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TEREPHTHALIC ACID
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Organic Chemical Manufacturing Volume 7: Selected Processes

Emission Standards and Engineering Division

**U.S. ENVIRONMENTAL PROTECTION AGENCY
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III. PROCESS DESCRIPTION

INTRODUCTION

The DMT or TPA used to make polyester must be of very high purity.¹ Crude terephthalic acid (C-TPA) that was formerly made by nitric acid oxidation of p-xylene contained impurities that were unacceptable to the polyester industry. The methanol esterification process for dimethyl terephthalate (DMT) provides a means of removing these impurities from C-TPA and produces a product of acceptable quality.²

(C-TPA made by air oxidation of p-xylene is of higher quality than that made by nitric acid oxidation but still requires purification for use in polyester fibers.) This can be done by esterification with methanol,³ as discussed above, or by hydrogenation and crystallization from water.^{1,2,4}

Another commercial route for producing DMT of polyester fiber quality is by air oxidation of a mixture of p-xylene and methyl toluate to toluic acid and monomethyl terephthalate, respectively, and subsequent methanol esterification. The methyl toluate that is formed in esterification is recycled to oxidation, and the DMT is recovered and purified by distillation.^{1,2,5}

This report is primarily concerned with the air-oxidation process for C-TPA, the methanol esterification process for DMT, and the hydrogenation and crystallization process for purified terephthalic acid (P-TPA). The process for oxidation of a mixture of p-xylene and methyl toluate as practiced by Hercofina is not likely to be selected for new construction. The nitric acid oxidation process for C-TPA is no longer practiced domestically^{1,6} and is not further considered in this report.

B. AIR-OXIDATION PROCESS FOR C-TPA

The model continuous process for the manufacture of C-TPA is shown in Fig. III-1. The oxidation and product recovery portion is essentially as is practiced by Amoco Chemicals, whereas the recovery and recycle of acetic acid and recovery of methyl acetate are essentially as practiced by Carolina Eastman.^{3,4}

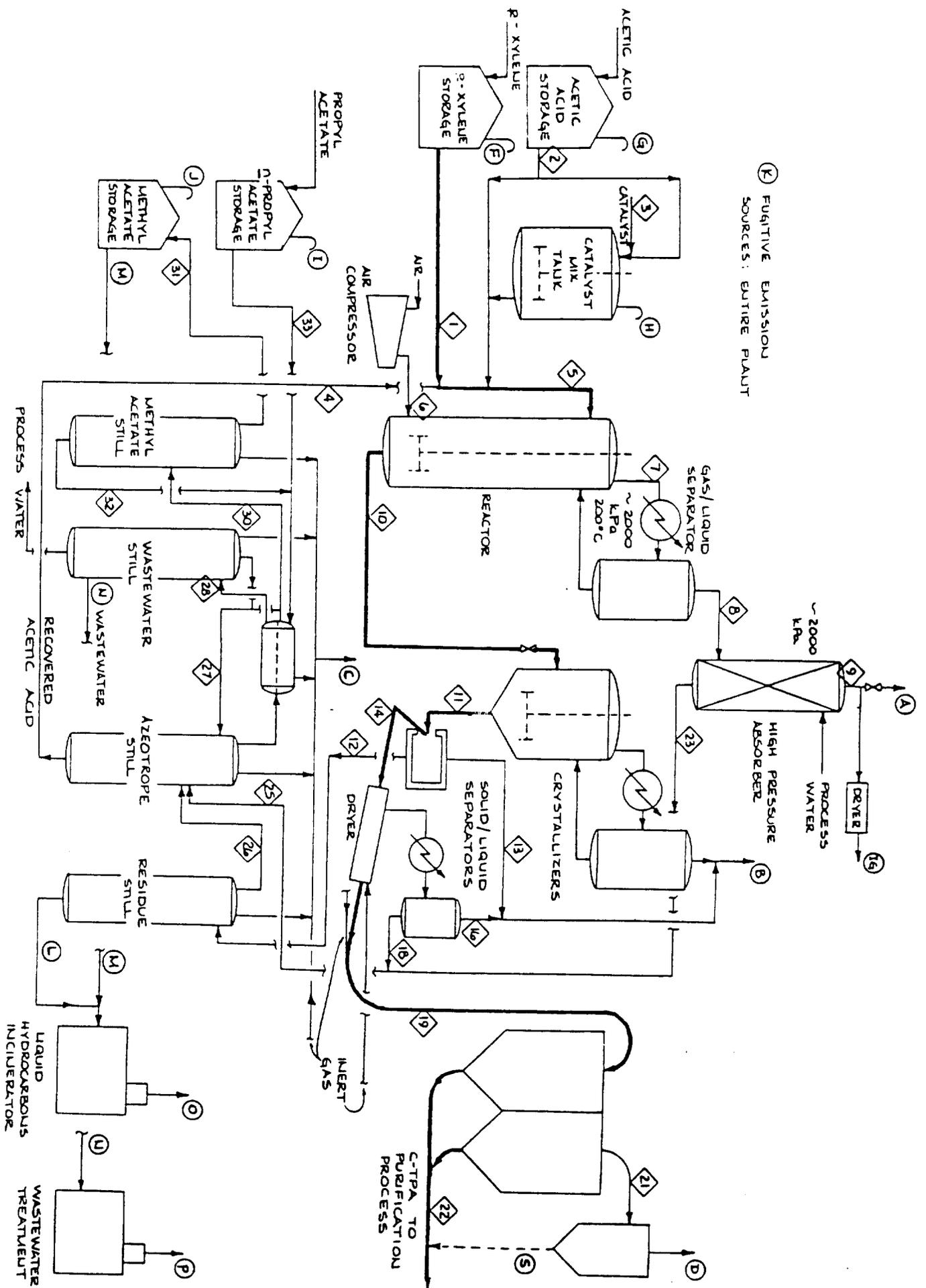
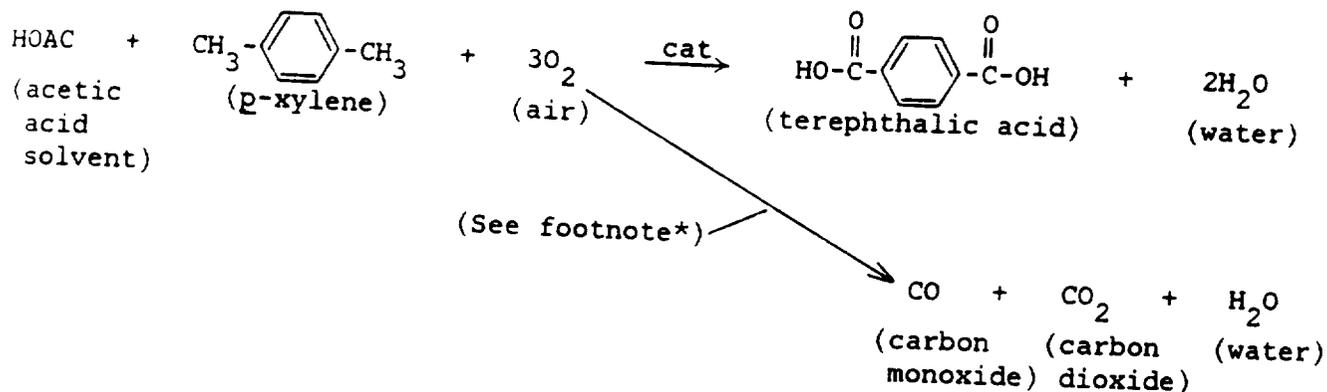


Fig. III-1. Crude Terephthalic Acid Process

Chemistry



Products of partial oxidation of p-xylene, such as p-toluic acid and p-formyl benzoic acid, are formed, with some of them appearing as impurities in TPA. Methyl acetate is also formed in significant amounts in the reaction.

2. Oxidation of p-Xylene

p-Xylene (stream 1), fresh acetic acid (stream 2), a catalyst system (stream 3), such as manganese or cobalt acetate and sodium bromide,⁷ and recovered acetic acid (stream 4) are combined to comprise the liquid stream entering the reactor (stream 5). Air (stream 6), compressed to reaction pressure (about 2000 kPa), is fed to the reactor. The temperature of the exothermic reaction is maintained at about 200°C by controlling the pressure at which the reaction mixture is permitted to boil and form the vapor stream (stream 7) leaving the reactor.

Inert gases, excess oxygen, CO, CO₂, and volatile organic compounds (VOC) (stream 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 (stream 9) with 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 (vent A). The underflow (stream 23) from the absorber is sent to the azeotrope still for recovery of acetic acid.

3. Crystallization and Separation

The reactor liquid containing TPA (stream 10) flows to a series of crystallizers, where the pressure is relieved and the liquid is cooled by the vaporization and

*Minor reaction.

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

4. Drying, Handling, and Storage

The wet cake (stream 14) from solid-liquid separation is sent to dryers, where with the use of heat and IG the moisture, predominantly acetic acid, is removed, leaving the product, C-TPA, as a dry flowable solid (stream 19).

The hot, VOC-laden IG is cooled to condense and recover VOC (stream 18). The cooled IG (stream 16) is vented to the atmosphere (vent B). The condensate (stream 18) is sent to the azeotrope still for recovery of acetic acid. IG is used to convey the product (stream 19) to storage silos. The transporting gas (stream 21) is vented from the silos to dust collectors (bag-type), where its particulate loading is reduced. It is then discharged to the atmosphere (vent D). The solids (S) from the bag filter can be forwarded to purification or be disposed of by incineration.

5. Distillation and Recovery

The mother liquor (stream 12) from solid-liquid separation flows to the residue still, where acetic acid, methyl acetate, and water are recovered overhead (stream 26). The bottoms (stream L) from the still contain the products of partial oxidation, tars, catalyst residue, and some acetic acid and are sent to a liquid-waste incinerator for destruction. The overhead (stream 26) from the still and the streams (25) from the high-pressure scrubber and the product dryer are processed in the azeotrope still to remove water as an overhead stream and produce a bottoms acetic acid stream (stream 4) essentially free of water.)
n-Propyl acetate, used as an azeotroping agent to facilitate the separation, enters the azeotrope still through stream 27. The vapors from the still containing water, n-propyl acetate, and methyl acetate are condensed and decanted.

The aqueous phase (stream 28) is forwarded to the wastewater still, whereas the organic phase (stream 27), mainly n-propyl acetate, is returned to the azeotrope still. The aqueous phase (stream 28) contains saturation amounts of n-propyl acetate and methyl acetate, which are stripped from the aqueous phase in the wastewater still. Part of the bottoms product is used as process water in absorption and the remainder (N) is sent to wastewater treatment. A purge stream of the organic phase (stream 30) is sent to the methyl acetate still, where methyl acetate and saturation amounts of water are recovered as an overhead product (stream 31) and disposed of as a fuel (discharge M). n-Propyl acetate, obtained as the bottoms product (stream 32), is returned to the azeotrope still. A small amount of inert gas, which is used for blanketing and instrument purging, is emitted to the atmosphere (vent C).) Process losses of n-propyl acetate are made up from storage (stream 33).

C. PROCESS VARIATION

In the model plant, acetic acid, used as a reaction solvent, is supplied as a raw material to replace losses of acetic acid as oxidation products and to emissions. A variation practiced by Carolina Eastman³ is the use of acetaldehyde as a source of acetic acid for the replacements of losses. Carolina Eastman uses a somewhat different catalyst system including bromine in the form of HBr, whereas others use a bromine salt. Otherwise, the processes are very similar.

The process used by Hercofina is different from the model plant in the majority of its processing steps. Air is used for oxidation of the p-xylene as in the model plant; however, in the Hercofina process the oxidation is conducted in an excess of methyl toluate solvent, where methyl toluate is oxidized to monomethyl terephthalate. Monomethyl terephthalate, which is the main oxidation product, is esterified subsequently to DMT; terephthalic acid is not recovered as a product or intermediate in this process.

D. DMT BY ESTERIFICATION OF C-TPA

The purpose of the typical process as shown in Fig. III-2 is to convert the terephthalic acid contained in C-TPA to a form that will permit its separation from the impurities. This process is representative of current DMT technology. Terephthalic acid is converted to the dimethyl ester and is separated by fractional distillation.

2. Sources and Emissions

Emission sources and quantities for the C-TPA process are summarized in Table I

- a. Reactor Vent—The reactor vent gas (A, Fig. III-1) contains nitrogen (from air oxidation); unreacted oxygen; unreacted p-xylene; acetic acid (reaction solvent carbon monoxide, carbon dioxide, and methyl acetate resulting from oxidation of p-xylene and acetic acid that are not recovered by the high-pressure absorber; and water, some of which results from oxidation and some from evaporation during absorption with water in the high-pressure absorber. Table IV-2 gives the composition of this stream based on consideration of data from several sources.^{3,4,7,8} The quantity of VOC emitted at vent A can be higher if the absorber is operated at a lower pressure than that in the model plant. The quantity can also vary with the temperature of the exiting vent gases.)
- b. Crystallization, Separation, and Drying Vent—The gases vented from the crystallization of terephthalic acid and the separation of the crystallized solids from the solvent by centrifugation or by filtration are the noncondensable gases that are released during crystallization and the VOC vapors that are carried by those gases. These vent gases and the C-TPA dryer vent gas are combined and released to the atmosphere (B, Fig. III-1). Different methods employed in this processing section can result in less noncondensable gases and less accompanying VOC being emitted from this vent. However, the VOC emission from the reactor vent may be commensurately increased.^{3,4,7,8}
- c. Distillation and Recovery Vent (C, Fig. III-1)—The gases vented from the distillation section are the small amount of gases dissolved in the feed stream to distillation, the inert gas used in inert blanketing, in instrument purging, and in pressure control, and the VOC vapors that are carried by the noncondensable gases. The quantity of this discharge is normally small.^{3,4,7,8}
- d. Product Transfer Vent—The gas vented (D Fig. III-1) from the bag filters on the product storage tanks (silos) is dry, reaction-generated, inert gas containing the VOC that were 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.^{3,4,7}

Table IV-1. Uncontrolled VOC Emissions from
Crude Terephthalic Acid Model Plant

Emission Source	Stream Designation (Fig.III-1)	Emissions			
		Ratio (g/kg) ^a		Rate (kg/hr) ^b	
		VOC	CO	VOC	CO
Reactor vent	A	14.6	17	383.3	446
Crystallization, separation, and drying vent	B	1.9		49.9	
Distillation and recovery vent	C	1.14		29.9	
Product transfer vent ^c	D	1.78 ^d	2	46.7 ^d	53
Storage and handling					
Raw material storage	F,G,I	0.112		2.94	
Other storage	H,J	0.006		0.17	
Fugitive	K	0.58		15.26	
Secondary					
Incinerator	L	0.00482		0.126	
	M	0.00123		0.0323	
Wastewater treatment	N	<0.004		<0.1	
Total		20.13	19	528.4	499

^a g of emission per kg of product produced.

^b Based on 8760 hr of operation per year.

^c Stream contains 0.7 g of TPA particulates/kg; not included.

^d VOC and CO emissions originated in reactor off-gas used for transfer.

V. APPLICABLE CONTROL SYSTEMS

A. CRUDE TEREPHTHALIC ACID PROCESS

1. Reactor Vent and Product Transfer Vent

There is demonstrated performance of carbon adsorption of VOC from a gas stream similar to the reactor vent gas and product transfer vent gas (A and D, respectively, Fig. III-1).¹ It is estimated that the vent stream from the model plant will perform similarly in carbon adsorption and effect a VOC emission reduction of 97% or greater. It should be noted that the CO emissions will not be reduced by carbon adsorption.

The reactor vent gas passes through one of the carbon beds, where the VOC are adsorbed, and is then released to the atmosphere. When the first carbon bed approaches breakthrough, the feed gas is routed to another carbon bed. At this point regeneration of the first bed by steam stripping is started. The VOC-laden stripping steam is then condensed and decanted. The p-xylene layer is returned to the reactor section, and the aqueous layer is forwarded to distillation for recovery of the water-soluble VOC. When essentially all the VOC are stripped from the first bed, a purge stream of VOC-depleted effluent from the second bed is forced by a blower through the first bed to purge the remaining VOC and to cool the bed for adsorption.

An alternative to the carbon adsorption system employed in the controlled model plant is a thermal oxidizer. With a properly designed system operating at 1100°C for efficient CO destruction, a reduction of 99% or greater in VOC and in CO can be achieved. Because of the high percentage of nitrogen present in the vent gas, 176 GJ of supplemental fuel per hour is needed to achieve the desired temperature. Although 133 GJ/hr of energy as steam can be recovered, the energy requirement balance of the plant needs to be considered. Thermal oxidation is covered by a separate EPA report.²

A reduction in emissions from vents A and D can be achieved by a change in the high-pressure absorber in the model plant by providing a compound system rather than the usual multistage system wherein the liquor from the lower portion is largely recycled and the upper portion is irrigated by once-through water, as is practiced by Carolina Eastman.³ This modification could reduce VOC

H. REFERENCES*

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.