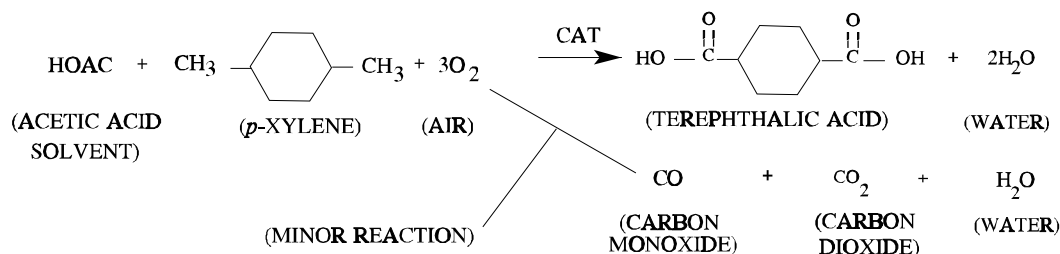


6.11 Terephthalic Acid

6.11.1 Process Description¹

Terephthalic acid (TPA) is made by air oxidation of *p*-xylene and requires purification for use in polyester fiber manufacture. A typical continuous process for the manufacture of crude terephthalic acid (C-TPA) is shown in Figure 6.11-1. The oxidation and product recovery portion essentially consists of the Mid-Century oxidation process, whereas the recovery and recycle of acetic acid and recovery of methyl acetate are essentially as practiced by dimethyl terephthalate (DMT) technology. The purpose of the DMT process is to convert the terephthalic acid contained in C-TPA to a form that will permit its separation from impurities. C-TPA is extremely insoluble in both water and most common organic solvents. Additionally, it does not melt, it sublimes. Some products of partial oxidation of *p*-xylene, such as *p*-toluic acid and *p*-formyl benzoic acid, appear as impurities in TPA. Methyl acetate is also formed in significant amounts in the reaction.



6.11.1.1 C-TPA Production -

Oxidation Of *p*-Xylene -

p-Xylene (stream 1 of Figure 6.11-1), fresh acetic acid (2), a catalyst system such as manganese or cobalt acetate and sodium bromide (3), and recovered acetic acid are combined into the liquid feed entering the reactor (5). Air (6), compressed to a reaction pressure of about 2000 kPa (290 psi), is fed to the reactor. The temperature of the exothermic reaction is maintained at about 200°C (392°F) by controlling the pressure at which the reaction mixture is permitted to boil and form the vapor stream leaving the reactor (7).

Inert gases, excess oxygen, CO, CO₂, and volatile organic compounds (VOC) (8) leave the gas/liquid separator and are sent to the high-pressure absorber. This stream is scrubbed with water under pressure, resulting in a gas stream (9) of reduced VOC content. Part of the discharge from the high-pressure absorber is dried and is used as a source of inert gas (IG), and the remainder is passed through a pressure control valve and a noise silencer before being discharged to the atmosphere through process vent A. The underflow (23) from the absorber is sent to the azeotrope still for recovery of acetic acid.

Crystallization And Separation -

The reactor liquid containing TPA (10) flows to a series of crystallizers, where the pressure is relieved and the liquid is cooled by the vaporization and return of condensed VOC and water. The partially oxidized impurities are more soluble in acetic acid and tend to remain in solution, while TPA crystallizes from the liquor. The inert gas that was dissolved and entrained in the liquid under pressure is released when the pressure is relieved and is subsequently vented to the atmosphere along

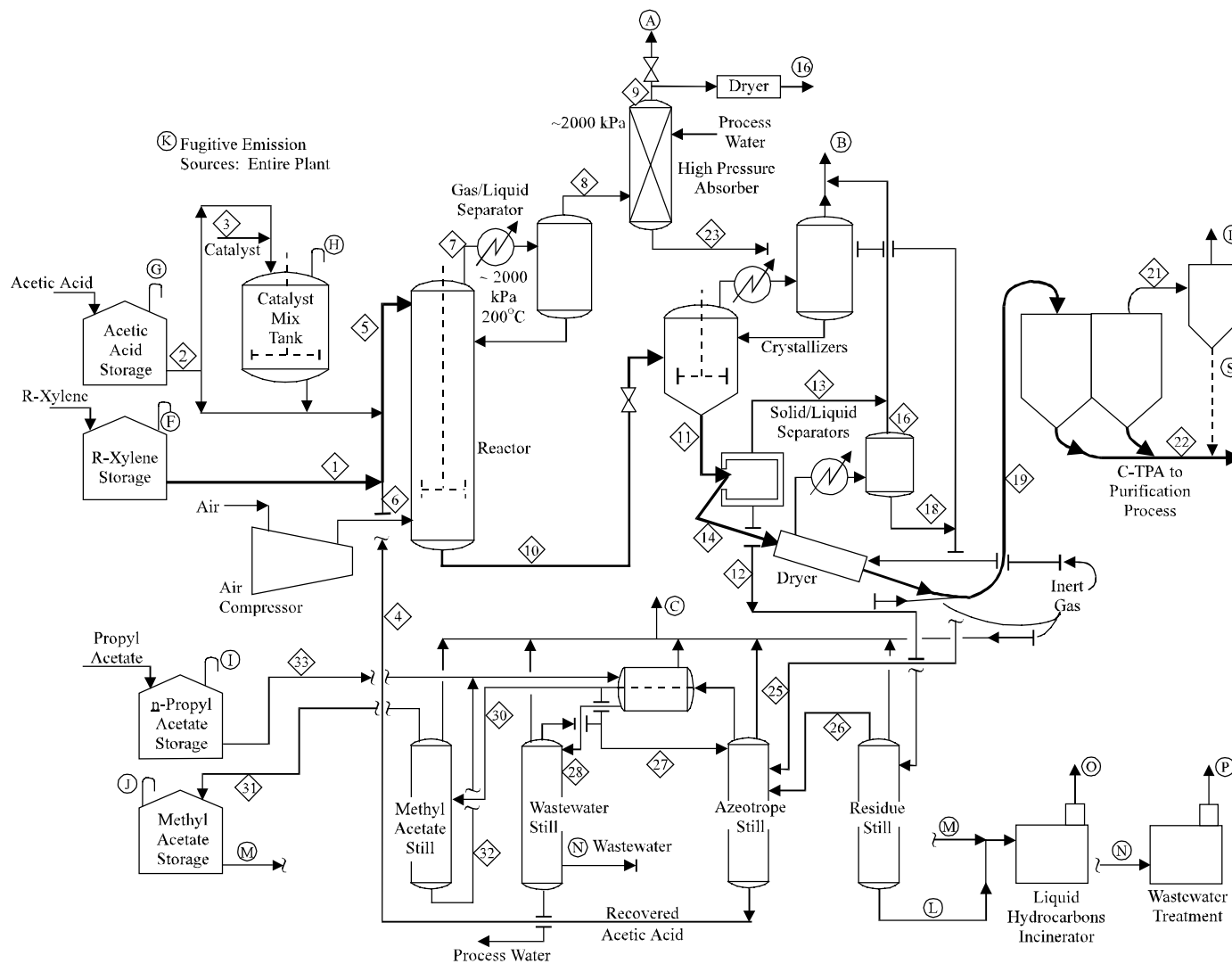


Figure 6.11-1. Crude terephthalic acid process.

with the contained VOC (B). The slurry (11) from the crystallizers is sent to solid/liquid separators, where the TPA is recovered as a wet cake (14). The mother liquor (12) from the solid/liquid separators is sent to the distillation section, while the vent gas (13) is discharged to the atmosphere (B).

Drying, Handling And Storage -

The wet cake (14) from solid/liquid separation is sent to dryers, where with the use of heat and IG, the moisture, predominately acetic acid, is removed leaving the product, C-TPA, as dry free-flowing crystals (19). IG is used to convey the product (19) to storage silos. The transporting gas (21) is vented from the silos to bag dust collectors to reduce its particulate loading, then is discharged to the atmosphere (D). The solids (S) from the bag filter can be forwarded to purification or can be incinerated.

Hot VOC-laden IG from the drying operation is cooled to condense and recover VOC (18). The cooled IG (16) is vented to the atmosphere (B), and the condensate (stream 18) is sent to the azeotrope still for recovery of acetic acid.

Distillation And Recovery -

The mother liquor (12) from solid/liquid separation flows to the residue still, where acetic acid, methyl acetate, and water are recovered overhead (26) and product residues are discarded. The overhead (26) is sent to the azeotrope still where dry acetic acid is obtained by using *n*-propyl acetate as the water-removing agent.

The aqueous phase (28) contains saturation amounts of *n*-propyl acetate and methyl acetate, which are stripped from the aqueous matter in the waste water still. Part of the bottoms product is used as process water in absorption, and the remainder (N) is sent to waste water treatment. A purge stream of the organic phase (30) goes to the methyl acetate still, where methyl acetate and saturation amounts of water are recovered as an overhead product (31) and are disposed of as a fuel (M). *n*-Propyl acetate, obtained as the bottoms product (32), is returned to the azeotrope still. Process losses of *n*-propyl acetate are made up from storage (33). A small amount of inert gas, which is used for blanketing and instrument purging, is emitted to the atmosphere through vent C.

6.11.1.2 C-TPA Purification -

The purification portion of the Mid-Century oxidation process involves the hydrogenation of C-TPA over a palladium-containing catalyst at about 232°C (450°F). High-purity TPA is recrystallized from a high-pressure water solution of the hydrogenated material.

The Olin-Mathieson manufacturing process is similar to the Mid-Century process except the former uses 95 percent oxygen, rather than air, as the oxidizing agent. The final purification step consists essentially of a continuous sublimation and condensation procedure. The C-TPA is combined with small quantities of hydrogen and a solid catalyst, dispersed in steam, and transported to a furnace. There the C-TPA is vaporized and certain of the contained impurities are catalytically destroyed. Catalyst and nonvolatile impurities are removed in a series of filters, after which the pure TPA is condensed and transported to storage silos.

6.11.2 Emissions And Controls¹⁻³

A general characterization of the atmospheric emissions from the production of C-TPA is difficult because of the variety of processes. Emissions vary considerably, both qualitatively and quantitatively. The Mid-Century oxidation process appears to be one of the lowest polluters, and its predicted preeminence will suppress future emissions totals.

The reactor gas at vent A normally contains nitrogen (from air oxidation); unreacted oxygen; unreacted *p*-xylene; acetic acid (reaction solvent); carbon monoxide, carbon dioxide, and methyl acetate from oxidation of *p*-xylene and acetic acid not recovered by the high-pressure absorber; and water. The quantity of VOC emitted at vent A can vary with absorber pressure and the temperature of exiting vent gases. During crystallization of TPA and separation of crystallized solids from the solvent (by centrifuge or filters), noncondensable gases carrying VOC are released. These vented gases and the C-TPA dryer vent gas are combined and released to the atmosphere at vent B. Different methods used in this process can affect the amounts of noncondensable gases and accompanying VOCs emitted from this vent.

Gases released from the distillation section at vent C are the small amount of gases dissolved in the feed stream to distillation; the IG used in inert blanketing, instrument purging pressure control; and the VOC vapors carried by the noncondensable gases. The quantity of this discharge is usually small.

The gas vented from the bag filters on the product storage tanks (silos) (D) is dry, reaction-generated IG containing the VOC not absorbed in the high-pressure absorber. The vented gas stream contains a small quantity of TPA particulate that is not removed by the bag filters.

Performance of carbon adsorption control technology for a VOC gas stream similar to the reactor vent gas (A) and product transfer vent gas (D) has been demonstrated, but CO emissions will not be reduced. An alternative to the carbon adsorption system is a thermal oxidizer that provides reduction of both CO and VOC.

Emission sources and factors for the C-TPA process are presented in Table 6.11-1.

Table 6.11-1 (Metric Units). UNCONTROLLED EMISSION FACTORS FOR CRUDE TEREPHTHALIC ACID MANUFACTURE^a

EMISSION FACTOR RATING: C

Emission Source	Stream Designation (Figure 6.11-1)	Emissions (g/kg)	
		Nonmethane VOC ^{b,c}	CO ^c
Reactor vent	A	15	17
Crystallization, separation, drying vent	B	1.9	NA
Distillation and recovery vent	C	1.1	NA
Product transfer vent ^d	D	1.8	2

^a Factors are expressed as g of pollutant/kg of product produced. NA = not applicable.

^b Reference 1. VOC gas stream consists of methyl acetate, *p*-xylene, and acetic acid. No methane was found.

^c Reference 1. Typically, thermal oxidation results in >99% reduction of VOC and CO. Carbon adsorption gives a 97% reduction of VOC only (Reference 1).

^d Stream contains 0.7 g of TPA particulates/kg. VOC and CO emissions originated in reactor offgas (IG) used for transfer.

References For Section 6.11

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3. J. W. Pervier, *et al.*, *Survey Reports On Atmospheric Emissions From The Petrochemical Industry, Volume II*, EPA-450/3-73-005b, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1974.