6.5 Phthalic Anhydride

6.5.1 General[1]

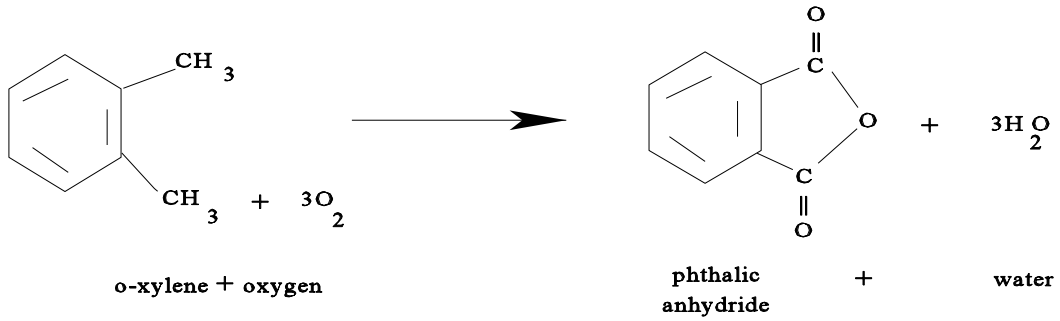
Phthalic anhydride (PAN) production in the United States in 1972 was 0.9 billion pounds per year; this total is estimated to increase to 2.2 billion pounds per year by 1985. Of the current production, 50 percent is used for plasticizers, 25 percent for alkyd resins, 20 percent for unsaturated polyester resins, and 5 percent for miscellaneous and exports. PAN is produced by catalytic oxidation of either orthoxylene or naphthalene. Since naphthalene is a higher-priced feedstock and has a lower feed utilization (about 1.0 lb PAN/lb o-xylene versus 0.97 lb PAN/lb naphthalene), future production growth is predicted to utilize o-xylene. Because emission factors are intended for future as well as present application, this report will focus mainly on PAN production utilizing o-xylene as the main feedstock.

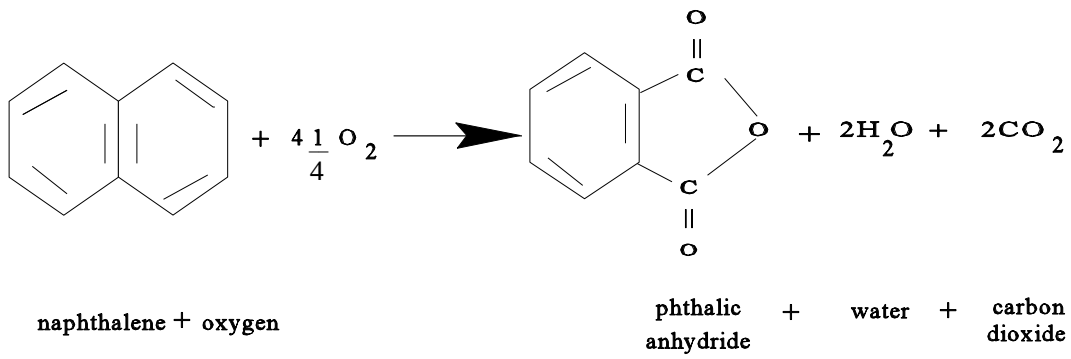
The processes for producing PAN by o-xylene or naphthalene are the same except for reactors, catalyst handling, and recovery facilities required for fluid bed reactors.

In PAN production using o-xylene as the basic feedstock, filtered air is preheated, compressed, and mixed with vaporized o-xylene and fed into the fixed-bed tubular reactors. The reactors contain the catalyst, vanadium pentoxide, and are operated at 650 to 725°F (340 to 385°C). Small amounts of sulfur dioxide are added to the reactor feed to maintain catalyst activity. Exothermic heat is removed by a molten salt bath circulated around the reactor tubes and transferred to a steam generation system.

Naphthalene-based feedstock is made up of vaporized naphthalene and compressed air. It is transferred to the fluidized bed reactor and oxidized in the presence of a catalyst, vanadium pentoxide, at 650 to 725°F (340 to 385°C). Cooling tubes located in the catalyst bed remove the exothermic heat, which is used to produce high-pressure steam. The reactor effluent consists of PAN vapors, entrained catalyst, and various byproducts and nonreactant gas. The catalyst is removed by filtering and returned to the reactor.

The chemical reactions for air oxidation of o-xylene and naphthalene are as follows.





The reactor effluent containing crude PAN plus products from side reactions and excess oxygen passes to a series of switch condensers where the crude PAN cools and crystallizes. The condensers are alternately cooled and then heated, allowing PAN crystals to form and then melt from the condenser tube fins.

The crude liquid is transferred to a pretreatment section in which phthalic acid is dehydrated to anhydride. Water, maleic anhydride, and benzoic acid are partially evaporated. The liquid then goes to a vacuum distillation section where pure PAN (99.8 wt. percent pure) is recovered. The product can be stored and shipped either as a liquid or a solid (in which case it is dried, flaked, and packaged in multi-wall paper bags). Tanks for holding liquid PAN are kept at 300°F (150°C) and blanketed with dry nitrogen to prevent the entry of oxygen (fire) or water vapor (hydrolysis to phthalic acid).

Maleic anhydride is currently the only byproduct being recovered.

Figure 6.5-1 and Figure 6.5-2 show the process flow for air oxidation of o-xylene and naphthalene, respectively.

6.5.2 Emissions And Controls[1]

Emissions from o-xylene and naphthalene storage are small and presently are not controlled.

The major contributor of emissions is the reactor and condenser effluent which is vented from the condenser unit. Particulate, sulfur oxides (for o-xylene-based production), and carbon monoxide make up the emissions, with carbon monoxide comprising over half the total. The most efficient (96 percent) system of control is the combined usage of a water scrubber and thermal incinerator. A thermal incinerator alone is approximately 95 percent efficient in combustion of pollutants for o-xylene-based production, and 80 percent efficient for naphthalene-based production. Thermal incinerators with steam generation show the same efficiencies as thermal incinerators alone. Scrubbers have a 99 percent efficiency in collecting particulates, but are practically ineffective in reducing carbon monoxide emissions. In naphthalene-based production, cyclones can be used to control catalyst dust emissions with 90 to 98 percent efficiency.

Pretreatment and distillation emissions—particulates and hydrocarbons—are normally processed through the water scrubber and/or incinerator used for the main process stream (reactor and condenser) or scrubbers alone, with the same efficiency percentages applying.

Product storage in the liquid phase results in small amounts of gaseous emissions. These gas streams can either be sent to the main process vent gas control devices or first processed through sublimation boxes or devices used to recover escaped PAN. Flaking and bagging emissions are negligible, but can be sent to a cyclone for recovery of PAN dust. Exhaust from the cyclone presents no problem.

Table 6.5-1 gives emission factors for controlled and uncontrolled emissions from the production of PAN.

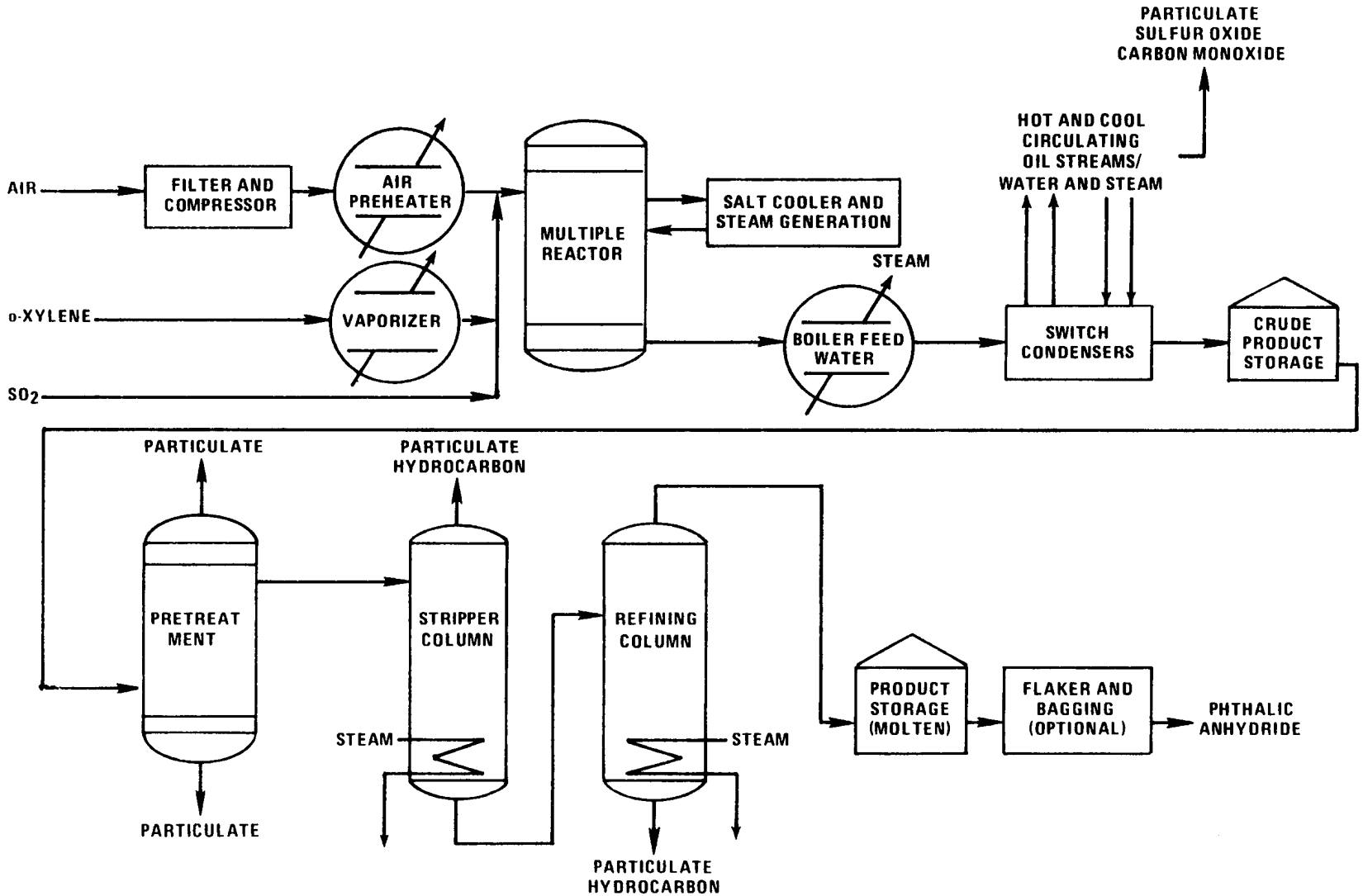


Figure 6.5-1. Flow diagram for phthalic anhydride using o-xylene as basic feedstock.[1]

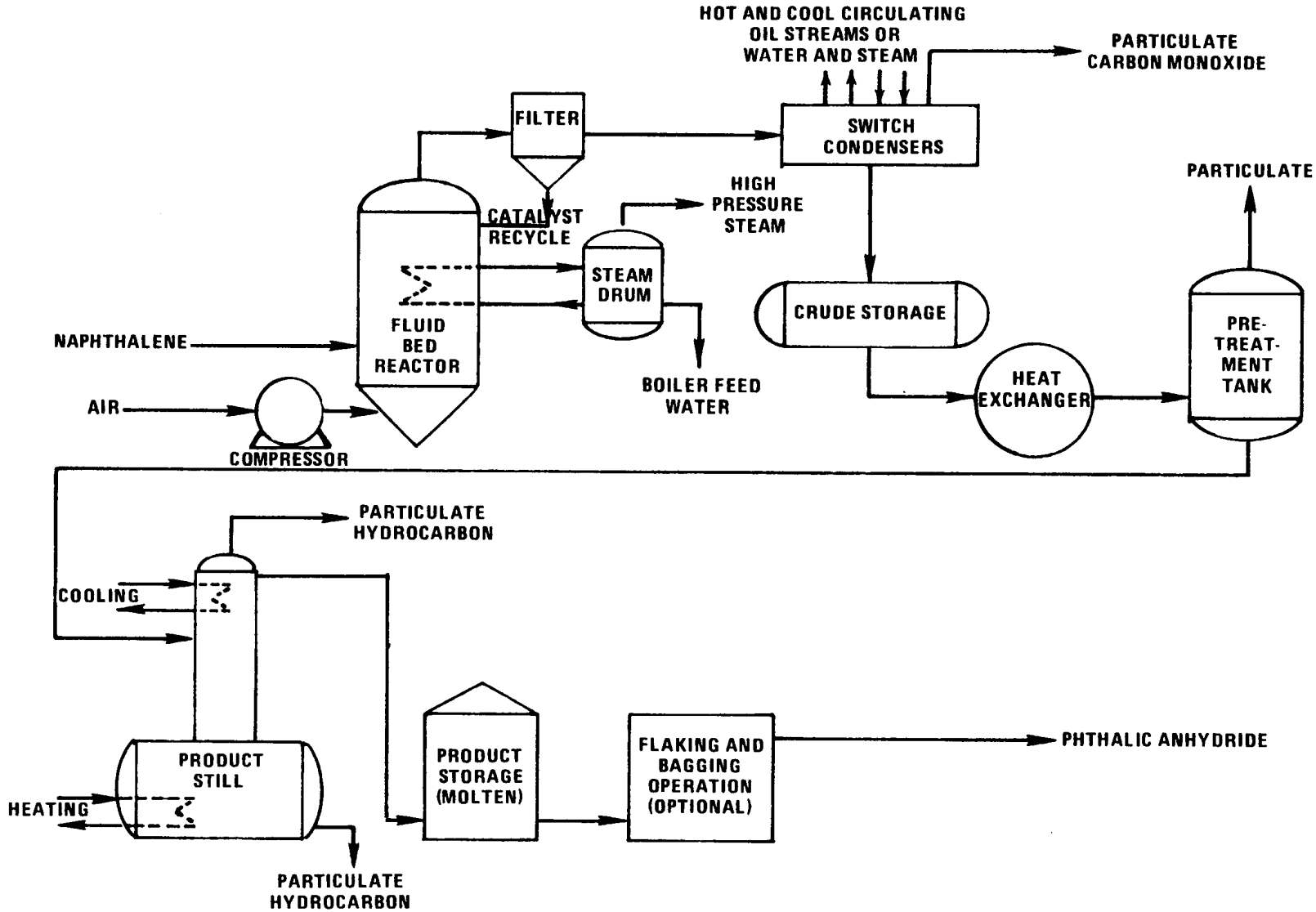


Figure 6.5-2. Flow diagram for phthalic anhydride using naphthalene as basic feedstock.[1]

Table 6.5-1 (Metric And English Units). EMISSION FACTORS FOR PHTHALIC ANHYDRIDE[a]

EMISSION FACTOR RATING: B

Process	Particulate		SO_x		Nonmethane VOC[b]		CO	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Oxidation of o-xylene[c]								
Main process stream[d]								
Uncontrolled	69[e]	138[e]	4.7[f]	9.4[f]	0	0	151	301
W/scrubber and thermal incinerator	3	6	4.7	9.4	0	0	6	12
W/thermal incinerator	4	7	4.7	9.4	0	0	8	15
W/incinerator with steam generator	4	7	4.7	9.4	0	0	8	15
Pretreatment								
Uncontrolled	6.4[g]	13[g]	0	0	0	0	0	0
W/scrubber and thermal incinerator	0.3	0.5	0	0	0	0	0	0
W/thermal incinerator	0.4	0.7	0	0	0	0	0	0
Distillation								
Uncontrolled	45[e]	89[e]	0	0	1.2[e,h]	2.4[e,h]	0	0
W/scrubber and thermal incinerator	2	4	0	0	<0.1	<0.1	0	0
W/thermal incinerator	2	4	0	0	<0.1	0.1	0	0
Oxidation of naphthalene[c]								
Main process stream[d]								
Uncontrolled	28[j,k]	56[j,k]	0	0	0	0	50	100
W/thermal incinerator	6	11	0	0	0	0	10	20
W/scrubber	0.3	0.6	0	0	0	0	50	100
Pretreatment								
Uncontrolled	2.5[m]	5[m]	0	0	0	0	0	0
W/thermal incinerator	0.5	1	0	0	0	0	0	0
W/scrubber	<0.1	<0.1	0	0	0	0	0	0

Table 6.5-1 (cont.).

Process	Particulate		SO_x		Nonmethane VOC[b]		CO	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Distillation								
Uncontrolled	19[j]	38[j]	0	0	5[h,j]	10[h,j]	0	0
W/thermal incinerator	4	8	0	0	1	2	0	0
W/scrubber	0.2	0.4	0	0	<0.1	0.1	0	0

[a] Reference 1. Factors are in kg of pollutant/Mg (lb/ton) of phthalic athydride produced.
[b] Emissions contain no methane.
[c] Control devices listed are those currently being used by phthalic anhydride plants.
[d] Main process stream includes reactor and multiple switch condensers as vented through condenser unit.
[e] Consists of phthalic anhydride, maleic anhydride, benzoic acid.
[f] Value shown corresponds to relatively fresh catalyst, which can change with catalyst age. Can be 9.5 - 13 kg/Mg (19 - 25 lb/ton) for aged catalyst.
[g] Consists of phthalic anhydride and maleic anhydride.
[h] Normally a vapor, but can be present as a particulate at low temperature.
[j] Consists of phthalic anhydride, maleic anhydride, naphthaquinone.
[k] Does not include catalyst dust, controlled by cyclones with efficiency of 90 - 98%.
[m] Particulate is phthalic anhydride.

Reference For Section 6.5

1. *Engineering And Cost Study Of Air Pollution Control For The Petrochemical Industry, Vol. 7: Phthalic Anhydride Manufacture From Ortho-xylene*, EPA-450/3-73-006g, U. S. Environmental Protection Agency, Research Triangle Park, NC, July 1975.