TEREPALIC ACID (TPA) & DIMETHYL TerePHTHALATE (DMT):

- Purified terephthalic acid (TPA) and dimethyl terephthalate (DMT) are used as raw materials for the production of saturated polyesters.
- Terephthalic acid, produced in technical or crude grades are not pure enough for manufacture of poly(ethylene terephthalate) [PET]. In almost all cases, the technical-grade material is immediately converted to purified terephthalic acid or dimethyl terephthalate, which together are the articles of commerce.
- Terephthalic acid and dimethyl terephthalate did not become large-volume industrial chemicals until after World War II.
- Imperial Chemical Industries in the United Kingdom in 1949 and Du Pont in the United States in 1953 commercialized fibers made from PET. Dimethyl terephthalate and ethylene glycol were the comonomers used by both companies. Initial production of the dimethyl terephthalate started with the oxidation of p-xylene to terephthalic acid using nitric acid; both companies reportedly used similar technology.
- Purified terephthalic acid became commercially available from Amoco Chemical Co. in 1965, by which time a considerable polyester industry based on dimethyl terephthalate had already developed. The Amoco technology is the most-used worldwide, but other processes have been developed and are operating commercially.
Physical and Chemical Properties:

**TPA:**
- White solid material
- M. W. = 166.14 g/mol
- M. P. = 300°C (sublimation)
- Freezing Point = 427°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature, °C</th>
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<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>in water</td>
<td>0.0017</td>
</tr>
<tr>
<td>in glacial acetic acid</td>
<td>0.013</td>
</tr>
<tr>
<td>in methanol</td>
<td>0.1</td>
</tr>
<tr>
<td>in dimethylformamide</td>
<td>6.7</td>
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<tr>
<td>in dimethyl sulfoxide</td>
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Terephthalic acid has a low order of toxicity. Inhalation by rats for 6 h/d, 5 d/wk for 4 wk produced no fatalities at a dust exposure level of 25 mg/m3. The mean acute oral toxicity for rats is over 18 g/kg (86), and for mice mover 6 g/kg. When terephthalic acid was fed as 3% of the diet to rats, urinary calculi formed in 90 d, some of which led to cancer.

High doses of terephthalic acid lead to formation of calcium terephthalate at levels exceeding its solubility in urine. This insoluble material leads to the calculi and provides a threshold below which cancer is not observed.

If ventilation is inadequate, a toxic-dust respirator should be used to avoid prolonged exposure.

**DMT:**
- White solid that melts to give distillable colorless liquid.
- Readily biodegradable.
- M. P. (decomposition) = 141°C
- B. P. = 280°C

<table>
<thead>
<tr>
<th>Property</th>
<th>Temperature, °C</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>150°C</td>
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<tr>
<td>Liquid density, g/cm³</td>
<td>1.068</td>
</tr>
<tr>
<td>Viscosity, mPa·s (cP)</td>
<td>0.965</td>
</tr>
<tr>
<td>Specific heat, J/(kg·K)</td>
<td>1921</td>
</tr>
<tr>
<td>Vapor density, g/cm³</td>
<td>1.068</td>
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<tr>
<td>Viscosity, mPa·s (cP)</td>
<td>0.0086</td>
</tr>
<tr>
<td>Specific heat, J/(kg·K)</td>
<td>1290</td>
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</tbody>
</table>
Dimethyl terephthalate also shows low toxicity.

Inhalation by rats of dust for 4 h/d for 58 d showed no toxicological effects at levels up to 86 mg/m³.

Urinary calculi were also formed when dimethyl terephthalate was added at 3% to the diet of rats.

As in the case of terephthalic acid, a toxic-dust respirator should be worn when ventilation is inadequate.

Molten dimethyl terephthalate burns if ignited.

Dimethyl terephthalate vapor and dust, and terephthalic acid dust form explosive mixtures with air.

Uses of Terephthalic Acid (TPA) and Dimethyl Terephthalate (DMT):

Essentially all polymer-grade terephthalic acid and dimethyl terephthalate are used to make saturated polyesters, the great majority being poly(ethylene terephthalate) [PET].

- **PET** is employed to make fiber and is the largest-volume synthetic fiber in the world. Fiber use makes up 73% of worldwide PET production. It is used for woven and knitted fabrics for clothing, draperies, upholstery, and carpeting. In clothing applications, it is usually blended with other fibers, primarily cotton.

- The fastest growing application for PET is in packaging, especially bottles. It currently accounts for 15% of production.

- PET is itself an engineering resin, although one more widely used is poly(butylene) terephthalate, formed by reaction with 1,4-butanediol as the comonomer.

Applications for high strength polyester continuous fibers are reinforcing cord for tires, V-belts, conveyor belts, and hoses.

Polyester film consumes 7% of production. When coated with a chemical emulsion, it is used as x-ray and microfilm; if coated with a magnetic emulsion, it is used for audio and video tapes; and if coated with an adhesive, it is used for wrapping and sealing tapes.

Small amounts of polymer-grade TPA and DMT are used as polymer raw materials for a variety of applications, e.g. adhesives and coatings. They are also used to make high performance polymers or engineering resins.

Terephthalic acid can also be the diacid in specialty nylons.
Purified terephthalic acid has replaced dimethyl terephthalate as the leading terephthalate source for PET. About 75% of PET production worldwide is based on the purified acid, and this percentage is increasing as virtually no new dimethyl terephthalate capacity is being built. This is because:

- Terephthalic acid offers distinct cost and product quality advantages to the manufacturer of PET. This has led to its use in almost all new polymer plants. Specifically, polyester processes that are based on DMT must have equipment for recovery of methanol, which is the by-product of the transesterification with ethylene glycol. Use of the pure acid produces water as a by-product of direct esterification.
- In addition, terephthalic acid provides a higher yield of polyester per kilogram of starting feedstock. While excess ethylene glycol is needed in both processes, the percentage of excess needed is much smaller using terephthalic acid, so less in the way of recovery and recycle process equipment is required.
- The need for transesterification catalysts with DMT introduces metals into the polyester which can cause undesirable side reactions.

**Production of 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.

Technical grade terephthalic acid does not yield products pure enough for use as raw materials in the production of polyester. However, polymer-grade terephthalic acid is produced through the use of a separate purification process. It is also produced by modifying the processes used for technical grade TPA. Most polymer-grade terephthalic acid made by modifying the liquid-phase oxidation process is used captively by the producing company or an affiliate, but some is sold on the open market. Polymer-grade terephthalic acid is also produced by hydrolyzing purified dimethyl terephthalate. Here too, though, the producing company also makes PET and uses most of it captively.

Some processes for the production of TPA are described in the following sections.
I. Amoco Process:

- Figure 2.1.3 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 and the 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.

Figure 2.1.3: Terephthalic Acid Production by catalytic, liquid-phase air oxidation of p-xylene.

- 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 TPA is at least 95 mol%.
• 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 [usually referred to as 4-carboxybenzaldehyde (4-CBA)], which is incompletely oxidized p-xylene.
• 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.

AMOCO Purification Process:
• The Amoco process is used to purify terephthalic acid produced by the bromine-promoted air oxidation of p-xylene.
• The main impurity in the oxidation product is 4-formylbenzoic acid and the Amoco process removes this to less than 25 ppm. Metals and colored organic impurities are also almost completely removed by the purification.
A flow diagram of the continuous process is presented in Figure 2.1.4.

Figure: 2.1.4: The Amoco Purification Process for Polymer grade Terephthalic Acid.

- Crude terephthalic acid and water are fed to a mixing tank to form a slurry of at least 15 wt.% terephthalic acid. The slurry is pumped to heat exchangers, which raise the slurry temperature sufficiently for the terephthalic acid to dissolve.
- The solution flows through a hydrogenation reactor that contains a palladium-on-carbon support catalyst.
- Hydrogen is added to the reactor, where it dissolves in the feed solution.
- In the reactor, 4-formylbenzoic acid is hydrogenated to p-toluic acid, and various colored impurities are hydrogenated to colorless products.
- The catalyst is highly selective; the loss of terephthalic acid by carboxylic acid reduction or ring hydrogenation is less than 1%.
- The overall effect of the hydrogenation is conversion of impurities to forms which remain in the mother liquor during the subsequent crystallization step.
- The terephthalic acid is purified by crystallization in a series of vessels where the pressure and therefore the temperature is sequentially decreased.
As was noted above, impurities remain in the mother liquor for the most part. The purified terephthalic acid crystals are recovered by centrifugation or filtration, followed by drying of the wet cake.

- Overall yield of a white, free-flowing powder is greater than 98%.

II. MOBIL Process:

- p-Xylene is oxidized in the presence of cobalt based catalyst without using any promoter.
- The reaction takes place in acetic acid medium at around 130°C.
- Methyl ethyl ketone is used as an activator.
- After cooling, washing and centrifuging, crude TPA is sent to purification section.
- Purification of TPA takes place in 2-steps:
  - Crude TPA is slurried with acetic acid and charged to leaching stage. During leaching, impurities like p-carboxybenzaldehyde and cobalt catalyst are removed from the crude TPA.
  - Crude TPA (about 99.5% pure) is further purified by sublimation. Crude TPA from leaching operation is dispersed in steam. Hydrogen and catalyst are added to the dispersed TPA, which is then passed through a heated furnace. Finally, purified TPA vapors after separating from impurities are condensed.
III. Henkel-I Process (Rearrangement of Benzoic Acid and Phthalic Anhydride):

- Henkel technology is based on the conversion of benzene carboxylic acids to their potassium salts.
- The salts are rearranged in the presence of carbon dioxide and a catalyst such as cadmium or zinc oxide to form dipotassium terephthalate, which is converted to terephthalic acid.
- Henkel technology is obsolete and is no longer practiced.

IV. Henkel-II Process:

- Henkel II technology starts with toluene to produce benzoic acid.
- Reaction of benzoic acid with potassium hydroxide resulted in potassium benzoate, which is subjected to a disproportionation reaction to produce dipotassium terephthalate and benzene.
- Dipotassium terephthalate reacted with sulfuric acid, and the resulting terephthalic acid is recovered by filtration and drying.
- Here, dipotassium sulfate is the by-product.
Production of DMT:

I. Route-1 (Hercules/ Dynamit Nobel Process):

- This is the most widely used route for the production of DMT where p-xylene and methanol comprise the feedstock.
- It involves four steps, which alternate between liquid-phase oxidation and liquid-phase esterification. Two reactors are used.
- First, p-xylene is oxidized with air to p-toluic acid in the oxidation reactor, and the contents are then sent to the second reactor for esterification with methanol to methyl p-toluate.
- The toluate is isolated by distillation and returned to the first reactor where it is further oxidized to monomethyl terephthalate, which is then esterified in the second reactor to dimethyl terephthalate.

- p-Xylene, air, and catalyst are fed continuously to the oxidation reactor where they are joined with recycle methyl p-toluate.
- Typically, the catalyst is a cobalt salt, but cobalt and manganese are also used in combination.
- The oxidation reactor is maintained at 140–180°C and 500–800 kPa (5–8 atm).
- The heat of reaction is removed by vaporization of water and excess p-xylene; these are condensed, water is separated, and p-xylene is returned continuously. Cooling coils can also be used.
- The oxidation reactor effluent and methanol are sent to the esterification reactor, which operates at up to 250°C and a pressure sufficient to maintain the liquid phase. This latter is about 2500 kPa (25 atm).
- The oxidation products are converted to methyl p-toluate and dimethyl terephthalate without a catalyst. Excess methanol is supplied, and steam and vaporized methanol are removed and enter a methanol recovery column.
The esterification products flow to a crude ester column, which separates the toluate from the terephthalate. The overhead stream of methyl p-toluate is returned to the oxidation reactor, and the bottom stream of dimethyl terephthalate goes to a primary distillation.

- The distillate is dissolved in methanol, crystallized, and solid dimethyl terephthalate is recovered.
- The dimethyl terephthalate can then be either recrystallized or distilled to yield the highly pure material needed for the polyesterification reaction.
- The overall yield of the process is at least 87 mol %.
- Figure 2.1.5 is a flow diagram which gives an example of the commercial practice of the Dynamit Nobel process for manufacturing DMT.

![Figure 2.1.5: The Dynamit Nobel Process for DMT Production](image)
II. Route-2 (Direct Esterification of Terephthalic Acid):

- Esterification of terephthalic acid is also used to produce DMT commercially, although the amount made by this process has declined.
- Esterification generally uses a large excess of methanol in a liquid process at 250–300°C.
- The reaction proceeds rapidly without a catalyst, but metal catalysts such as zinc, molybdenum, antimony, and tin can be used.

\[
\text{COOH} + 2\text{CH}_3\text{OH} \xrightarrow{\text{0-xylene}} \text{COOCH}_3 + 2\text{H}_2\text{O}
\]

- Conversion to dimethyl terephthalate is limited by equilibrium, but yields of 96% have been reported.
- The crude DMT is recovered and purified by distillation in most processes.
- Although distillation is generally a powerful separation technique, the mode of production of the terephthalic acid determines its impurity content, which in turn may make purification by distillation difficult.
- Generally, this method is adopted when highly impure Terephthalic Acid is available.