Report Abstract

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1 INTRODUCTION

Bisphenol A (BPA) is the basic monomer for the production of two major polymers: epoxy resins and polycarbonates. As such, it is the fastest growing end use of phenol and acetone. The two aromatic rings joined together by a propyl group lend strength and toughness to materials made from BPA; properties that both epoxy resins and polycarbonates are well known for.

2 TECHNOLOGY

Bisphenol A (BPA) is prepared by the reaction of one mole of acetone and two moles of phenol to give primarily the para, para’-condensation product, para, para’-isopropylidene-diphenol:

The first step in the acid catalyzed reaction consists of the reaction of acetone and the strong acid to form a carbonium ion. This carbonium ion adds one mole of phenol and subsequently forms a second carbonium ion. The second carbonium ion eliminates a mole of water and then reacts with a second mole of phenol to form BPA. The heat of reaction for reactants and products in their usual physical states at 25°C is calculated from heats of formation as 18.4 kilocalories per mol of BPA. The major by-products are the ortho, para-isomer, and to a lesser extent the ortho, ortho’-isomer. Reaction of BPA already formed with the tertiary carbonium ion intermediate gives a higher phenol containing three aromatic rings, called trisphenol or BPX.

Strong mineral acids such as hydrochloric or sulfuric can be used as catalysts. Hydrochloric acid is much preferred due to its lower boiling point and relative ease of removal from the reaction mixture. Instead of strong mineral acids, strongly acidic cation exchange resins such as the styrene/divinyl benzene type can be used with or without activity enhancing modifiers. Resin catalysts eliminate catalyst recycle and greatly mitigate equipment corrosion and wastewater treatment problems. To compensate for any activity deficit, reaction temperatures with resin catalysts can be increased to 70 to 80°C, compared to 50°C with concentrated aqueous or gaseous dry HCl catalyst.

Crude reaction mixtures of phenol and acetone, made from the cumene hydroperoxide process for phenol production and acetone by-product, can be used to make BPA. Since 0.62 pound of acetone is made per pound of phenol in the cumene hydroperoxide phenol process and 0.26 pound of acetone is used per pound of phenol in bisphenol A production, the mixture must be depleted in acetone by distillation or enriched in phenol by addition to adjust to the desired ratio for BPA synthesis.
2.1 Dow Ion Exchange Resin Catalyzed Process

Dow initially developed a BPA technology in the 1960s for use in the production of epoxy resins. The first BPA production was located in Midland, Michigan. Dow’s continuing process development and improvements during the late 1960s led to a new technology based on proprietary cation exchange resin catalysts to produce a polycarbonate-grade BPA product. In 1972, Dow started up their first commercial plant based on this new resin-based technology at Freeport, Texas. Since then, Dow has continued to improve the technology, especially in the areas of product quality, higher operating efficiency, and reduced capital cost. At present, Dow is one of the world’s leading producers of BPA with a total production capacity of 370 thousand metric tons per year in four plants located in Texas, U.S. and Stade, Germany.

The first license to a Dow BPA technology was granted to Nan Ya Plastics Corporation, who selected Dow's Generation I technology for its 90,700 metric tons per year grassroots BPA plant at Mailiao, Taiwan. The plant was brought on-stream early in 1999 and expanded to 100 thousand metric tons per year in 2005.

Dow has continued to improve its BPA process and has successfully demonstrated its High-Purity Bisphenol-A Generation II process at its Stade site.

The Bisphenol A reaction is catalyzed by a DOWEX® cation exchange resin. The catalyst is batch-promoted via a proprietary system to achieve the proper selectivity to the \textit{para, para} isomer. The reaction is carried out in a significant excess of phenol and the reactors run adiabatically.

The process minimizes the formation of rearrangeable and non-rearrangeable by-products. By utilizing a process recycle stream, the rearrangeable impurities reach equilibrium such that the reaction of phenol and acetone primarily produces high-purity \textit{p,p}-bisphenol.

The plant has multiple fixed bed reactors. When a reactor's catalyst activity becomes too low that reactor is taken off-line; the spent catalyst is removed and replaced with a unique DOWEX® catalyst before the reactor is brought back on-line. One reactor is typically on standby after having its spent catalyst replaced.

3 ECONOMICS

Two cases have been considered for the production of bisphenol A at a capacity of 220 million pounds per year, but different catalysts, under a consistent U.S. Gulf Coast first quarter 2007 price scenario.

Furthermore, production cost estimates have been generated for the production of phenol since it is the raw material used in the production of bisphenol A. It is assumed in all cases that phenol is available over the fence at a price that reflects cost of production plus ten percent return on investment.
The selected cases are:

- Bisphenol A (U.S. Gulf Coast, HCl catalyst)
- Bisphenol A (U.S. Gulf Coast, Dow High-Purity BPA Generation II Process, ion exchange resin catalyst)

Our cost analysis finds the following:

- Net raw material costs are essentially the same for both processes.
- The ion-exchange catalyst process has a lower utility cost.
- Investment related expenses such as maintenance, insurance, property taxes, and general plant overhead (partial dependence) are lower for the ion exchange resin catalyzed process.

4 HEALTH AND SAFETY CONCERNS

At the beginning of the year, the European Food Safety Authority (EFSA) stated that infants’ and children’s BPA exposure was below the new tolerable daily intake (TDI) of 5 milligrams per kg body weight per day. However, based on new data EFSA will increase the TDI from 5 micrograms per kg body weight per day to 50 micrograms per kg body weight per day that will reflect the change of the uncertainty factor needed to translate the “no observed adverse effect level” (NOAEL) standard to a TDI level.

In May 2007, the European Parliament recommended 28 additional substances (including BPA) be put on a list of pollutants that should be limited in surface water in order to reach a “good chemical status.”

In the United States, debates are ongoing over the safety and/or risks of the use of bisphenol A. California, Maryland, Massachusetts and Maine have introduced legislation involving the ban of BPA in children’s products while in San Francisco, the ban on BPA has been put on hold. In May 2007, San Francisco withdrew BPA’s limits from the ban, making phthalates the only chemicals applicable to the “Toxic Toy Law”. The city will reassess the restrictions to BPA in 2008.

California is now considering three bills that will ban many kinds of plastics in packaging products therefore reducing marine litter in California’s oceans. One of the bills (approved by California’s Senate and now before the Assembly) is the Toxic Free Oceans Act of 2007. The bill will ban companies from manufacturing, processing or distributing plastics packing products (in sizes between 8 ounces up to 5 gallons) that contain not just BPA but also several other chemicals such as vinyl chloride, styrene, perfluorooctanoic acid, nonylphenol, and alkylphenol. Several industry representatives claimed that the plastic bans are not sustained by science and that they disregard health concerns shown by the public.

As of June 2007, bans on bisphenol A (BPA) in San Francisco, California, Maryland, and Minnesota where either lifted, withdrawn, or didn’t pass. These same decisions are expected to follow in other bans involving BPA in other cities (i.e., Massachusetts) of the United States.
The latest controversy between studies can be found on the reports issued by scientists that participated in a BPA workshop in Chapel Hill, NC (organized by the National Institute of Environmental Health Sciences (NIEHS)) and the Center for the Evaluation of Risks to Human Reproduction (CERHR). The NIEHS found that low doses on BPA in rodents caused breast cancer, hypospadias, type 2 diabetes, enlarged prostates, reduced sperm counts, early onset of puberty in females, and adverse neurological effects. On the other hand, the CERHR panel concluded that it has “minimal concern” that BPA exposure can cause enlarged prostates or accelerates puberty, “some concern” that prenatal BPA exposure can affect brain development and “negligible concern” on reproductive tract abnormalities as a result of humans exposed prenatally to BPA. The conclusions of these two government panels will be evaluated by the FDA (according to the deputy director “FDA absolutely still considers BPA safe for uses in food containers”) and the NTP (who is in the last stage of the BPA hazard assessment).

5 COMMERCIAL ANALYSIS

The major demand for bisphenol A is in polycarbonates and epoxies, shown in Figure 1.

Figure 1 United States Bisphenol A Demand by End Use, 2006

Polycarbonate is one of the largest volume engineering thermoplastics and has enjoyed strong demand growth reflecting its combination of technical performance characteristics. The strongest growth in end use for polycarbonate is expected in the optical storage media sector (i.e., recordable CDs and DVDs). The second most significant application is in the electrical and electronics industries. Polycarbonate is also an attractive option for construction, packing, car headlamp lenses, and domestic appliance housings. In the medical field, polycarbonate is used in dialysers and blood oxygenators.
Bisphenol A used in epoxy resin production is expected to grow more slowly than polycarbonate. Demand is more heavily focused on coatings than in other areas, and less reliant on construction applications. Demand for coatings and adhesives in the automotive sector is expected to continue to grow. The electronics manufacturing sector in the United States is not expected to be a major growth driver for epoxy demand.

Other uses for bisphenol A include polysulfone resins, polyarylate resins, specialty phenolic resins, polyetherimide resins, unsaturated polyester resins, tetrabromobisphenol A flame retardants, and stabilizers for various polymers.

Capacity, supply/demand and trade forecasts out to 2012 for the United States, Western Europe and Japan are provided.