

KIRK-OTHMER

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## PHTHALIC ACIDS AND OTHER BENZENEPOLYCAR- BOXYLIC ACIDS

This article discusses the benzenepolycarboxylic acids, their anhydrides, and their esters. Table 1 includes IUPAC nomenclature, common names, and CAS Registry Numbers for the benzenepolycarboxylic acids. These acids and anhydrides are highly stable. The carboxylic acid groups provide from two to six sites for reaction for a wide variety of products, mostly polymers and plasticizers.

Phthalic anhydride (1) is the commercial form of phthalic acid (2). The worldwide production capacity for the anhydride was ca  $3.5 \times 10^6$  metric tons in 1993, and it was used in the manufacture of plasticizers (qv), unsaturated polyesters, and alkyd resins (qv) (see POLYESTERS, UNSATURATED). Sales of terephthalic acid (3) and its dimethyl ester are by far the largest of any of the benzenepolycarboxylic acids;  $14.3 \times 10^6$  t were produced in 1993. This is 80% of the total tonnage of all commercial forms of the benzenepolycarboxylic acids.

**Technical-Grade Terephthalic Acid.** All technical-grade terephthalic acid is produced by catalytic, liquid-phase air oxidation of *p*-xylene. Several processes have been developed, but they all use acetic acid as a solvent and a multivalent heavy metal or metals as catalysts. Cobalt is always used. In the most popular process, cobalt and manganese are the multivalent heavy-metal catalysts and bromine is the renewable source for free radicals (51,52). This catalyst system is used in about 70% of the *p*-xylene oxidations, and the percentage is increasing as new plants almost invariably employ it. Process conditions are highly corrosive owing to the acetic acid and bromine, and titanium must be used in contact with some parts of the process.

Figure 2 is a typical flow sheet for the process using technology originally developed and licensed by Amoco and Mitsui Petrochemical. Acetic acid, air, *p*-xylene, and catalyst are fed continuously into an oxidation reactor that is maintained at 175–225°C and 1500–3000 kPa (~15–30 atm). Air is added in amounts in excess of stoichiometric requirements to minimize formation of by-products. The oxidation is exothermic to the extent of  $2 \times 10^8$  J/kg of *p*-xylene reacted, and this heat is removed by allowing the acetic acid solvent to boil. The vapor is condensed and refluxed to the reactor, and this sets the temperature–pressure relationship. The condensing vapor is used to generate steam, which is employed as a heat source in other parts of the process. Two moles of water are formed per mole of *p*-xylene reacted. The residence time is 30 min–2 h depending on the process. More than 98% of the *p*-xylene is converted and the yield to terephthalic acid is at least 95 mol % in modern plants. Further, this is on a once-through basis. The near exclusive selection of this technology for all new capacity follows from these yield and conversion values.

The effluent from the reactor is a slurry of terephthalic acid because it dissolves to a limited extent in almost all solvents, including the acetic acid–water solvent used here. This slurry passes through a surge vessel that operates at a lower pressure than the reactor. More terephthalic acid crystallizes and the slurry is then ready to be processed at close to atmospheric conditions. The terephthalic acid crystals are recovered by filtration, washed, dried, and conveyed to storage, from which they are in turn fed to the purification step.

This is called a technical or crude grade of terephthalic acid, but the purity is typically greater than 99%. It is not, however, pure enough for the poly(ethylene terephthalate) made from it to reach the required degree of polymerization. The main impurity is 4-formylbenzoic acid [619-66-9], which is incompletely oxidized *p*-xylene and is monofunctional with regard to esterification. 4-Formylbenzoic acid is usually referred to as 4-carboxybenzaldehyde (4-CBA) in the industry.

Water formed in the reaction as well as some undesirable by-products must be removed from the acetic acid solvent. Therefore, mother liquor from the filter is purified in a residue still to remove heavies, and in a dehydration tower to remove water. The purified acetic acid from the bottom of the dehydration tower is recycled to the reactor. The water overhead is sent to waste treatment, and the residue still bottoms can be processed for catalyst recovery. Alternatively, some mother liquor from the filter can be recycled directly to the reactor.

Cleanup of waste streams from the process has been highly developed and is widely practiced commercially. The nitrogen and unused oxygen from the