6.14 Maleic Anhydride

6.14.1 General[1]

The dominant end use of maleic anhydride (MA) is in the production of unsaturated polyester resins. These laminating resins, which have high structural strength and good dielectric properties, have a variety of applications in automobile bodies, building panels, molded boats, chemical storage tanks, lightweight pipe, machinery housings, furniture, radar domes, luggage, and bathtubs. Other end products are fumaric acid, agricultural chemicals, alkyd resins, lubricants, copolymers, plastics, succinic acid, surface active agents, and more. In the United States, one plant uses only n-butane and another uses n-butane for 20 percent of its feedstock, but the primary raw material used in the production of MA is benzene. The MA industry is converting old benzene plants and building new plants to use n-butane. MA also is a byproduct of the production of phthalic anhydride. It is a solid at room temperature but is a liquid or gas during production. It is a strong irritant to skin, eyes, and mucous membranes of the upper respiratory system.

The model MA plant, as described in this section, has a benzene-to-MA conversion rate of 94.5 percent, has a capacity of 22,700 megagrams (Mg) (25,000 tons) of MA produced per year, and runs 8000 hours per year.

Because of a lack of data on the n-butane process, this discussion covers only the benzene oxidation process.

6.14.2 Process Description[2]

Maleic anhydride is produced by the controlled air oxidation of benzene, illustrated by the following chemical reaction:

$2\ C_6H_6$	+	$9\ O_2$	$\xrightarrow[MoO_3]{V_2O_5}$	$2\ C_4H_2O_3$	+	H_2O	+	$4\ CO_2$
Benzene		Oxygen	Catalyst ——>	Maleic anhydride		Water		Carbon dioxide

Vaporized benzene and air are mixed and heated before entering the tubular reactor. Inside the reactor, the benzene/air mixture is reacted in the presence of a catalyst that contains approximately 70 percent vanadium pentoxide (V_2O_5), with usually 25 to 30 percent molybdenum trioxide (MoO_3), forming a vapor of MA, water, and carbon dioxide. The vapor, which may also contain oxygen, nitrogen, carbon monoxide, benzene, maleic acid, formaldehyde, formic acid, and other compounds from side reactions, leaves the reactor and is cooled and partially condensed so that about 40 percent of the MA is recovered in a crude liquid state. The effluent is then passed through a separator that directs the liquid to storage and the remaining vapor to the product recovery absorber. The absorber contacts the vapor with water, producing a liquid of about 40 percent maleic acid. The 40 percent mixture is converted to MA, usually by azeotropic distillation with xylene. Some processes may use a double-effect vacuum evaporator at this point. The effluent then flows to the xylene stripping column where the xylene is extracted. This MA is then combined in storage with that from the separator. The molten product is aged to allow color-forming impurities to polymerize. These are then removed in a fractionation column, leaving the finished product. Figure 6.14-1 represents a typical process.

MA product is usually stored in liquid form, although it is sometimes flaked and pelletized into briquets and bagged.

6.14.3 Emissions And Controls[2]

Nearly all emissions from MA production are from the main process vent of the product recovery absorber, the largest vent in the process. The predominant pollutant is unreacted benzene, ranging from 3 to 10 percent of the total benzene feed. The composition of uncontrolled emissions from the product recovery absorber is presented in Table 6.14-1. The refining vacuum system vent, the only other exit for process emissions, produces 0.28 kilograms (kg) (0.62 pounds [lb]) per hour of MA and xylene.

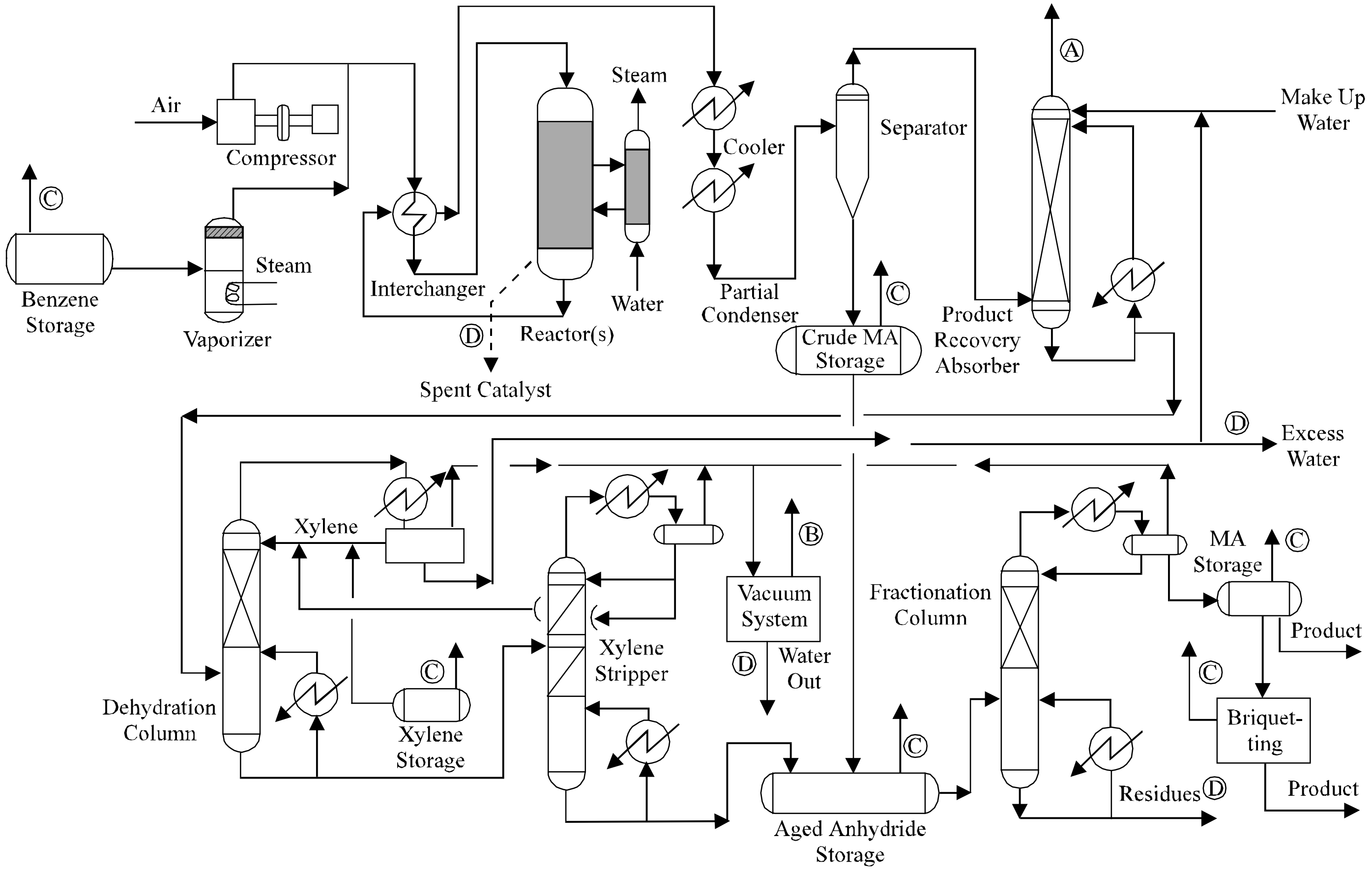
Table 6.14-1 (Metric And English Units). COMPOSITION OF UNCONTROLLED EMISSIONS FROM PRODUCT RECOVERY ABSORBER[a]

Component	Wt.%	kg/Mg	lb/ton
Nitrogen	73.37	21,406.0	42,812.0
Oxygen	16.67	4,863.0	9,726.0
Water	4.00	1,167.0	2,334.0
Carbon dioxide	3.33	972.0	1,944.0
Carbon monoxide	2.33	680.0	1,360.0
Benzene	0.33	67.0	134.0
Formaldehyde	0.05	14.4	28.8
Maleic acid	0.01	2.8	5.6
Formic acid	0.01	2.8	5.6
Total		29,175.0	58,350.0

[a] Reference 2.

Fugitive emissions of benzene, xylene, MA, and maleic acid also arise from the storage (see Chapter 7) and handling (see Section 5.1.3) of benzene, xylene, and MA. Dust from the briquetting operations can contain MA, but no data are available on the quantity of such emissions.

Potential sources of secondary emissions are spent reactor catalyst, excess water from the dehydration column, vacuum system water, and fractionation column residues. The small amount of residual organics in the spent catalyst after washing has low vapor pressure and produces a small percentage of total emissions. Xylene is the principal organic contaminant in the excess water from the dehydration column and in the vacuum system water. The residues from the fractionation column are relatively heavy organics, with a molecular weight greater than 116, and they produce a small percentage of total emissions.



KEY

A - Product Recovery Absorber Vent
B - Vacuum System Vent
C - Storage and Handling Emissions
D - Secondary Emission Potential

Figure 6.14-1. Process flow diagram for uncontrolled model plant.

Benzene oxidation process emissions can be controlled at the main vent by means of carbon adsorption, thermal incineration, or catalytic incineration. Benzene emissions can be eliminated by conversion to the n-butane process. Catalytic incineration and conversion from the benzene process to the n-butane process are not discussed for lack of data. The vent from the refining vacuum system is combined with that of the main process as a control for refining vacuum system emissions. A carbon adsorption system or an incineration system can be designed and operated at a 99.5 percent removal efficiency for benzene and volatile organic compounds with the operating parameters given in Appendix R of Reference 2.

Fugitive emissions from pumps and valves may be controlled by an appropriate leak detection system and maintenance program. No control devices are presently being used for secondary emissions. Table 6.14-2 presents emission factors for MA production.

Table 6.14-2 (Metric And English Units). EMISSION FACTORS FOR MALEIC ANHYDRIDE PRODUCTION[a]

EMISSION FACTOR RATING: C

Source	Nonmethane VOC[b]		Benzene	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Product vents (recovery absorber and refining vacuum system combined vent)				
Uncontrolled	87	174	67.0	134.0
With carbon adsorption[c]	0.34	0.68	0.34	0.68
With incineration	0.43	0.86	0.34	0.68
Storage and handling emissions[d]	—[d]	—[d]	—[d]	—[d]
Fugitive emissions[e]	—[e]	—[e]	—[e]	—[e]
Secondary emissions[f]	ND	ND	ND	ND

[a] No data are available for catalytic incineration or for plants producing MA from n-butane. ND = no data.

[b] VOC also includes the benzene. For recovery absorber and refining vacuum, VOC can be MA and xylene; for storage and handling, MA, xylene and dust from briquetting operations; for secondary emissions, residual organics from spent catalyst, excess water from dehydration column, vacuum system water, and fractionation column residues. VOC contains no methane.

[c] Before exhaust gas stream goes into carbon adsorber, it is scrubbed with caustic to remove organic acids and water soluble organics. Benzene is the only likely VOC remaining.

[d] See Chapter 7.

[e] See Section 5.1.3.

[f] Secondary emission sources are excess water from dehydration column, vacuum system water, and organics from fractionation column. No data are available on the quantity of these emissions.

References For Section 6.14

1. B. Dmuchovsky and J. E. Franz, "Maleic Anhydride", *Kirk-Othmer Encyclopedia of Chemical Technology*, *Volume 12*, John Wiley and Sons, Inc., New York, NY, 1967, pp. 819-837.

2. J. F. Lawson, *Emission Control Options For The Synthetic Organic Chemicals Manufacturing Industry: Maleic Anhydride Product Report*, EPA Contract No. 68-02-2577, Hydroscience, Inc., Knoxville, TN, March 1978.