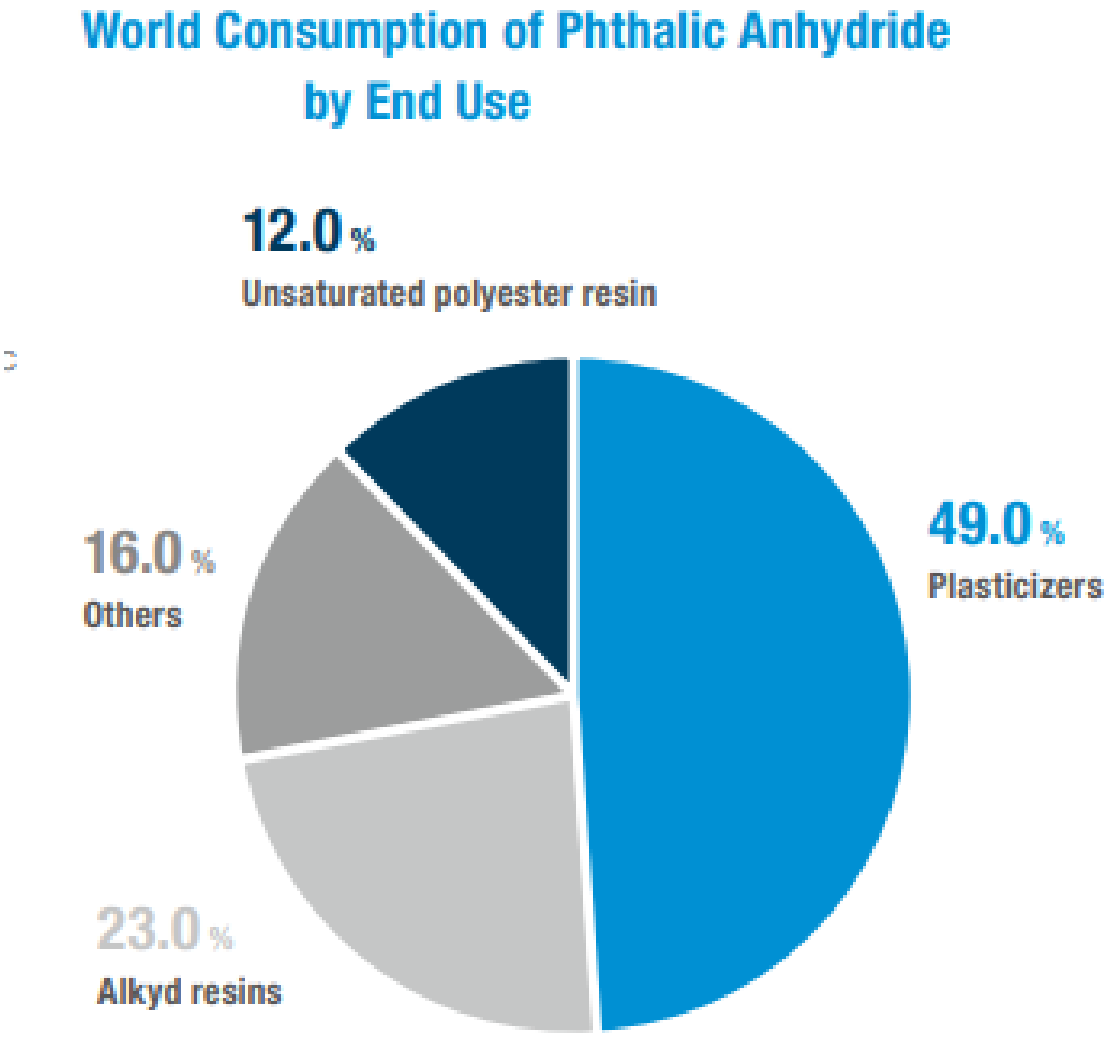
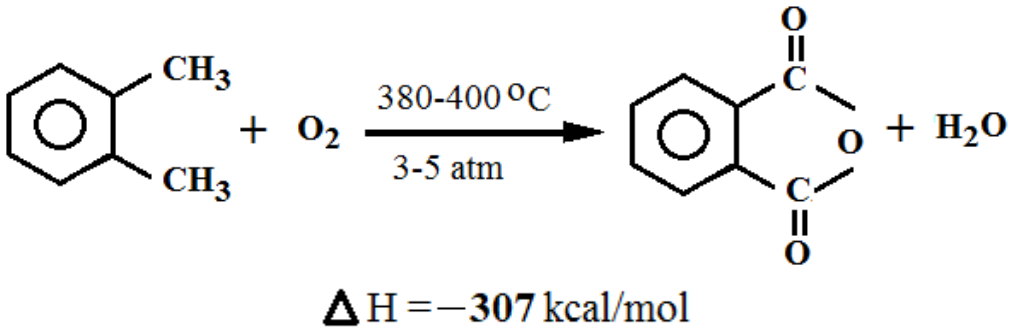
Petrochemical Technology

Chemicals from Xylenes

Chemicals from *o*-Xylene



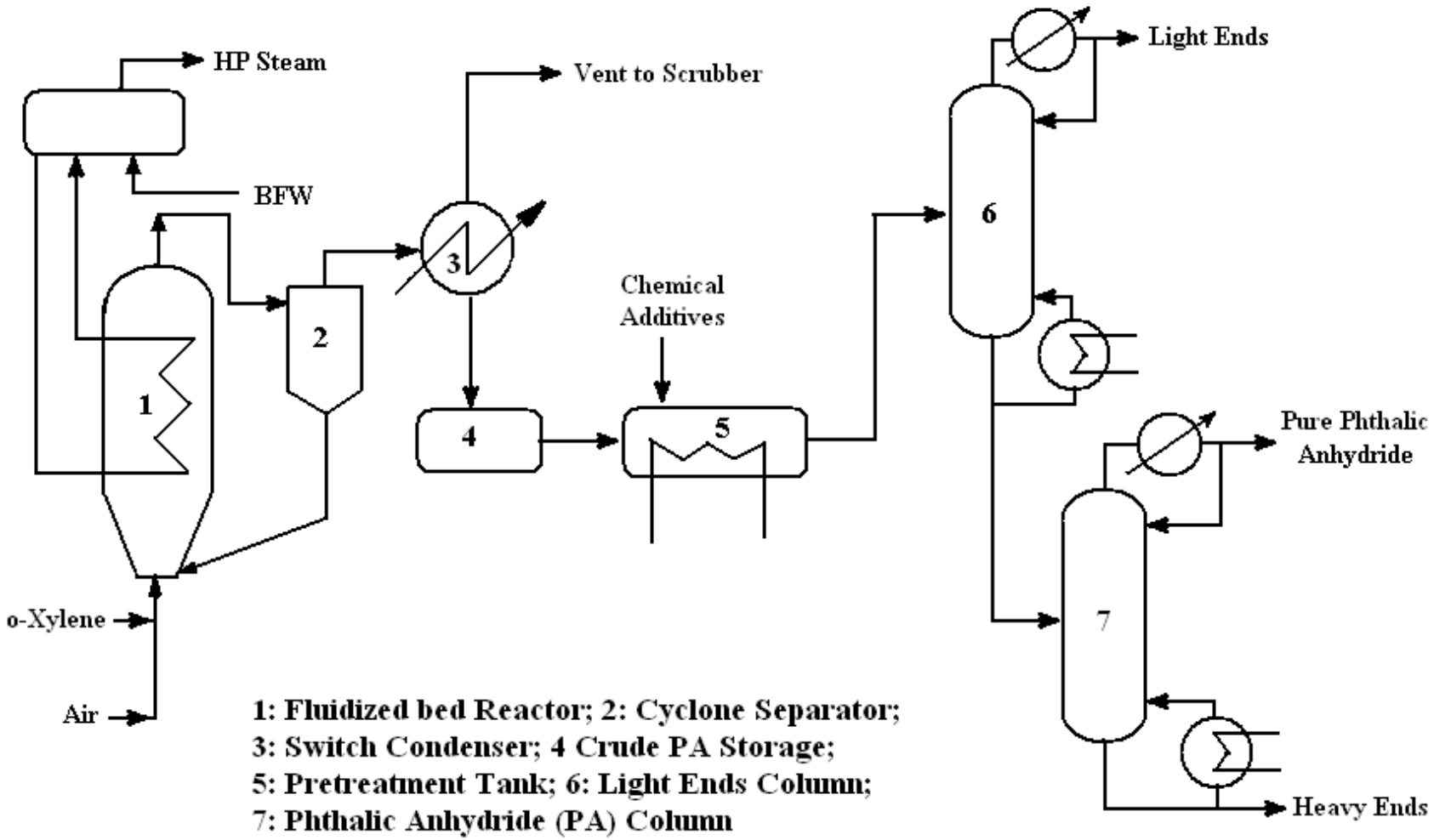
Phthalic Anhydride from *o*-Xylene



$\Delta H = -307$ kcal/mol

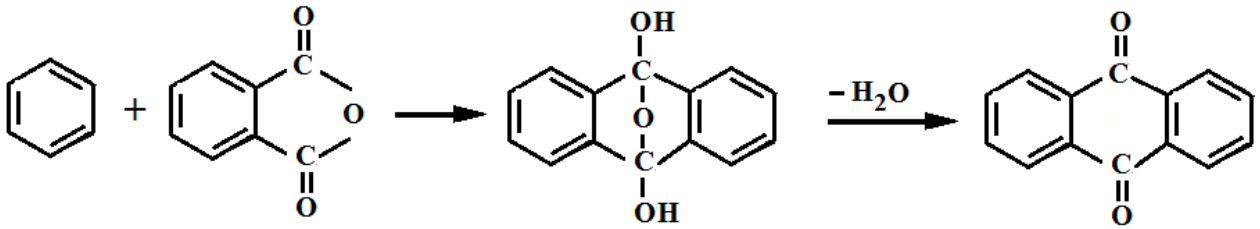
Catalyst: V_2O_5 combined with TiO_2 and these active materials are coated on an inert nonporous carrier. TiO_2 increases the catalyst's affinity for oxygen and improves the selectivity of the reaction to form PA. The yield of PA can be as high as 1.395 kg/kg *o*-X.

The selectivity of the PA reaction is 70%, for the complete combustion of *o*-X is 15%, for the incomplete combustion of *o*-X is 5%, for maleic anhydride is 9% and for the heavy impurity is 1%.



Production of Phthalic Anhydride from *o*-Xylene

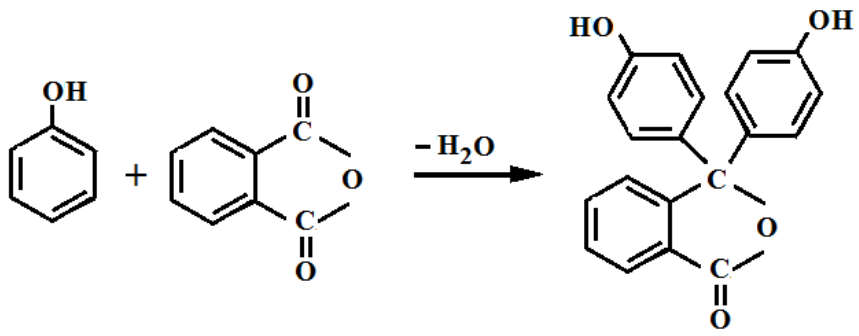
About one half of the phthalic anhydride production is used in plasticizers. One quarter goes into alkyd resins and an equal amount into unsaturated polyesters.



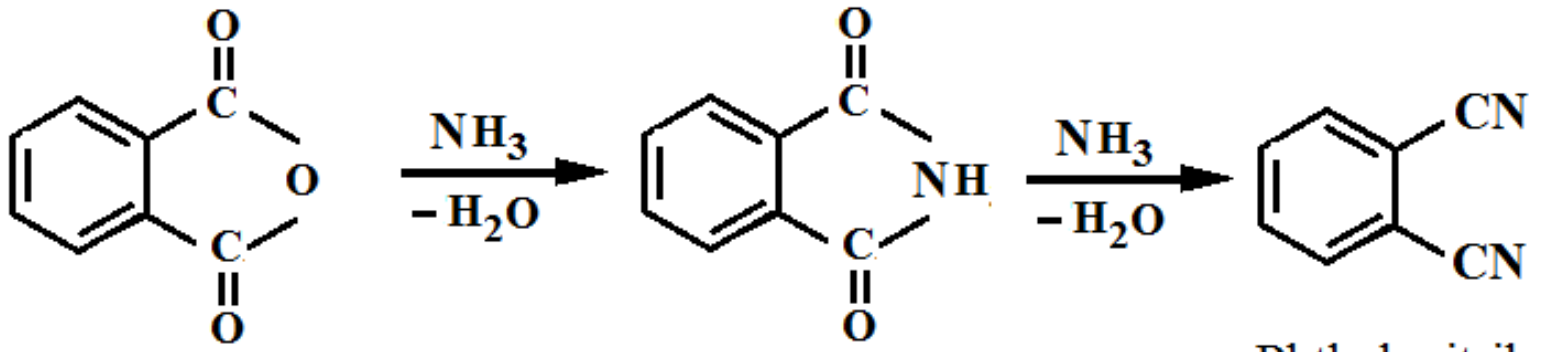
Anthraquinone

Anthraquinone is used to make dyes, digester additive in paper making and anthracenedione class of drugs.

Phthalic anhydride reacts with phenol in presence of sulphuric acid to form the pH indicator, Phenolphthalein.

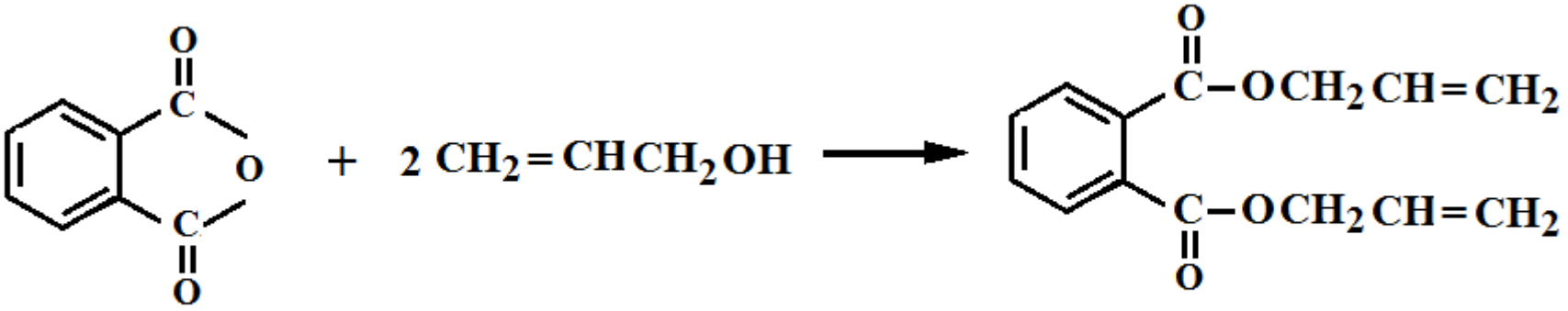


Phenolphthalein



Phthalonitrile

Phthalonitrile is the starting material for phthalocyanine dyes.

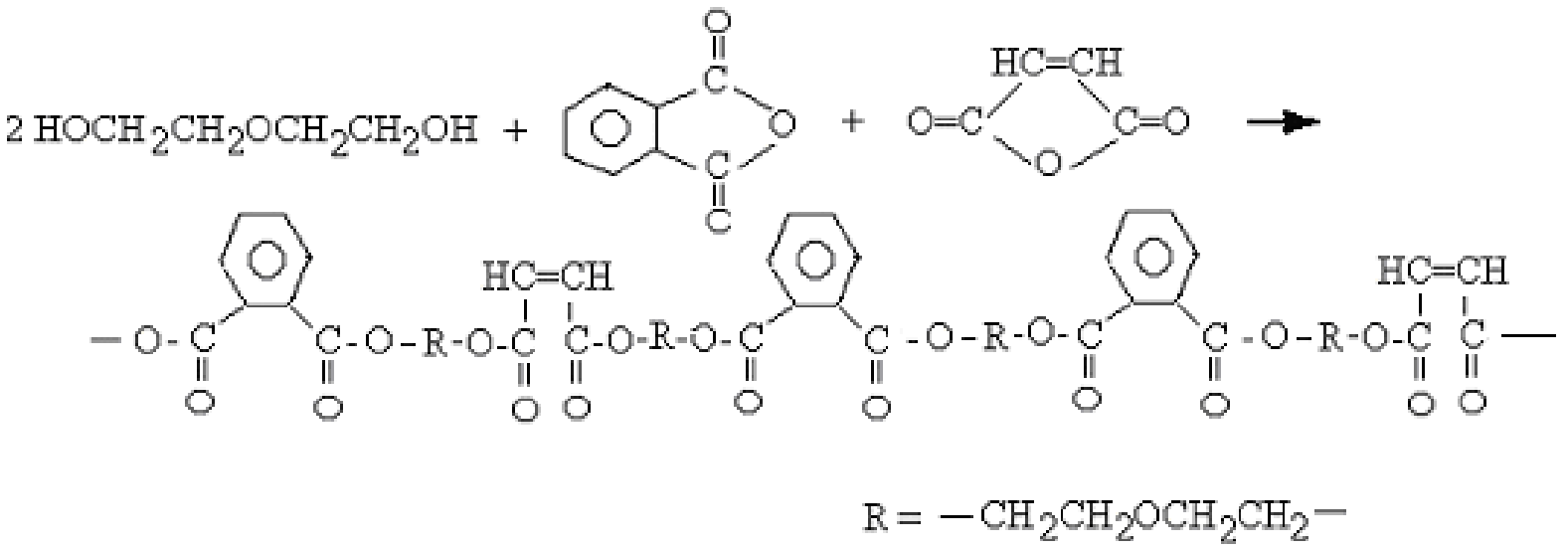


Diallylphthalate

Diallylphthalate is used as a monomer for high performance thermoset polymers, useful for glass-reinforced plastics.

Dioctyl phthalate and di-2-ethylhexyl phthalate are used as plasticizers for polymers, principally polyvinyl chloride (PVC).

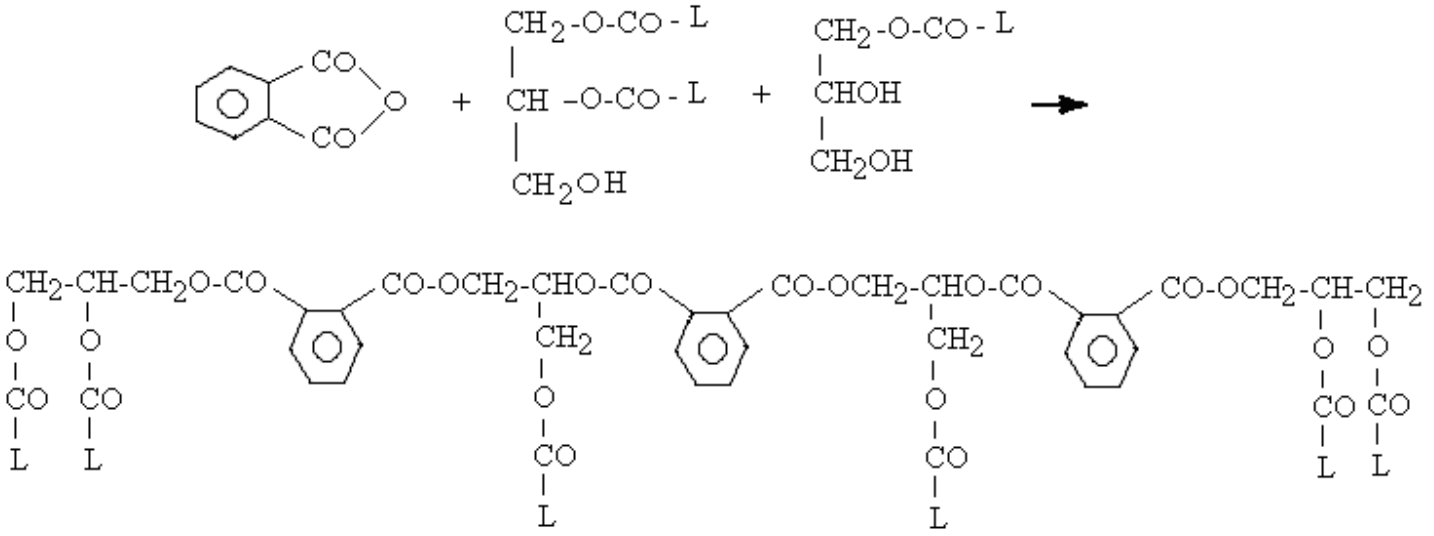
Unsaturated Polyester Resin



Unsaturated polyesters reinforced with glass, cloth or fibers are used for the automobiles. They are used as a metal replacement for the fabrication of pipe and storage tanks, and in the manufacture of small boats and even large minesweepers, where the absence of metal is essential.

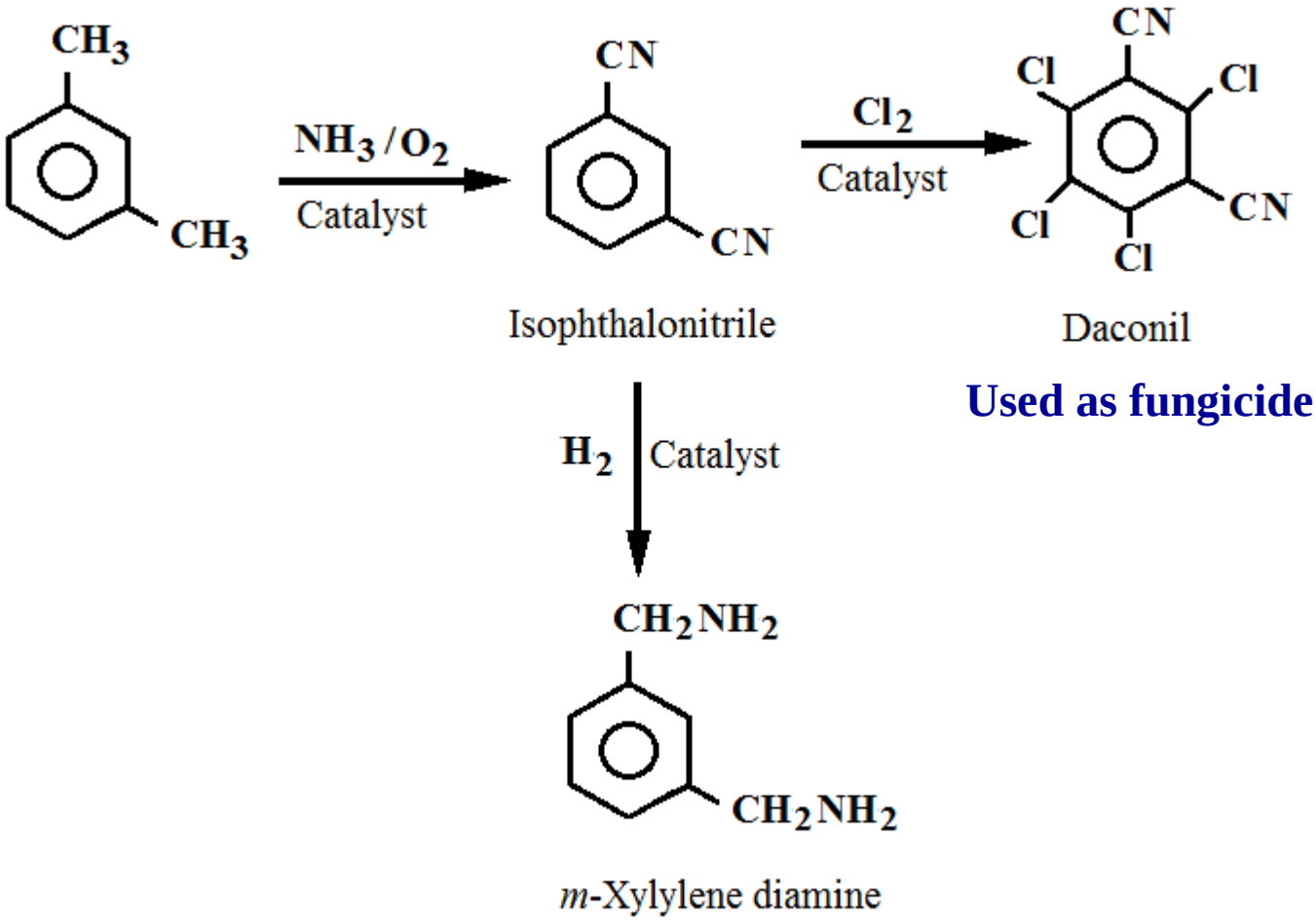
Alkyd Resins

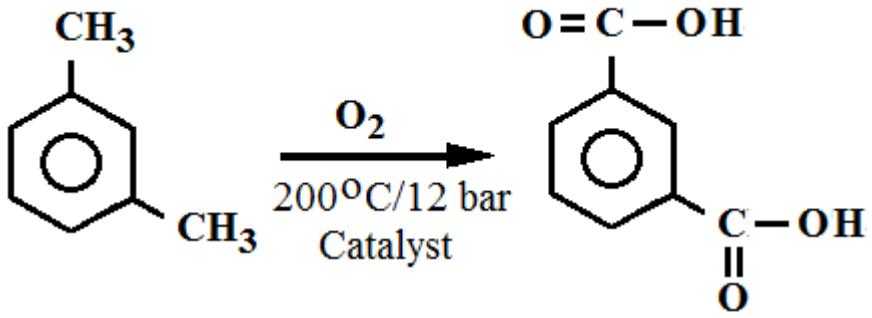
Alkyd resins are oligomers in which polyester functions have been inserted into natural "drying oils".



The incorporation of the polyester function gives the paint film greater solvent and ultraviolet resistance and also imparts somewhat greater corrosion-resistance.

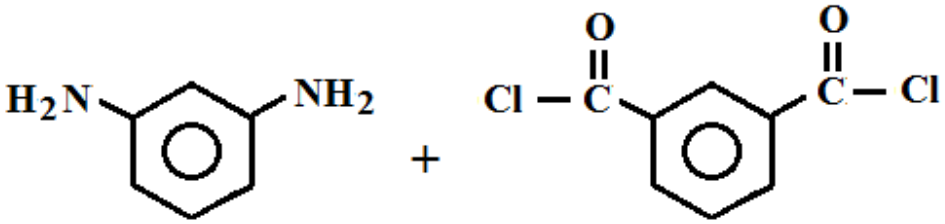
Chemicals from *m*-Xylene



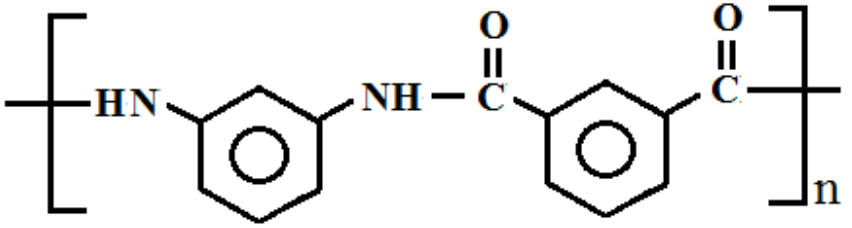


Isophthalic acid

Catalyst: Mn or Co salt with Br as promoter
Or Manganous and Cobaltous
Bromide in acetic acid medium

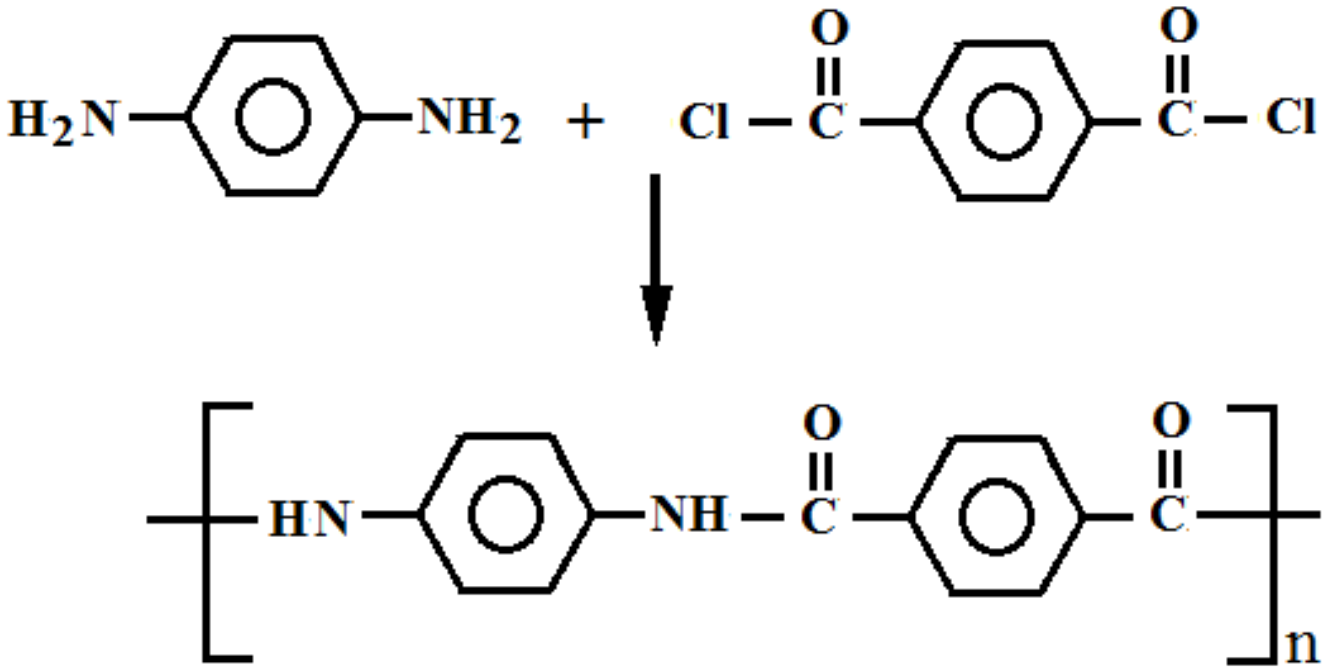


Nomex is used for making fire-resistant cloth for fire fighters and race car drivers uniform and for plant workers clothings.



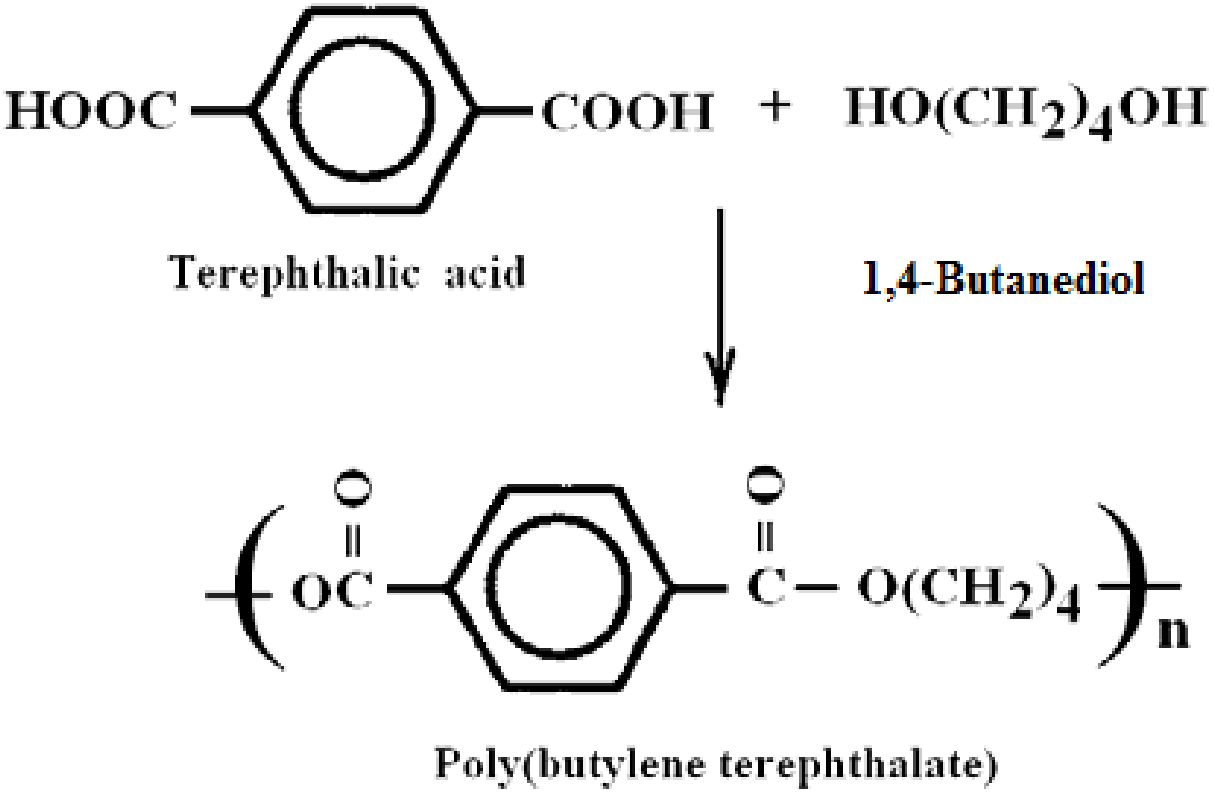
Nomex

Chemicals from *p*-Xylene

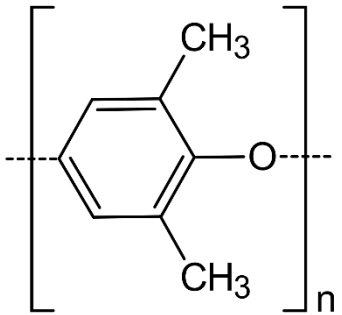


Kevlar

Kevlar finds its major application as an asbestos replacement. Other uses include cord for tires for large vehicles and reinforcement for bullet-proof vests and military helmets. It is used in combination with epoxy resin for canoe manufacture and as cloth for boat sails.



PBT is an inexpensive moulding resin useful for pipe, automotive parts, and toothbrush bristles. It is also alloyed with poly(phenylene oxide) to give a plastic useful for automobile bumpers and even for side panels.



PPO

Terephthalic Acid (TPA)

The global purified terephthalic acid (PTA) market is valued at US$ 61.78 Billion in 2023. The increasing use of polyester fibres due to their ability to combine with various natural and synthetic fibres is likely to boost demand throughout this decade. The overall demand for PTA is projected to grow at a CAGR of 5.5% between 2022 and 2032, totaling around US$ 99.50 Billion by 2032.

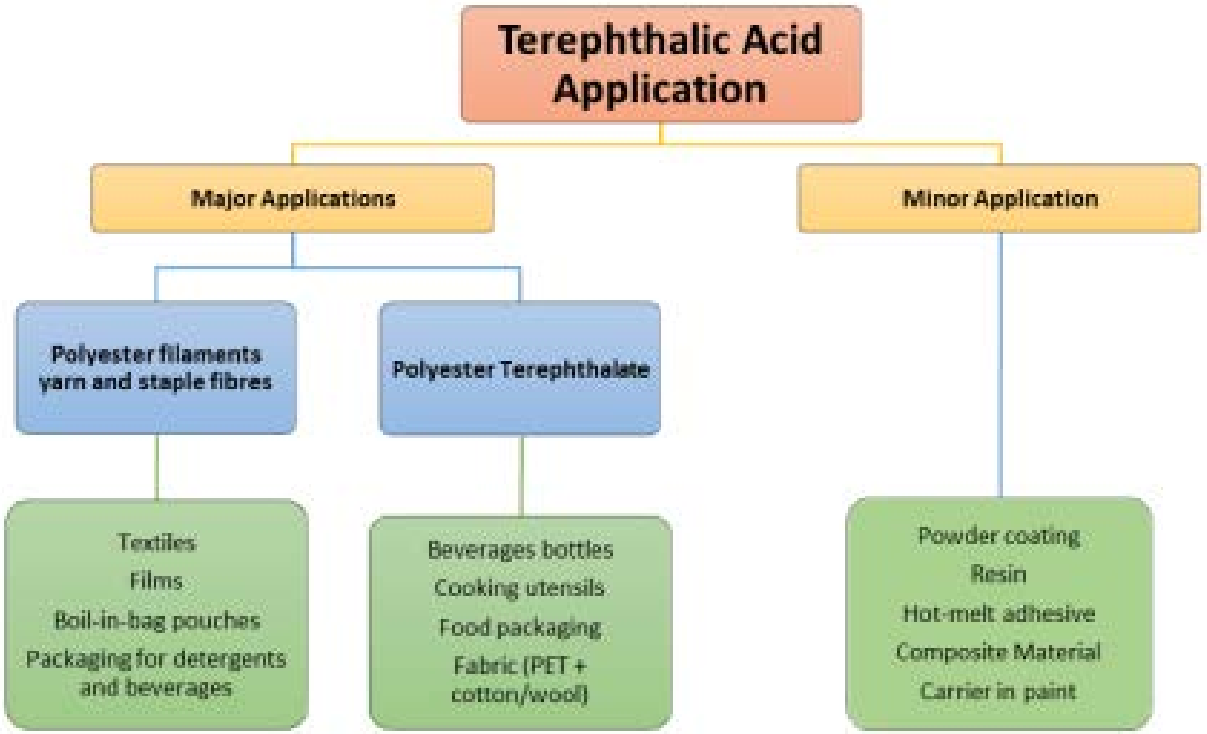
Over the forecast period of 2022-2032, the worldwide PTA market is expected to develop at a high CAGR. Market participants are investigating development opportunities in the maritime, construction, transportation, and wind energy industries.

Globally, there is an installed capacity of ca. 81.6 MMT per year, and this is estimated to increase to 105.6 MMT per year by the end of 2029.

Applications

Purified terephthalic acid (PTA) is a critical component in the production of synthetic fibres. Purified terephthalic acid accounts for 70-80% of polyester goods. PTA is a less expensive alternative to dimethyl terephthalate (DMT). PTA is widely used in the textile and packaging industries.

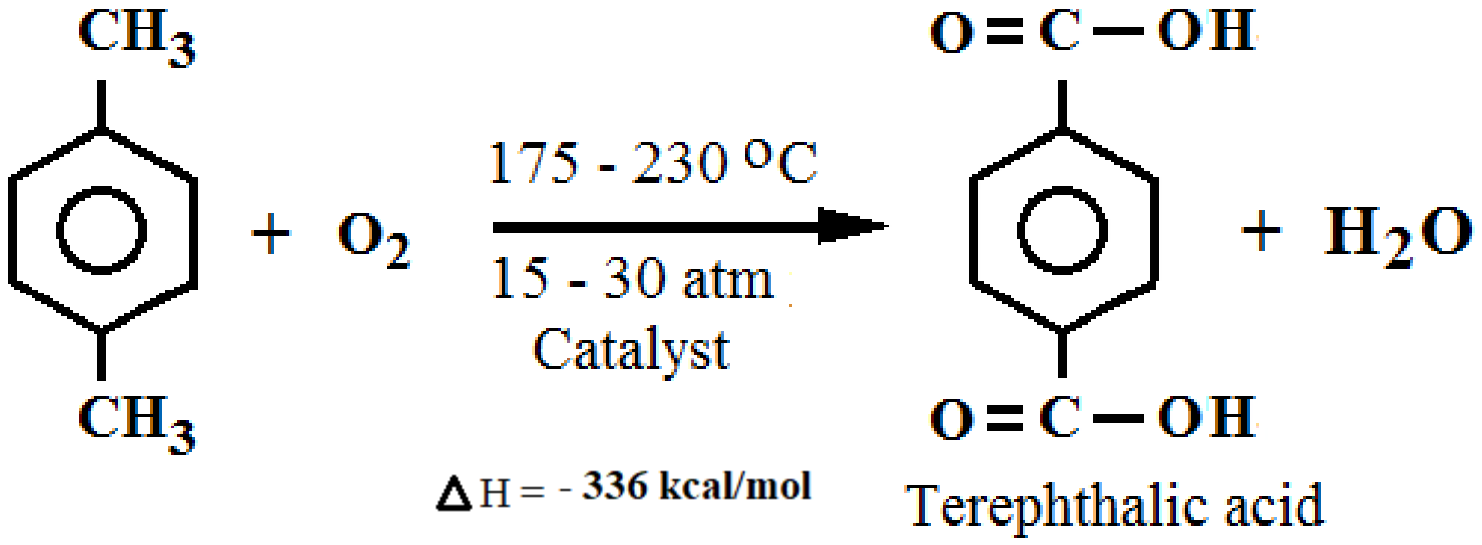
Furthermore, PTA is being used in the medical field to treat peptic ulcers, reflux esophagitis, and gastroesophageal reflux disease (GERD).



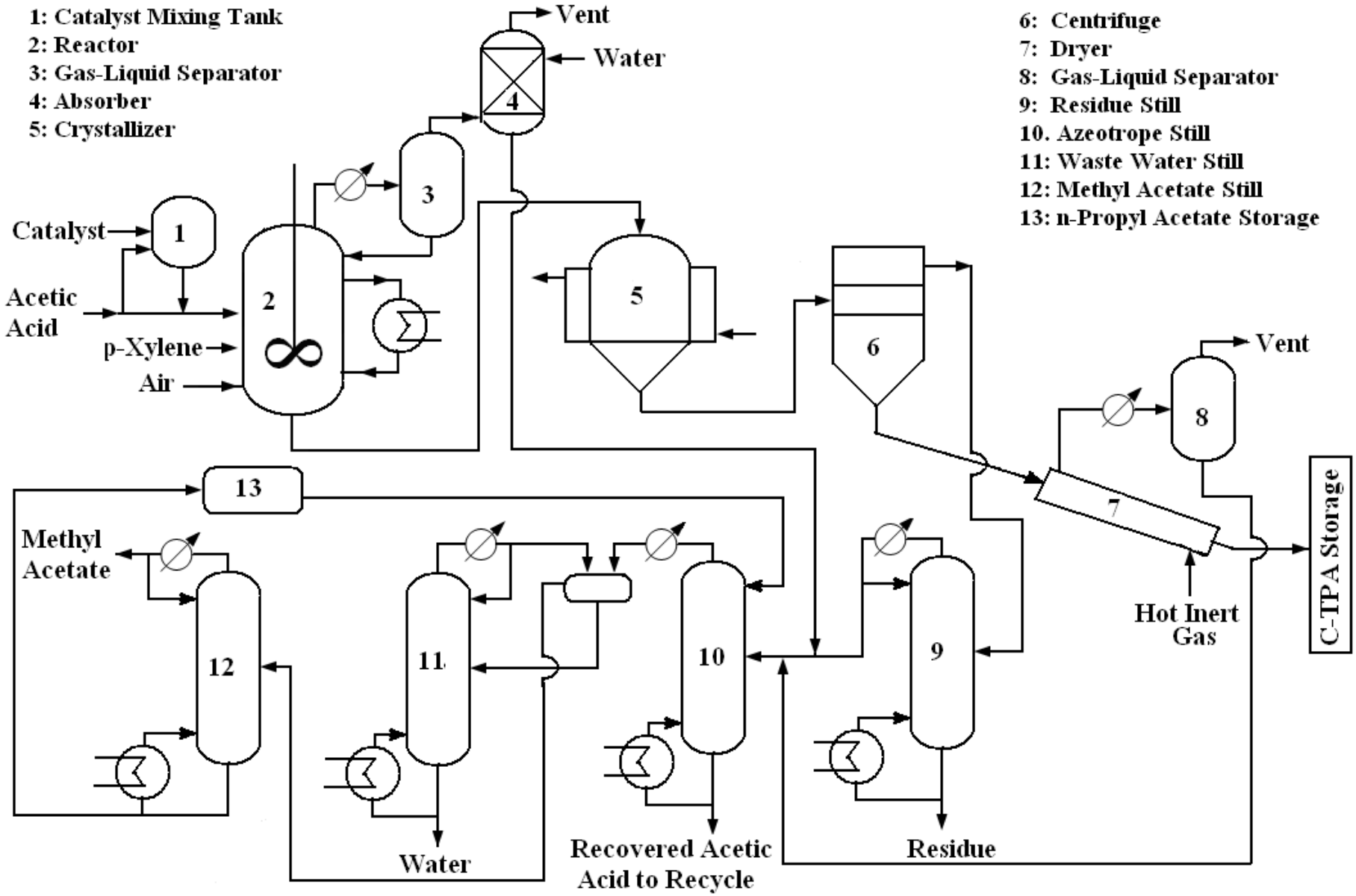
Manufacture of Terephthalic Acid

Terephthalic acid is produced by oxidation of *p*-xylene. The oxidation is carried out in acetic acid solution with a catalyst comprising of a manganese or cobalt salt with a bromine promoter, which may actually be bromine itself but is usually manganous or cobaltous bromide. The bromide converts the recalcitrant methyl group to a free radical, which is then much more susceptible to oxidation.

Acetic acid is used as solvent because terephthalic acid (TPA) is much less soluble in it than are the intermediate products, and this allows for the separation of relatively pure TPA. Much of the acetic acid is oxidized and must be replaced. Even in the presence of acetic acid, impurities are formed in the reaction, the most important of which is 4-formylbenzoic acid (also called *p*-carboxylic benzaldehyde). A flow sheet for the production of TPA from *p*-xylene is shown below. Crude TPA produced this way is purified by Amoco purification process to get polymer grade TPA. The specification for polymer grade TPA is given below.



Catalyst: Mn or Co salt with Br as promoter
Or Manganous and Cobaltous
Bromide in acetic acid medium



Production of Terephthalic Acid

Specification for Polymer Grade TPA

Property	Specification
Acid number, mg KOH/gm	675±2
Ash, ppm	15 max
Total significant metals, ppm (Mo, Cr, Ni, Co, Fe, Ti, Mg)	10 max
4-Formyl benzoic acid, ppm	25 max
Moisture, wt%	0.5 max
5% Dimethyl formamide solution colour, APHA*	10 max

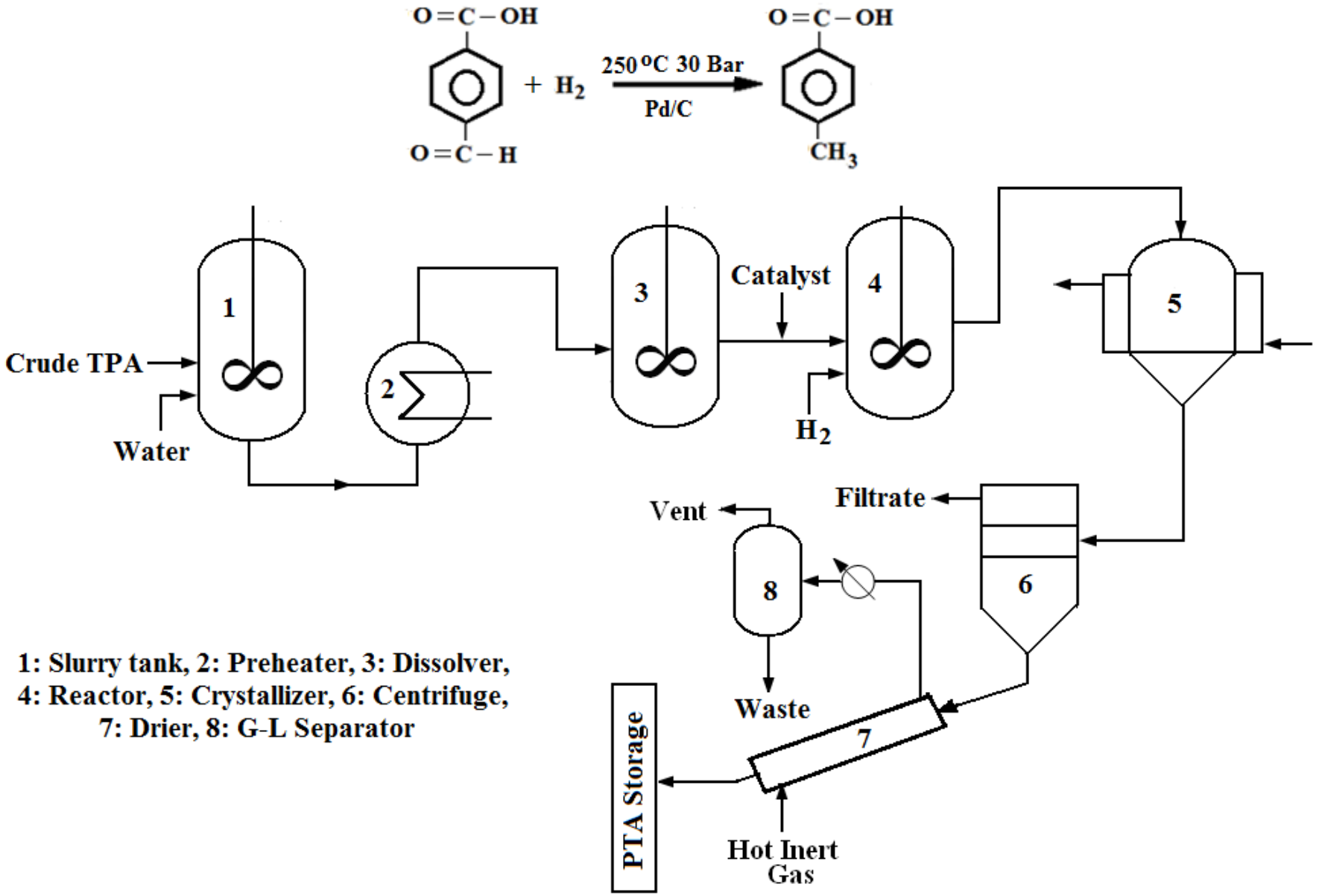
***APHA: American Public Health Association**

Amoco Purification Process

The Amoco process is used to purify terephthalic acid produced by bromine-promoted air oxidation of *p*-xylene. The product contains >25 ppm of 4-formyl benzoic acid, which is the main impurity in the feed. Metals and coloured organic impurities in the feed are almost completely eliminated by the purification.

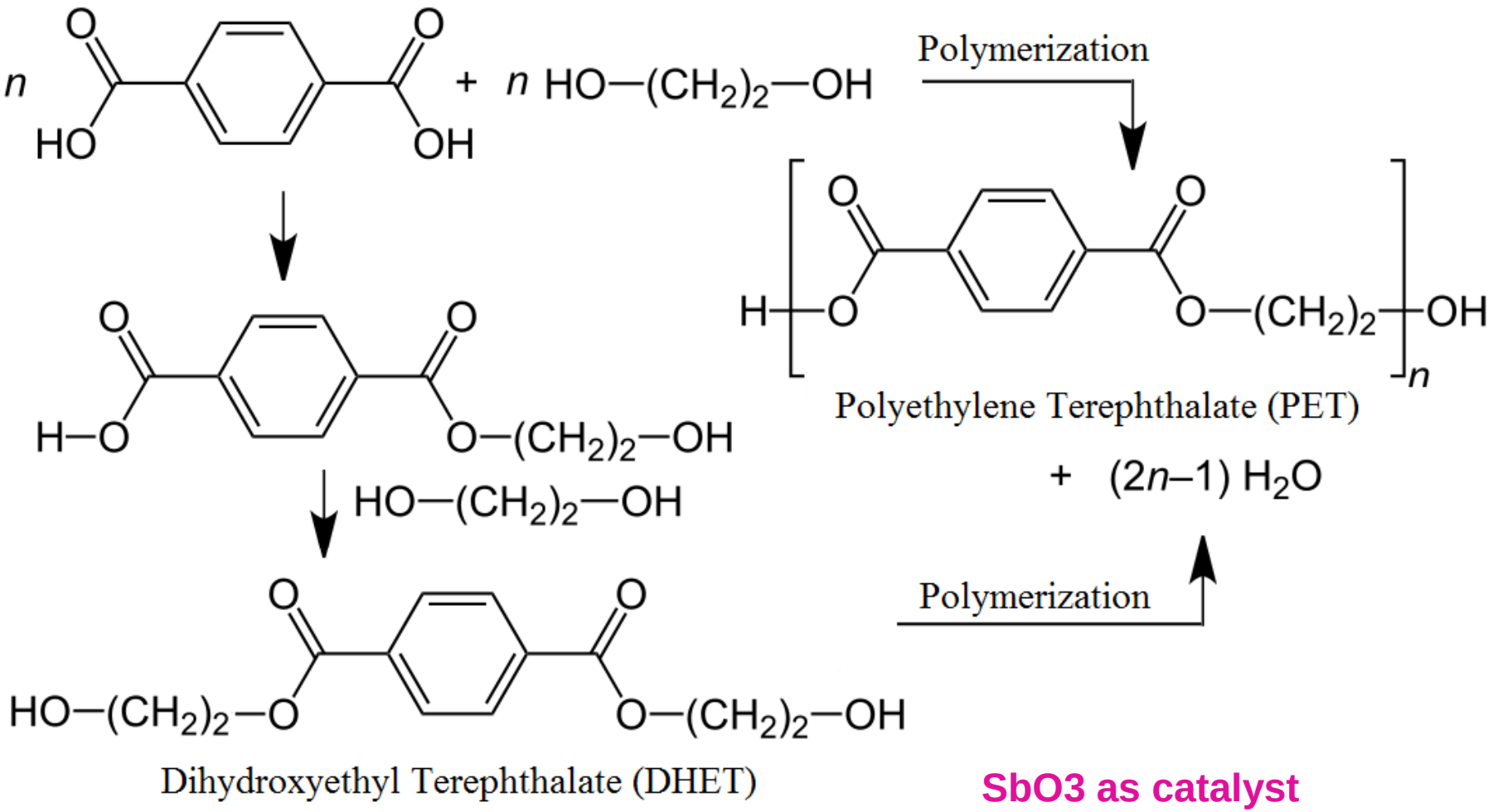
Crude TPA and water are fed into a mixing tank to give a slurry containing at least 10 wt% TPA. The slurry is pumped through a preheater and into a dissolver, which operates at $\geq 250^{o}C$. The effluent from the dissolver is a solution and it flows through the hydrogenation reactor, which contains a noble metal (Pd) catalyst on a carbon support. The pressure in the reactor is sufficient (around 30 bar) to maintain a liquid phase and to ensure an adequate supply of hydrogen. The reactor temperature is same as that of the dissolver ($250^{o}C$).

In the reactor 4-formyl benzoic acid is reduced to *p*-toluic acid and various colour bodies are hydrogenated to colourless products. Catalyst activity does not cause a significant yield loss; ring hydrogenation and reduction of the TPA carbonyl groups proceed at slow rates. The overall effect of the hydrogenation step is conversion of impurities to forms that remain in the mother liquor during subsequent crystallization. Purified TPA is recovered by crystallization, centrifugation and drying. The particle size distribution can be modified using grinders. Overall yield for the process is >97%.

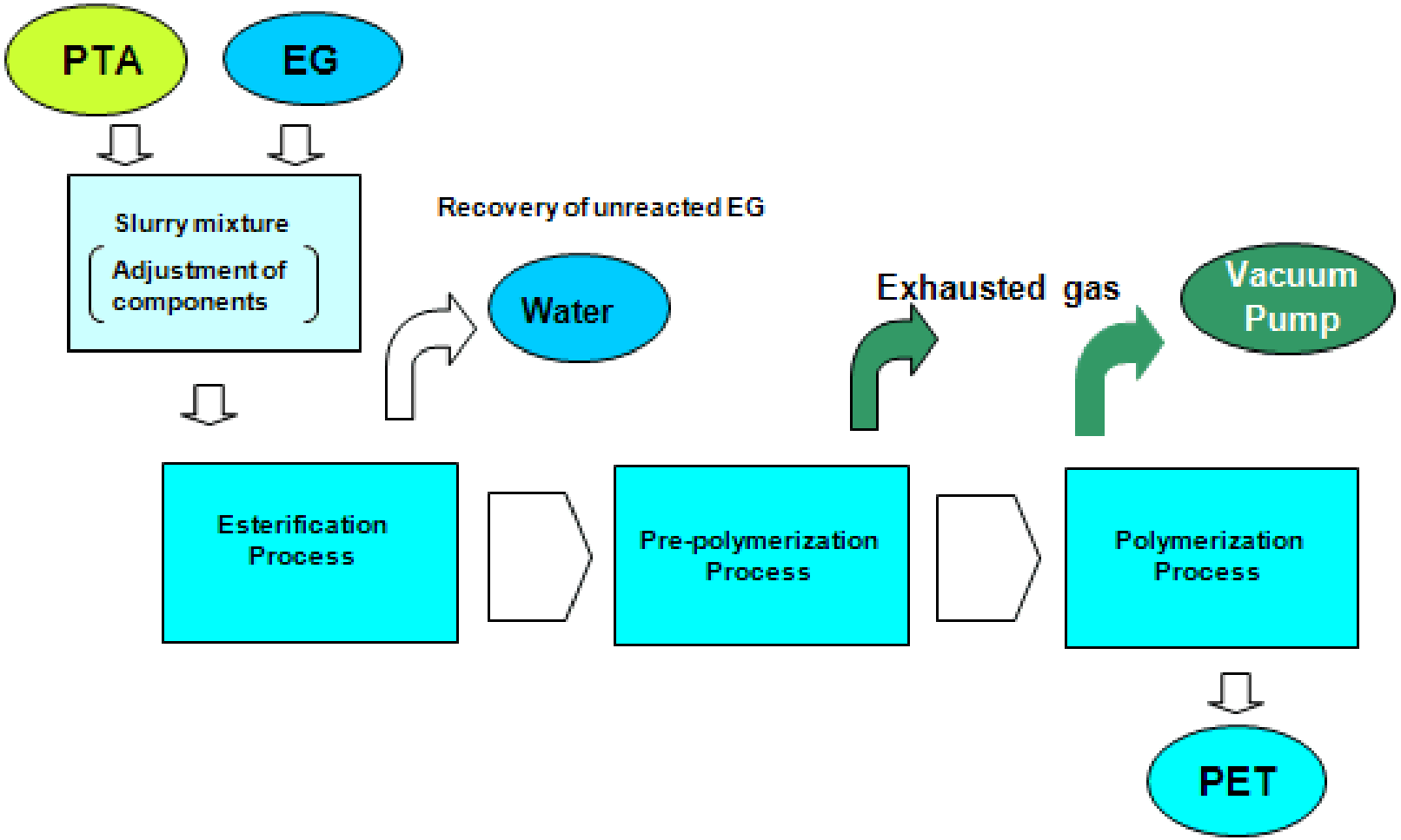


Production of Purified Terephthalic Acid (PTA)

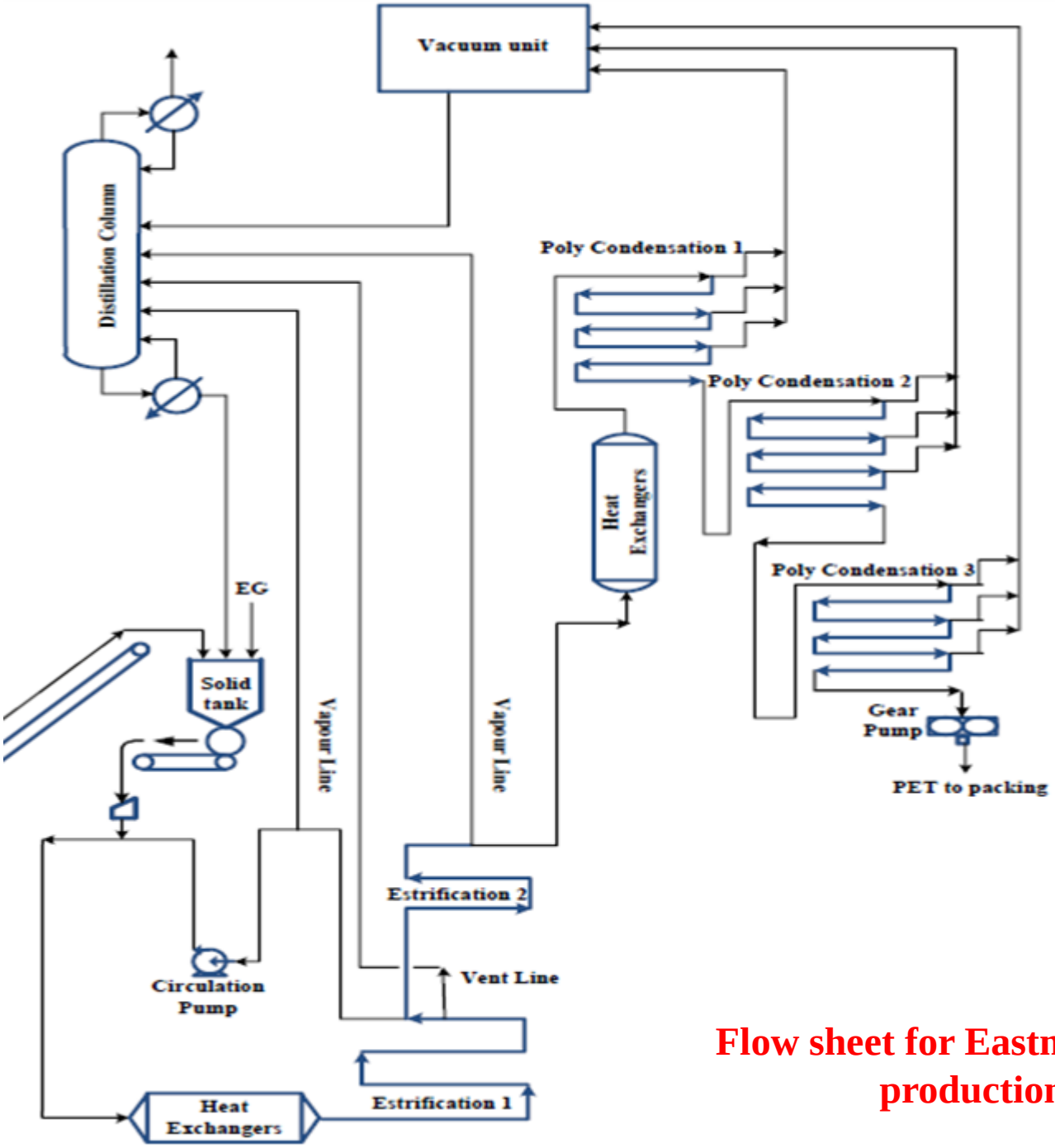
Synthesis of Polyester, Polyethylene Terephthalate (PET)



SbO3 as catalyst at 270-280°C
Last stage: at 285°C, 2 mm Hg

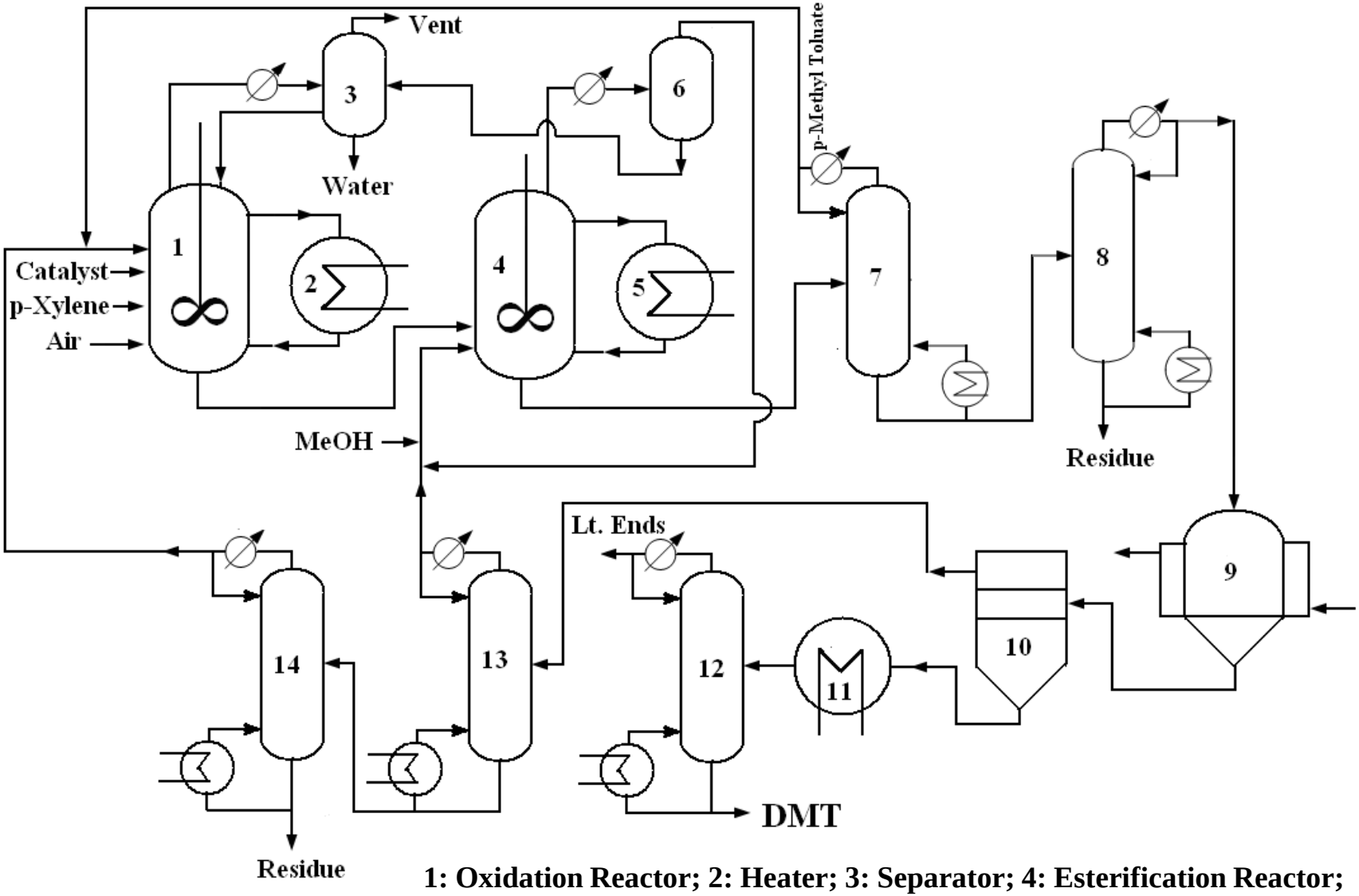


Block Diagram of PET Production Process



The main unit is a tubular reactor that leads to a significant reduction of energy, raw materials consumptions, operation costs and capital costs.

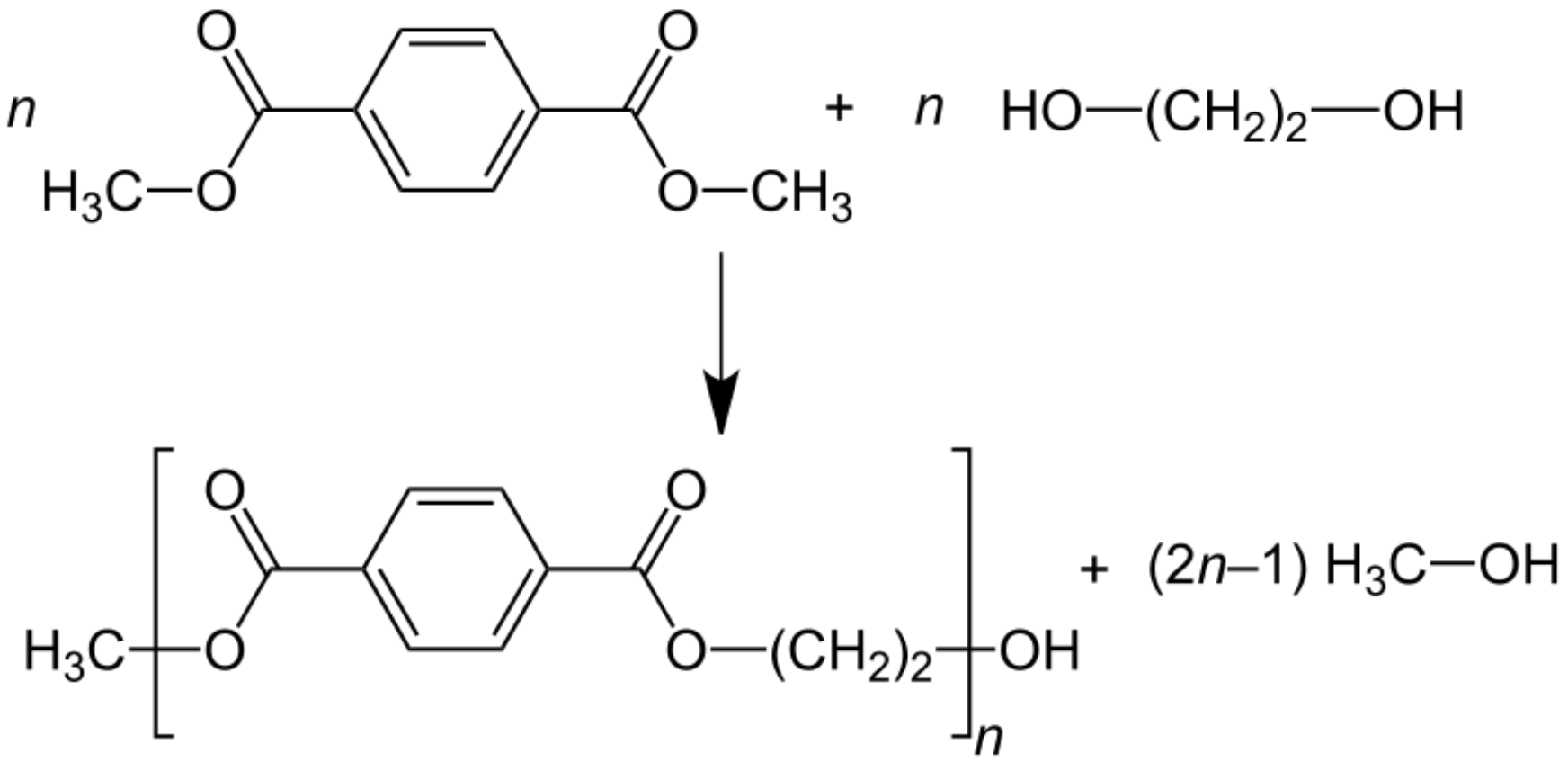
Flow sheet for Eastman IntegRex PET production process



1: Oxidation Reactor; 2: Heater; 3: Separator; 4: Esterification Reactor; 5: Heater; 6: Reactants Recovery Column; 7: By-product Recovery Column; 8: Purification Column; 9: Crystallizer; 10: Centrifuge; 11: Heater; 12: DMT Column; 13: MeOH Recovery Column; 14: Residue Still

Production of Dimethyl Terephthalate (DMT)

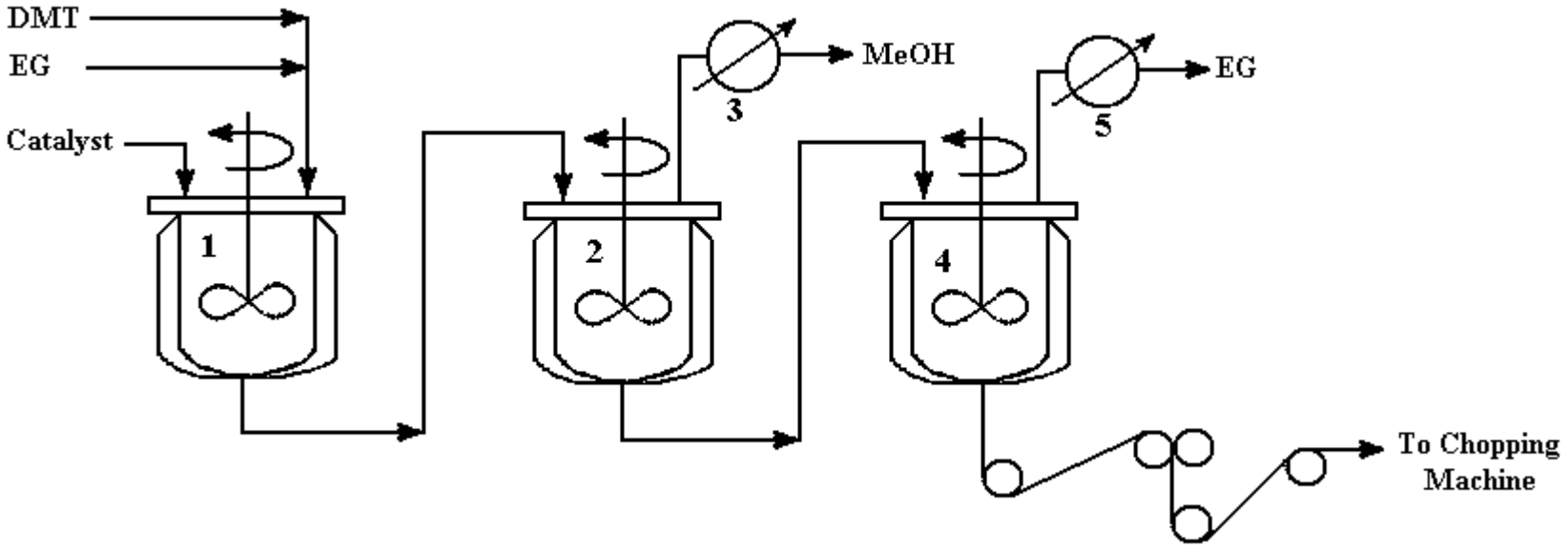
Polyethylene Terephthalate from DMT



Polyethylene Terephthalate (PET)

Polyethylene Terephthalate from DMT

Dimethyl terephthalate (DMT) and ethylene glycol (EG) in a ratio of 1:2 with catalyst are charged into autoclave (1), where the contents are heated upto 150°C. The whole mass is transferred into another autoclave (2) under nitrogen pressure, where the transesterification concludes. Simultaneously, methanol liberated is distilled off to collect in the condensation system (3). After all the methanol is driven off, the product is again transferred under nitrogen pressure to autoclave (4), where polycondensation occurs at about 230°C in presence of catalyst like antimony trioxide under low pressure. Excess glycol are distilled off and condensed (5). Distillation is necessary to shift the equilibrium in the forward direction and ultimately a molecular mass of 25,000 to 35,000 results. The melt is forced out by nitrogen pressure in the form of a ribbon onto a drum and the solidified ribbon to finally machines for chopping. The polymer is fabricated into terelene by melt spinning, after which the fibers are stretched and given twist and allowed to set at a temperature of 120°C.



Production of Polyethylene Terephthalate (PET)

Thank you!