



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

1. S. W. Dylewski, *Organic Chemical Manufacturing, Volume 7: Selected Processes*, EPA-450/3-80-028b, U. S. Environmental Protection Agency, Research Triangle Park, NC, January 1981.
2. D. F. Durocher, *et al.*, *Screening Study To Determine Need For Standards Of Performance For New Sources Of Dimethyl Terephthalate And Terephthalic Acid Manufacturing*, EPA Contract No. 68-02-1316, Radian Corporation, Austin, TX, July 1976.
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.