of ca.0.3-0.35. As the ratio is increased, more side reactions, such as transalkylation and

isomeric rearrangement, occur. Further alkylation of ethylbenzene leads to the reversible formation of lower molecular mass polyalkylbenzenes. The loss in net yield due to residue is minimized by recycling this material to the alkylation reactor. In addition, because the reaction occurs close to thermodynamic equilibrium, the traditional processes use a single reactor to alkylate benzene and transalkylate polyalkylbenzenes.

The reaction temperature is generally limited to 130°C; a higher temperature rapidly deactivates the catalyst and favors formation of non aromatics and polyalkylbenzenes, which are preferential absorbed by the highly acidic catalyst complex, resulting in byproduct formation. Sufficient pressure is maintained to keep the reactants in the liquid phase. High -alloy materials of construction are also required for the piping and handling systems.

The liquid reactor effluent is cooled and discharged into a settler, where the heavy catalyst phase is decanted from the organic liquid phase and recycled. The organic phase is washed with water and caustic to remove dissolved AlCl<sub>3</sub> and promoter. The aqueous phase from these treatment steps is first neutralized and then recovered as a saturated aluminum chloride solution and wet aluminum hydroxide sludge.

Removal of dissolved catalyst from the catalyst from the organic stream has long been a problem for ethylbenzene producers. Recently CdF chime found that more complete recovery of AlCl<sub>3</sub> could be achieved by first contacting the organic phase with ammonia instead of sodium hydroxide.

**Separation:** Purification of the ethylbenzene product is usually accomplished in a series of three distillation columns. The unreacted benzene is recovered by the first columns as an overhead distillate. The second column separates the ethylbenzene product from the heavier polyalkylated components. The bottoms product of the second column is fed to a final column, where the recyclable polyalkylbenzenes are stripped from non recyclable high molecular mass residue compounds. The residue or flux oil, consisting primarily of polycyclic aromatics, is burned as fuel.

Because the alkylation mixture can tolerate only minor amounts of water, the recycled benzene and fresh benzene must be dried thoroughly prior to entering the reactor. Water not only increases corrosion, but also decreases catalyst activity. Benzene dehydration is accomplished in a separate column.

The improved Monsanto process (see fig 2) has distinct advantages compared to conventional  $\text{AlCl}_3$  processes. The most important of these is a significant reduction in the  $\text{AlCl}_3$  catalyst use, thus lessening the problem of waste catalyst disposal. Monsanto found that by an increase in temperature and by careful control of ethylene addition, the required  $\text{AlCl}_3$  concentration could be reduced to the solubility limit, thereby eliminating the separate catalyst complex phase.[7]. Therefore, alkylation occurs in a single homogeneous liquid phase instead of the two liquid phases in earlier processes. Monsanto claims that a separate catalyst complex phase may actually prevent the attainment of maximum reactor yields. With a few exceptions, the flow scheme of the Monsanto process is nearly the same as that of more traditional processes. The process is also capable of operating with low-concentration ethylene feed. The process is also capable of operating with low concentration ethylene feed. Typically, the alkylation temperature is maintained at 160-180<sup>0</sup>C. This higher operating temperature enhances catalyst activity, with the additional benefit that the heat of reaction can be recovered as low-pressure steam. Whereas the traditional process accomplishes alkylation and transalkylation in a single reactor, the homogeneous catalyst system must employ a separate transalkylation reactor. At lower catalyst concentrations, the recycle of substantial amounts of polyalkylbenzenes terminates the alkylation reaction. Therefore, only dry benzene, ethylene, and catalyst are fed to the alkylation reactor. The recycle polyethylbenzene stream is mixed with the alkylation reactor effluent prior to entering the transalkylation reactor. The transalkylation reactor is operated at much lower temperature than the primary alkylation reactor.

After transalkylation, the reaction products are washed and neutralized to remove residual  $\text{AlCl}_3$ . With the homogeneous process, all of the catalyst remains in solution. The catalyst-free organic reaction mixture is then purified using the sequence described previously for the conventional  $\text{AlCl}_3$  process. As with other  $\text{AlCl}_3$  process, the organic residue is used as fuel and the aluminum chloride waste streams are usually sold, or sent to treatment facilities.

## **PRODUCTION BY VAPOR-PHASE ALKYLATION:**

Vapor-phase alkylation has been practiced since the early 1940s, but at that time processes were unable to compete with liquid-phase aluminum chloride based technology. The alkar process developed by UOP, based on boron trifluoride catalyst, had modest success in the 1960s, but fell from favor because of high maintenance costs resulting from the severe corrosion caused by small quantities of water. Nevertheless, some ethylbenzene units continue to use this process.

The *Mobil –badger* ethylbenzene process represents the latest and most successful vapor phase technology to be introduced. The process was developed in the 1970s around Mobil's versatile ZSM-5 synthetic zeolite catalyst. Earlier attempts at using zeolite or molecular sieves for benzene alkylation had suffered from rapid catalyst deactivation because of coke formation and poor transalkylation capabilities. The Mobil catalyst combines superior resistance to coke formation with high catalytic activity for both alkylation and transalkylation by American Hoechst Corp. at their  $408 \times 10^3$  t/a Bayport, Texas plant. Currently nine commercial plants have been licensed, representing ca.  $3 \times 10^{10}$  t/a of production capacity.

**ALKAR PROCESS:** This process produces a high purity ethylbenzene product and can use dilute ethylene feed stock. If the entry of water into the process is strictly prevented, the corrosion problems associated with aluminum chloride processors are avoided. However, even small amounts of water (<1mg/kg) hydrate the BF<sub>3</sub> catalyst.

The alkylation reaction takes place at high pressure (2.5-3.5 Mpa; 25-35 bar) and low temperature (100-150°C). Dehydrated benzene, ethylene, and make up BF<sub>3</sub> catalysts are fed to the reactor. Typically, ethylene; benzene molar ratios between 0.15 and 0.2 are used. The reactor inlet temperature is controlled by recycling a small portion of the reactor effluent.

Transalkylation takes place in a separate reactor. Dry benzene, BF<sub>3</sub> catalyst, and recycled polyethylbenzene are fed to the transalkylation reactor. The effluent streams from the two reactors are combined and passed to a benzene recovery column, where benzene is separated for recycle to the reactors. Boron trifluoride and light hydrocarbons are taken over head as a vapor stream from which the BF<sub>3</sub> is recovered for recycle. The bottom for the benzene recovery column is sent to a product column, where ethylbenzene of > 99.9%

purity is taken overhead. A final column serves to recover polyethylenbenzenes for recycle to the transalkylation reactor.

The alkar process can operate with ethylene feed containing as low as 8-10 mol% ethylene, enabling a variety of refinery and coke-oven gas streams to be used. However, purification of these streams is necessary to remove components that poison the  $\text{BF}_3$  catalyst, e.g., trace amounts of water sulfur compound, and oxygenates.

**MOBIL-BADGER PROCESS:** The fixed –bed ZSM-5 catalyst promotes the same overall alkylation chemistry as those used in the other processes; however, the reaction mechanism is different. Ethylene molecules are adsorbed onto the Bronsted acid sites within the catalyst, which activates the ethylene molecule and allows bonding with benzene molecules to occur. Hence, the range of higher alkylated aromatic byproducts formed by the Mobil – Badger process is some what different than that for the Friedel Crafts processes. These components do not affect the ethylbenzene product purity and are recycled to the reactor for transalkylation or dealkylation.

The Mobil-Badger heterogeneous catalyst system offers several advantages when compared to the other commercially available processes. The most important are that it is noncorrosive and nonpolluting. The catalyst is essentially silica – alumina, which is environmentally inert. Because no aqueous waste streams are produced by the process, the equipment for waste treatment and for catalyst recovery is eliminated. In addition, carbon steel is the primary material of construction, high-alloy materials and brick linings are not required.

The reactor typically operates at 400-450<sup>0</sup>C and 2-3 Mpa (20-30 bar). At this temperature >99% of the net process heat input and exothermic heat of reaction can be recovered as steam. The reaction section includes two parallel multibed reactors, a fired heater, and heat recovery equipment. The high-activity catalyst allows transalkylation and alkylation to occur simultaneously in a single reactor.

Because the catalyst slowly deactivates as a result of coke formation and requires periodic regeneration, two reactors are included to allow uninterrupted production: one is on stream while the other is regenerated. Regeneration takes ca. 36h and is necessary

after 6-8 weeks of operation. The catalyst is less sensitive to water, sulfur, and other poisons than the Lewis acid catalysts.

The reactor effluent passes to the purification section as a hot vapor. This steam is used as the heat source for the first distillation column, which recovers the bulk of the unreacted benzene for recycle to the reactor. The remaining benzene is recovered from a second distillation column. The ethylbenzene product is taken as the overhead product from the third column. The bottoms product from this column is sent to the last column, where the recyclable alkylbenzenes and polyalkylbenzenes are separated from heavy nonrecyclable residue. The low-viscosity residue stream, consisting mainly of diphenylmethane and diphenylethane, is burned as fuel.

The Mobil-Badger process also can use dispute ethylene feedstocks. In semi commercial applications, the process has operated on streams containing as little as 15 mol% ethylene.