6.6.2 Poly(ethylene Terephthalate)¹⁻²

6.6.2.1 General

Poly(ethylene terephthalate), or PET, is a thermoplastic polyester resin. Such resins may be classified as low-viscosity or high-viscosity resins. Low-viscosity PET typically has an intrinsic viscosity of less than 0.75, while high-viscosity PET typically has an intrinsic viscosity of 0.9 or higher. Low-viscosity resins, which are sometimes referred to as "staple" PET (when used in textile applications), are used in a wide variety of products, such as apparel fiber, bottles, and photographic film. High-viscosity resins, sometimes referred to as "industrial" or "heavy denier" PET, are used in tire cord, seat belts, and the like.

PET is used extensively in the manufacture of synthetic fibers (i. e., polyester fibers), which compose the largest segment of the synthetic fiber industry. Since it is a pure and regulated material meeting FDA food contact requirements, PET is also widely used in food packaging, such as beverage bottles and frozen food trays that can be heated in a microwave or conventional oven. PET bottles are used for a variety of foods and beverages, including alcohol, salad dressing, mouthwash, syrups, peanut butter, and pickled food. Containers made of PET are being used for toiletries, cosmetics, and household and pharmaceutical products (e. g., toothpaste pumps). Other applications of PET include molding resins, X-ray and other photographic films, magnetic tape, electrical insulation, printing sheets, and food packaging film.

6.6.2.2 Process Description³⁻¹⁵

PET resins are produced commercially from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). DMT and TPA are solids. DMT has a melting point of 140°C (284°F), while TPA sublimes (goes directly from the solid phase to the gaseous phase). Both processes first produce the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer and either methanol (DMT process) or water (TPA process). The BHET monomer is then polymerized under reduced pressure with heat and catalyst to produce PET resins. The primary reaction for the DMT process is:

$$\begin{array}{c} \mathrm{CH_3OOC} & \bigodot \mathrm{COOCH_3} + \mathrm{HOCH_2CH_2OH} \\ \mathbf{DMT} & \mathbf{EG} \end{array} \\ \mathbf{PET} \\ \end{array} \\ \mathrm{PET} \\ \end{array} \\ \mathrm{PET}$$

The primary reaction for the TPA process is:

Both processes can produce low- and high-viscosity PET. Intrinsic viscosity is determined by the high polymerizer operating conditions of: (1) vacuum level, (2) temperature, (3) residence time, and (4) agitation (mechanical design).

The DMT process is the older of the two processes. Polymerization grade TPA has been available only since 1963. The production of methanol in the DMT process creates the need for methanol recovery and purification operations. In addition, this methanol can produce major VOC emissions. To avoid the need to recover and purify the methanol and to eliminate the potential VOC emissions, newer plants tend to use the TPA process.

DMT Process -

Both batch and continuous operations are used to produce PET using DMT. There are three basic differences between the batch process and continuous process: (1) a column-type reactor replaces the kettle reactor for esterification (ester exchange between DMT and ethylene glycol), (2) "no-back-mix" (i. e., no stirred tank) reactor designs are required in the continuous operation, and (3) different additives and catalysts are required to ensure proper product characteristics (e. g., molecular weight, molecular weight distribution).

Figure 6.6.2-1 is a schematic representation of the PET/DMT continuous process, and the numbers and letters following refer to this figure. Ethylene glycol is drawn from raw material storage (1) and fed to a mix tank (2), where catalysts and additives are mixed in. From the mix tank, the mixture is fed, along with DMT, to the esterifiers, also known as ester exchange reactors (3). About 0.6 pounds (lb) of ethylene glycol and 1.0 lb of DMT are used for each pound of PET product. In the esterifiers, the first reaction step occurs at an elevated temperature (between 170 and 230°C [338 and 446°F]) and at or above atmospheric pressure. This reaction produces the intermediate BHET monomer and the byproduct methanol. The methanol vapor must be removed from the esterifiers to shift the conversion to produce more BHET.

The vent from the esterifiers is fed to the methanol recovery system (11), which separates the methanol by distillation in a methanol column. The recovered methanol is then sent to storage (12). Vapor from the top of the methanol column is sent to a cold water (or refrigerated) condenser, where the condensate returns to the methanol column, and noncondensables are purged with nitrogen before being emitted to the atmosphere. The bottom product of methanol column, mostly ethylene glycol from the column's reboiler, is reused.

The BHET monomer, with other esterifier products, is fed to a prepolymerization reactor (4) where the temperature is increased to 230 to 285°C (446 to 545°F), and the pressure is reduced to between 1 and 760 millimeters (mm) of mercury (Hg) (typically, 100 to 200 mm Hg). At these operating conditions, residual methanol and ethylene glycol are vaporized, and the reaction that produces PET resin starts.

Product from the prepolymerizer is fed to one or more polymerization reactors (5), in series. In the polymerization reactors, sometimes referred to as end finishers, the temperature is further increased to 260 to 300°C (500 to 572°F). The pressure is further reduced (e. g., to an absolute pressure of 4 to 5 mm Hg). The final temperature and pressure depend on whether low- or high-viscosity PET is being produced. For high-viscosity PET, the pressure in the final (or second) end finisher is less than 2 mm Hg. With high-viscosity PET, more process vessels are used than low-viscosity PET to achieve the higher temperatures and lower pressures needed.

The vapor (ethylene glycol, methanol, and other trace hydrocarbons from the prepolymerization and polymerization reactors) typically is evacuated through scrubbers (spray condensers) using spent ethylene glycol. The recovered ethylene glycol is recirculated in the scrubber system, and part of the spent ethylene glycol from the scrubber system is sent to storage in process tanks (13), after which it is sent to the ethylene glycol recovery system (14).

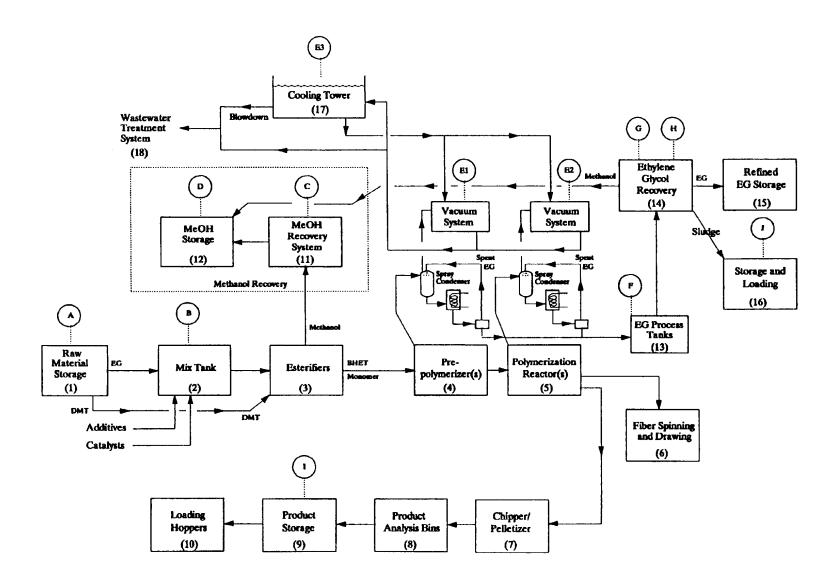


Figure 6.6.2-1. Simplified flow diagram of PET/DMT continuous process.

The ethylene glycol recovery system (14) usually is a distillation system composed of a low boiler column, a refining column, and associated equipment. In such a system, the ethylene glycol condensate is fed to the low boiler column. The top product from this column is sent to a condenser, where methanol is condensed and sent to methanol storage. The noncondensable vent (from the low boiler condenser) is purged with nitrogen and sent to the atmosphere (Stream G in the flow diagram). The bottom product of the low boiler column goes to its reboiler, with the vapor recycled back to the low boiler column and the underflow sent to the refining column. The refining column is under vacuum and is evacuated to the atmosphere. Top product from the refining column goes through a condenser, and the condensate is collected in a reflux tank. Part of the ethylene glycol condensate returns to the refining column. The remaining liquid goes to refined ethylene glycol storage (15). The reflux tank is purged with nitrogen. (The purge gas vented to the atmosphere from the reflux tank consists of only nitrogen.) The bottom product of the refining column goes to a reboiler, vapor returns to the column, and what remains is a sludge byproduct (16).

The vacuum conditions in the prepolymerization and polymerization reactors are created by means of multistage steam jet ejector (venturi) systems. The vacuum system typically is composed of a series of steam jets, with condensers on the discharge side of the steam jet to cool the jets and to condense the steam. The condensed steam from the vacuum jets and the evacuated vapors are combined with the cooling water during the condensation process. This stream exiting the vacuum system goes either to a cooling tower (17), where the water is cooled and then recirculated through the vacuum system, or to a waste water treatment plant (once-through system) (18).

Product from the polymerization reactor (referred to as the polymer melt) may be sent directly to fiber spinning and drawing operations (6). Alternatively, the polymer melt may be chipped or pelletized (7), put into product analysis bins (8), and then sent to product storage (9) before being loaded into hoppers (10) for shipment to the customer.

TPA Process -

Figure 6.6.2-2 is a schematic diagram of a continuous PET/TPA process, and the numbers and letters following refer to this figure. Raw materials are brought on site and stored (1). Terephthalic acid, in powder form, may be stored in silos. The ethylene glycol is stored in tanks. The terephthalic acid and ethylene glycol, containing catalysts, are mixed in a tank (2) to form a paste. In the mix tank, ethylene glycol flows into a manifold that sprays the glycol through many small slots around the periphery of the vent line. The terephthalic acid and ethylene glycol are mixed by kneading elements working in opposite directions. Combining these materials into a paste is a simple means of introducing them to the process, allowing more accurate control of the feed rates to the esterification vessels. A portion of the paste is recycled to the mix tank. This paste recycle and feed rates of TPA and ethylene glycol are used to maintain an optimum paste density or weight percent of terephthalic acid.

The paste from the mix tanks is fed, using gear pumps to meter the flow, to a series of esterification vessels (referred to as esterifiers, or ester exchange reactors). Two or more esterifiers may be used. Residence time is controlled by valves in the transfer lines between each vessel. These esterifiers are closed, pressurized reactors. Pressure and temperature operating conditions in the primary esterifier (3) are between 30 and 50 pounds per square inch gauge (psig) and 230 to 260°C (446 to 500°F), respectively. Vapors, primarily water (steam) and glycol, are vented to a reflux column or distillation column. A heat exchanger cools the vapors. Recovered glycol is returned to the primary esterifier. The water vapor is condensed using 29°C (85°F) cooling water in a shell-and-tube condenser and then is discharged to the waste water treatment system. The monomer formed in the primary esterifier and the remaining reactants are pumped to the secondary esterifier.

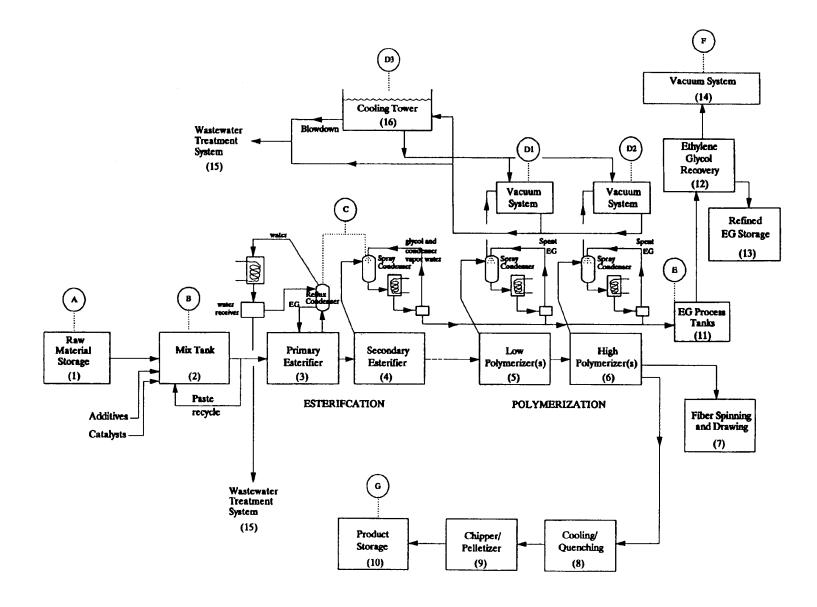


Figure 6.6.2-2. Simplified flow diagram of PET/TPA continuous process.

The secondary esterifier (4) is operated at atmospheric pressure and at a temperature of 250 to 270 °C (482 to 518 °F). The vapors from the secondary esterifier, primarily water vapor, are vented to a spray condenser, and this condensate is sent to a central ethylene glycol recovery unit (12). The condensate water is cooled by cooling water in a shell-and-tube heat exchanger and then recycled.

At one plant, the secondary esterifiers for the staple PET lines have a manhole (or rotary valve on some lines) through which chips and reworked yarn pellets are recycled. These manholes are not present on the secondary esterifiers for the industrial PET lines. Water vapor and monomer are emitted from the manholes, and the monomer sublimates on piping near the manhole.

Monomer (BHET) from the secondary esterifier is then pumped to the polymerization reactors. The number of reactors and their operating conditions depends on the type of PET being produced. Typically, there will be at least two polymerization reaction vessels in series, an initial (low) polymerizer and a final (high) polymerizer. The former is sometimes referred to as a prepolymerizer or a prepolycondensation reactor. The latter is sometimes called an end finisher. In producing high-viscosity PET, a second end finisher is sometimes used.

In the initial (low) polymerizer (5), esterification is completed and polymerization occurs (i. e., the joining of short molecular chains). Polymerization is "encouraged" by the removal of ethylene glycol. This reactor is operated under pressures of 20 to 40 mm Hg and at 270 to 290°C (518 to 554°F) for staple (low-viscosity) PET, and 10 to 20 mm Hg and 280 to 300°C (536 to 572°F) for industrial filament PET. The latter conditions produce a longer molecule, with the greater intrinsic viscosity and tenacity required in industrial fibers. Glycol released in the polymerization process and any excess or unreacted glycol are drawn into a contact spray condenser (scrubber) countercurrent to a spent ethylene glycol spray. (At one facility, both the low and high polymerizer spray condensers have four spray nozzles, with rods to clear blockage by solidified polymer. Care is taken to ensure that the spray pattern and flow are maintained.) Recovered glycol is pumped to a central glycol recovery unit, a distillation column. Vacuum on the reactors is maintained by a series of steam jets with barometric intercondensers. At one plant, a two-stage steam ejector system with a barometric intercondenser is used to evacuate the low polymerizer. The condensate from the intercondensers and the last steam jets is discharged to an open recirculating water system, which includes an open trough (referred to as a "hot well") and cooling tower. The recirculation system supplies cooling water to the intercondensers.

In the production of high-viscosity PET, the polymer from the low polymerizer is pumped to a high polymerizer vessel (6). In the high polymerizer, the short polymer chains formed in the low polymerizer are lengthened. Rotating wheels within these vessels are used to create large surface exposure for the polymer to facilitate removal of ethylene glycol produced by the interchange reaction between the glycol ester ends. The high polymerizer is operated at a low absolute pressure (high vacuum), 0.1 to 1.0 mm Hg, and at about 280 to 300°C (536 to 572°F). Vapors evolved in the high polymerizer, including glycol, are drawn through a glycol spray condenser. If very "hard" vacuums are drawn (e. g., 0.25 mm Hg), such spray condensers are very difficult, if not impossible, to use. At least one facility does not use any spray condensers off the polymerizers (low and high). Recovered glycol is collected in a receiver and is pumped to a central ethylene glycol recovery unit. At one plant, chilled water between -3.9 and 1.7°C (25 and 35°F) is used on the heat exchanger associated with the high polymerizer spray condenser.

At least one facility uses two high polymerizers (end finishers) to produce high-viscosity PET. At this plant, the first end finisher is usually operated with an intermediate vacuum level of about 2 mm Hg. The polymer leaving this reactor then enters a second end finisher, which may have a vacuum level as low as 0.25 mm Hg.

Vapors from the spray condenser off the high polymerizers are also drawn through a steam jet ejector system. One facility uses a five-jet system. After the first three ejectors, there is a barometric intercondenser. Another barometric intercondenser is located between the fourth and fifth ejectors. The ejectors discharge to the cooling water hot well. The stream exiting the vacuum system is sent either to a cooling tower (16) where the water is recirculated through the vacuum system, or to a waste water treatment plant (once-through system) (15).

Vacuum pumps were installed at one plant as an alternative to the last two ejectors. These pumps were installed as part of an energy conservation program and are used at the operator's discretion. The vacuum pumps are operated about 50 percent of the time. The vacuum system was designed for a maximum vapor load of about 10 kilograms per hour (kg/hr). If vacuum is lost, or is insufficient in the low or high polymerizers, off-specification product results. Each process line has a dual vacuum system. One five-stage ejector/vacuum pump system is maintained as a standby for each industrial filament (high-viscosity) process line. The staple (low-viscosity) lines have a standby ejector system, but with only one vacuum pump per process line. Steam ejectors reportedly recover faster from a slug of liquid carryover than do vacuum pumps, but the spare system is used in the production of either high- or low-viscosity PET.

At many facilities, molten PET from the high polymerizer is pumped at high pressure directly through an extruder spinerette, forming polyester filaments (7). The filaments are air cooled and then either cut into staple or wound onto spools. Molten PET can also be pumped out to form blocks as it cools and solidifies (8), which are then cut into chips or are pelletized (9). The chips or pellets are stored (10) before being shipped to the customer, where they are remelted for end-product fabrication.

Ethylene glycol recovery (12) generally involves a system similar to that of the DMT process. The major difference is the lack of a methanol recovery step. At least one TPA facility has a very different process for ethylene glycol recovery. At this plant, ethylene glycol emissions from the low and high polymerizers are allowed to pass directly to the vacuum system and into the cooling tower. The ethylene glycol is then recovered from the water in the cooling tower. This arrangement allows for a higher ethylene glycol concentration in the cooling tower.

6.6.2.3 Emissions And Controls^{3,5,11,13,16-21}

Table 6.6.2-1 shows the VOC and particulate emissions for the PET/DMT continuous process, with similar levels expected for batch processes. The extensive use of spray condensers and other ethylene glycol and methanol recovery systems is economically essential to PET production, and these are not generally considered "controls".

Total VOC emissions will depend greatly on the type of system used to recover the ethylene glycol from the prepolymerizers and polymerization reactors, which give rise to emission streams E1, E2, E3, F, G, H, and J. The emission streams from the prepolymerizers and polymerization reactors are primarily ethylene glycol, with small amounts of methanol vapors and volatile impurities in the raw materials. Of these emission streams, the greatest emission potential is from the cooling tower (Stream E3). The amount of emissions from the cooling tower depends on a number of factors, including ethylene glycol concentration and windage rate. The ethylene glycol concentration depends on a number of factors, including use of spray condensers off the polymerization vessels, circulation rate of the cooling water in the cooling tower, blowdown rate (the rate are which water is drawn out of the cooling tower), and sources of water to cooling tower (e. g., dedicated cooling tower versus plant-side cooling tower).

Table 6.6.2-1 (Metric Units). EMISSION FACTORS FOR PET/DMT PROCESS^a

Stream Identification	Emission Stream	Nonmethane VOC ^b	Particulate	EMISSION FACTOR RATING	References
A	Raw material storage	0.1	0.165 ^c	С	17
В	Mix tanks	negligible ^d	ND	С	13
С	Methanol recovery system	0.3 ^e	ND	С	3, 17
D	Recovered methanol storage	0.09 ^f	ND	С	3, 17
Е	Polymerization reaction				
E1	Prepolymerizer vacuum system	0.009	ND	С	17
E2	Polymerization reactor vacuum system	0.005	ND	С	17
E3	Cooling tower ^g	0.2 3.4	ND	С	18 - 19
F	Ethylene glycol process tanks	0.0009	ND	С	17
G	Ethylene glycol recovery condenser	0.01	ND	С	17
Н	Ethylene glycol recovery vacuum system	0.0005	ND	С	17
I	Product storage	ND	0.0003 ^h	С	17
J	Sludge storage and loading	0.02	ND	С	17
Total Plant		0.73 ^j 3.9 ^k	0.17		

^a Stream identification refers to Figure 6.6.2-1. Units are grams per kilogram of product. ND = no data.

$$E = [EG_{wt\%} \times CT_{cr} \times 60 \times WR] \times [(4.2 \times EG_{wt\%}) + (3.78 \times H_2O_{wt\%})]$$

^b Rates reflect extensive use of condensers and other recovery equipment as part of normal industry economical practice.

^c From storage of DMT.

d Assumed same as for TPA process.

^e Reference 3. For batch PET production process, estimated to be 0.15 grams VOC per kilogram of product.

f Reflects control by refrigerated condensers.

Based on ethylene glycol concentrations at two PET/TPA plants. The lower estimate reflects emissions where spray condensers are used off the prepolymerizers and the polymerization reactors. The higher estimate reflects emissions where spray condensers are not used off the prepolymerizers and the polymerization reactors. A site-specific calculation is highly recommended for all cooling towers, because of the many variables. The following equation may be used to estimate windage emissions from cooling towers:

where:

E = Mass of VOC emitted (kilograms per hour)

 $EG_{wt\%}$ = Concentration of ethylene glycol, weight percent (fraction)

60 = Minutes per hour

 CT_{cr} = Cooling tower circulation rate, gallons per minute

WR = Windage rate, fraction

4.2 = Density of ethylene glycol (kilograms per gallon)

3.78 = Density of water (kilograms per gallon)

 $H_2O_{wt\%}$ = Concentration of water, weight percent (fraction)

Example: The VOC emissions from a cooling tower with an ethylene glycol concentration of 8.95% by weight, a water concentration of 91.05% by weight, a cooling tower circulation rate of 1270 gallons per minute, and a windage rate of 0.03% are estimated to be:

 $E = [0.0895 \times 1270 \times 60 \times 0.0003] \times [(4.2 \times 0.0895) + (3.78 \times 0.9105)]$

= 7.8 kilograms per hour

Most plants recover the ethylene glycol by using a spent ethylene glycol spray scrubber condenser directly off these process vessels and before the stream passes through the vacuum system. The condensed ethylene glycol may then be recovered through distillation. This type of recovery system results in relatively low concentrations of ethylene glycol in the cooling water at the tower, which in turn lowers emission rates for the cooling tower and the process as a whole. At one PET/TPA plant, a typical average concentration of about 0.32 weight percent ethylene glycol was reported, from which an emission rate of 0.2 grams VOC per kilogram (gVOC/kg) of product was calculated.

Alternatively, a plant may send the emission stream directly through the vacuum system (typically steam ejectors) without using spent ethylene glycol spray condensers. The steam ejectors used to produce a vacuum will produce contaminated water, which is then cooled for reuse. In this system, ethylene glycol is recovered from the water in the cooling tower by drawing off water from the tower (blowdown) and sending the blowdown to distillation columns. This method of recovering ethylene glycol can result in much higher concentrations of ethylene glycol in the cooling tower than when the ethylene glycol is recovered with spray condensers directly off the process vessels. (The actual concentration of ethylene glycol in the cooling water depends, in part, on the blowdown rate.) Higher concentrations in the cooling tower result in greater ethylene glycol emissions from the cooling tower and, in turn, from the process as a whole. At one PET/TPA plant recovering the ethylene glycol from the cooling tower, emissions from the cooling tower were approximately 3.4 gVOC/kg of product.

h Emission rate is for "controlled" emissions. Without controls, the estimated emission rate is 0.4 grams per kilogram of product.

^j With spray condensers off all prepolymerizers and the polymerization reactors.

^k With no spray condensers off all prepolymerizers and the polymerization reactors.

Next to the cooling tower, the next largest potential emission source in the PET/DMT process is the methanol recovery system. Methanol recovery system emissions (Stream C) from a plant using a continuous process are estimated to be approximately 0.3 gVOC/kg of product and about 0.09 gVOC/kg of product from the recovered methanol storage tanks. The emissions from the methanol recovery system (Stream C) for a batch process were reported to be 0.15 gVOC/kg of product, and typically are methanol and nitrogen.

The other emission streams related to the prepolymerizer and polymerization reactors are collectively relatively small, being about 0.04 gVOC/kg of product. VOC emissions from raw material storage (mostly ethylene glycol) are estimated to be about 0.1 gVOC/kg of product. Fixed roof storage tanks (ethylene glycol) and bins (DMT) are used throughout the industry. Emissions are vapors of ethylene glycol and DMT result from vapor displacement and tank breathing. Emissions from the mix tank are believed to be negligible.

Particulate emissions occur from storage of both raw material (DMT) and end product. Those from product storage may be controlled before release to the atmosphere. Uncontrolled particulate emissions from raw material storage are estimated to be approximately 0.17 g/kg of product. Particulate emissions from product storage are estimated to be approximately 0.0003 g/kg of product after control and approximately 0.4 g/kg of product before control.

Total VOC emissions from a PET/DMT continuous process are approximately 0.74 gVOC/kg of product if spray condensers are used off all of the prepolymerizers and polymerization reaction vessels. For a batch process, this total decreases to approximately 0.59 gVOC/kg of product. If spray condensers are not used, the ethylene glycol concentration in the cooling tower is expected to be higher, and total VOC emissions will be greater. Calculation of cooling tower emissions for site-specific plants is recommended. Total particulate emissions are approximately 0.17 g/kg of product, if product storage emissions are controlled.

Table 6.6.2-2 summarizes VOC and particulate emissions for the PET/TPA continuous process, and similar emission levels are expected for PET/TPA batch processes. VOC emissions are generally "uncontrolled", in that the extensive use of spray condensers and other ethylene glycol recovery systems are essential to the economy of PET production.

Emissions from raw material storage include losses from the raw materials storage and transfer (e. g., ethylene glycol). Fixed roof storage tanks and bins with conservation vents are used throughout the process. The emissions, vapors of ethylene glycol, TPA, and TPA dust, are from working and breathing losses. The VOC emission estimate for raw materials storage is assumed to be the same as that for the PET/DMT process. No emission estimate was available for the storage and transfer of TPA.

VOC emissions from the mix tank are believed to be negligible. They are emitted at ambient temperatures through a vent line from the mixer.

VOC emissions from the esterifiers occur from the condensers/distillation columns on the esterifiers. Emissions, which consist primarily of steam and ethylene glycol vapors, with small amounts of feed impurities and volatile side reaction products, are estimated to be 0.04 gVOC/kg of product. Exit temperature is reported to be approximately 104°C (220°F). At least one plant controls the primary esterifier condenser vent with a second condenser. At this plant, emissions were 0.0008 gVOC/kg of product with the second condenser operating, and 0.037 gVOC/kg of product without the second condenser operating. The temperature for the emission stream from the second

Table 6.6.2-2 (Metric Units). EMISSION FACTORS FOR PET/TPA PROCESS^a

Stream Identification	Emission Stream	Nonmethane VOC ^b	Particulate	EMISSION FACTOR RATING	References
A	Raw material storage	0.1 ^c	ND	С	17
В	Mix tanks	negligible	ND	С	13
С	Esterification	0.04 ^d	ND	A	20 - 21
D	Polymerization reaction				
D1	Prepolymerizer vacuum system	0.009 ^c	ND	С	17
D2	Polymerization reactor vacuum system	0.005 ^c	ND	С	17
D3	Cooling tower ^e	0.2 3.4	ND	С	18 - 19
Е	Ethylene glycol process tanks	0.0009 ^c	ND	С	17
F	Ethylene glycol recovery vacuum system	0.0005 ^c	ND	С	17
G	Product storage	ND	0.0003 ^{c,f}	С	17
Total Plant		0.36 ^g 3.6 ^h			

^a Stream identification refers to Figure 6.6.2⁻². Units are grams per kilogram of product. ND = no data.

condenser was reported to be 27 to 38°C (80 to 100°F). The emissions from the second condenser were composed of di-iso-propyl amine (DIPA) and acetaldehyde, with small amounts of ethylene.

^b Rates reflect extensive use of condensers and other recovery equipment as part of normal industry economical practice.

^c Assumed same as for DMT process.

d At least one plant controls the primary esterifier condenser vent with a second condenser. Emissions were 0.0008 grams VOC per kilogram of product with the second condenser operating, and 0.037 grams VOC per kilogram of product without the second condenser operating.

e Based on ethylene glycol concentrations at two PET/TPA plants. The lower estimate reflects emissions where spray condensers are used off the prepolymerizers and the polymerization reactors. The higher estimate reflects emissions where spray condensers are not used off the prepolymerizers and the polymerization reactors. It is highly recommended that a site-specific calculation be done for all cooling towers as many variables affect actual emissions. The equation found in footnote g for Table 6.6.2-1 may be used to estimate windage emissions from cooling towers.

f Reflects control of product storage emissions. Without controls, the estimated emission rate is 0.4 grams per kilogram of product.

^g With spray condensers off all prepolymerizers and the polymerization reactors.

^h With no use of spray condensers off all prepolymerizers and the polymerization reactors.

Emissions from the prepolymerizers and polymerization reaction vessels in both PET/TPA and PET/DMT processes should be very similar. The emissions were discussed earlier under the DMT process.

The estimates of VOC emissions from the ethylene glycol process tanks and the ethylene glycol recovery system, and of particulate emissions from product storage, are assumed to be the same as for the DMT process.

Total VOC emissions from the PET/TPA process are approximately 0.36 gVOC/kg of product if spray condensers are used with all of the prepolymerizers and polymerization reaction vessels. If spray condensers are not used with all of these process vessels, the concentration in the cooling tower can be expected to be higher, and total VOC emissions will be greater. For example, at one plant, emissions from the cooling tower were calculated to be approximately 3.4 gVOC/kg of product, resulting in a plantwide estimate of 3.6 gVOC/kg of product. Calculation of cooling tower emissions for site-specific plants is recommended. Excluding TPA particulate emissions (no estimate available), total particulate emissions are expected to be small.

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- 18. K. Meardon, "Revised Costs For PET Regulatory Alternatives", Docket No. A-82-19, Item II-B-90. U. S. EPA, Air Docket Section, Waterside Mall, 401 M Street, SW, Washington, DC, August 20, 1984.
- 19. Written communication from J. W. Torrance, Allied Fibers and Plastics, Petersburg, VA, to J. R. Farmer, U. S. Environmental Protection Agency, Research Triangle Park, NC, September 4, 1984.
- 20. Written communication from A. T. Roy, Allied-Signal, Petersburg, VA, to K. Meardon, Pacific Environmental Services, Inc., Durham, NC, August 18, 1989.
- 21. Telephone communication between K. Meardon, Pacific Environmental Services, Inc., Durham, NC, and A. Roy, Allied-Signal, Petersburg, VA, August 18, 1989.