CHE654 – Plant Design Project #6
Semester 1, 2022

DESIGN OF A MALEIC ANHYDRIDE PRODUCTION PROCESS

(Courtesy of the Department of Chemical Engineering at West Virginia University)

Introduction

Maleic anhydride is a chemical intermediate that is used to produce resins, surface coatings, lubricant additives, and agricultural chemicals. The compound's chemical formula is $C_2H_2(CO)_2O$ and is the acid anhydride of maleic acid. In its pure state, the compound is colorless or white solid with an acrid odor. Maleic anhydride was traditionally manufactured by the oxidation of benzene or other aromatic compounds. As of 2006, only a few smaller plants continue to use benzene; due to rising benzene prices, most maleic anhydride plants now use *n*-butane as a feedstock.

The purpose of this project is to do a preliminary analysis to determine the feasibility of constructing a chemical plant to manufacture 40,000 ton/year maleic anhydride. The raw material is benzene. Your job is to analyze a simplified maleic anhydride production process, to suggest profitable operating conditions, and to write a final report summarizing your findings. Note that although you are to look for a "best" solution in your design, optimization is <u>NOT</u> required in this design project.

Chemical Reactions

The raw material is benzene. The primary reaction is one in which benzene is partially oxidized to form maleic anhydride (Equation 1). There are three undesired side reactions, the subsequent combustion of maleic anhydride (Equation 2), the complete combustion of benzene (Equation 3), and the formation of the by-product, quinone (Equation 4).

The reactions and reaction kinetics are:

$$\underset{\text{benzene}}{C_6H_6(g)} + 4.5O_2(g) \xrightarrow{k_1} \underset{\text{maleic anhydride}}{C_4H_2O_3(g)} + 2CO_2(g) + 2H_2O(g) \qquad (1)$$

$$\underset{\text{benzene}}{C_6H_6(g)} + 7.5O_2(g) \xrightarrow{k_2} 6CO_2(g) + 3H_2O(g) \qquad (2)$$

$$\underset{\text{maleic anhydride}}{C_4H_2O_3(g)} + 3O_2(g) \xrightarrow{k_3} 4CO_2(g) + H_2O(g) \qquad (3)$$

$$C_6H_6(g) + 1.5O_2(g) \xrightarrow{k_4} C_6H_4O_2(g) + H_2O(g) \tag{4}$$

benzene quinone

where

$$-r_i = k_i C_{benzene} \text{ or } -r_3 = k_3 C_{maleic\ anhydride} \tag{5}$$

and

$$k_1 = 7.7 \times 10^6 \exp(-25{,}143/RT) \tag{6}$$

$$k_2 = 6.31 \times 10^7 \exp(-29{,}850/RT) \tag{7}$$

$$k_3 = 2.33 \times 10^4 \exp(-21{,}429/RT) \tag{8}$$

$$k_4 = 7.20 \times 10^5 \exp(-27{,}149/RT) \tag{9}$$

The units of reaction rate, r_i, are kmol/m^3(reactor)s, the activation energy is given in cal/mol (which is equivalent to kcal/kmol), the units of k_i are m^3(gas)/m^3 (reactor)s, and the units of concentration are kmol/m^3(gas).

The catalyst is a mixture of vanadium and molybdenum oxides on an inert support. Typical inlet reaction temperatures are in the range of 350-400°C. The maximum temperature that the catalyst can be exposed to without causing irreversible damage (sintering) is 650°C. The catalyst diameter is 5 mm, and the void fraction of the bed is 0.5.

Process Description

The PFD for the (starting) process is given in Figure 1.

C-501	E-501	H-501	E-502	R-501	V-501	T-501	T-502	E-503	H-502
Air Feed Compressor	BenzeneFeed Vaporizer	Feed Fired Heater	Reactor Effluent Cooler	Maleic Anhydride Reactor	Dibutyl Phthalate Mixing Vessel	Maleic Anhydride Absorber	Maleic Anhydride Distillation Column	Maleic Tower Condenser	Maleic Tower Reboiler/Fired Heater

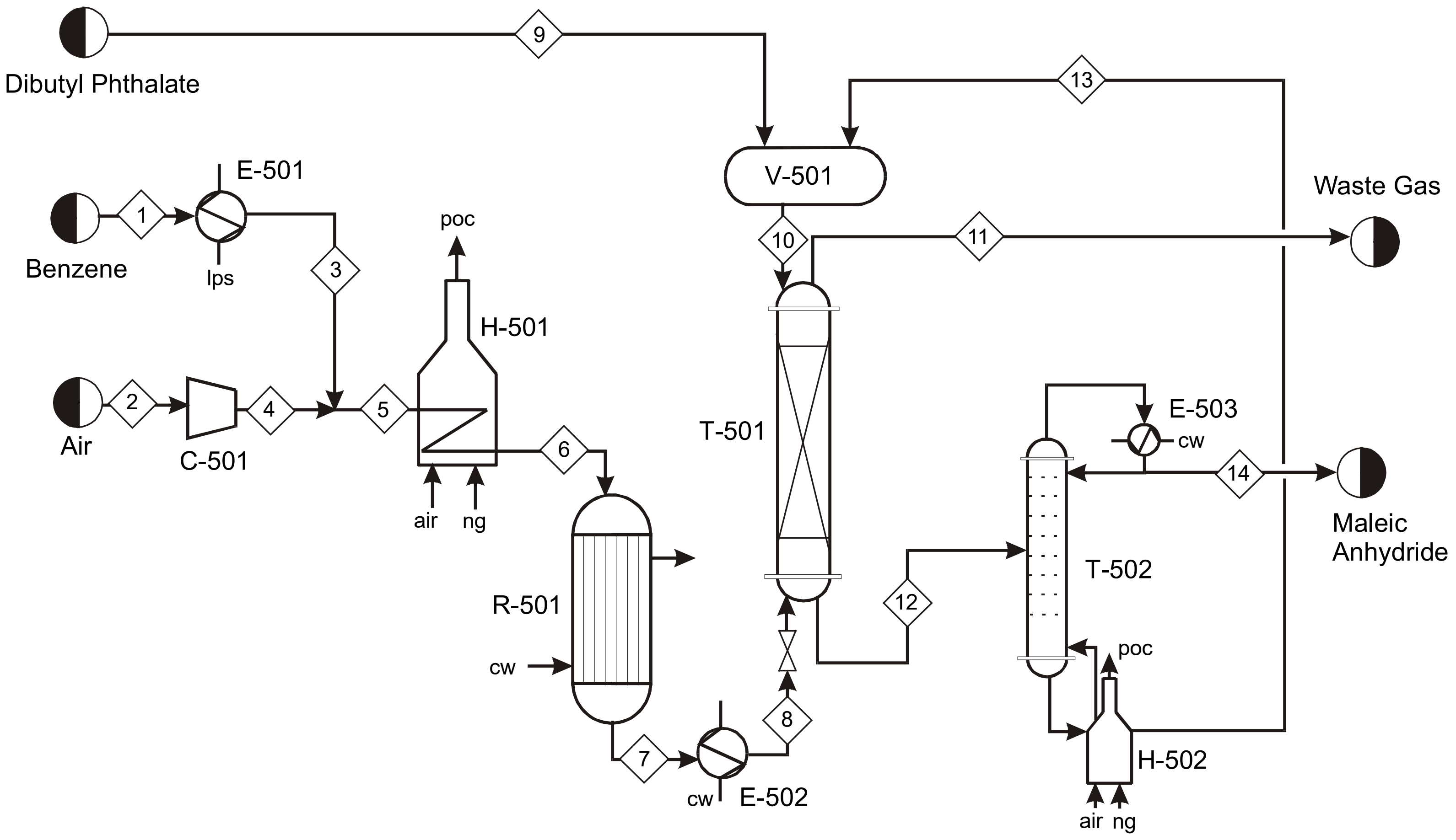

Figure 1: Maleic Anhydride Production Process

Process Details

Feed Stream and Effluent Streams

Stream 1: Benzene – stored as a liquid at the desired pressure of the reaction. The cost of benzene is \$4.73/L (liquid).

Stream 2: Air or "pure" oxygen – present at 200% excess based on maleic anhydride formation reaction (note: 100% excess is double the stoichiometric amount). Consider air to have zero cost and to have 79 mol % N_2, 21 mol % O_2. The cost for "pure" oxygen is \$0.20/100 std ft^3 (60°F, 1 atm). Oxygen is available at 60°F and 1 atm.

Stream 9: Dibutyl phthalate solvent – make-up stream for amount lost in Streams 11 and 14. The cost is \$1.72/kg.

Stream 11: Waste gas – contains unreacted benzene and O_2, N_2, CO_2, and H_2O, plus some dibutyl phthalate – sent to treatment process, the cost of which may be considered negligible.

Stream 14: Maleic anhydride product. Specifications for this stream are given below. The product is to be sold at \$1.08/kg of maleic anhydride in the stream.

Equipment

Compressor (C-501)

The compressor increases the pressure of the feed air or oxygen to the reactor pressure. The compressor may be assumed to be adiabatic. In that case, the compressor work, W_s, may be calculated as

$$W_s = 4.5R(T_{out} - T_{in}) \tag{10}$$

where W_s is in [kJ/kmol] and the inlet and outlet temperatures, T_{in} and T_{out}, respectively are in [K]. The outlet and inlet temperatures are related through:

$$T_{out} = T_{in}\left(\frac{P_{out}}{P_{in}}\right)^{0.286} \tag{11}$$

The cost of electricity to run the compressor is a utility cost.

Heat Exchanger (E-501)

This heat exchanger vaporizes the benzene feed to 10°C of superheat at the stream pressure. The cost of the heat source is a utility cost.

Fired Heater (H-501)

This heats reactor feed vapor to reaction temperature. Natural gas is used as the fuel, and the amount needed is based on the LHV of natural gas. The cost of natural gas is a utility cost.

Reactor (R-501)

This is where the reactions in Equations 1-3 occur. Details of the reactor are presented below. There are two possible reactor configurations. The one illustrated in Figure 1 shows heat removal to maintain a constant temperature. In this case, the cost of the medium to remove heat (cooling water, cw, in Figure 1) is a utility cost. The alternative reactor configuration is an adiabatic reactor, in which there is no heat removal. The heat generated by the reaction raises the temperature of the exit stream. The temperature constraints described below must be obeyed.

Absorber (T-501)

The absorber runs at 1.5 atm and 100°C (outlet streams and Stream 8). In the absorber, 99% of the maleic anhydride in Stream 8 is absorbed into the solvent dibutyl phthalate. For accounting purposes, all maleic anhydride in the recycle stream (Stream 13) may be assumed to go to Stream 12. You should assume that 0.001% of the dibutyl phthalate in Stream 10 is lost into Stream 11. This plus the dibutyl phthalate in Stream 14 is the amount of dibutyl phthalate needed in Stream 9. The cost of Stream 9 is a raw material cost.

Distillation Column (T-502)

This column runs at 1 atm. (The pressure is controlled by a valve in the product stream from R-501.) Separation of maleic anhydride and dibutyl phthalate occurs in this column. Of the maleic anhydride in Stream 12, 99% enters Stream 14. Similarly, 99% of dibutyl phthalate in Stream 12 enters Stream 13.

Heat Exchanger (E-503):

In this heat exchanger, the contents of the top of T-502 are condensed from saturated vapor to saturated liquid at the column pressure. It may be assumed that this stream condenses at the boiling point of maleic anhydride at the column pressure. The flowrate of the stream from T-502 to E-503 is three times the flowrate of Stream 14. (That is to say, one-third of the condensate becomes Stream 14, and the remainder is returned to the column.) There is a cost for the amount of cooling water needed; this is a utility cost. The cooling water leaving E-503 must always be at a lower temperature than that of the stream being condensed.

Fired Heater (H-502):

In this heat exchanger, you may assume that the stream that has been vaporized and is being returned to T-502 has the same flowrate as Stream 13. The stream from H-502 is vaporized from saturated liquid to saturated vapor at the boiling point of dibutyl phthalate at the column pressure. Natural gas is used as the fuel, and the amount needed is based on the LHV of natural gas. The cost of natural gas is a utility cost.

Vessel (V-501)

In this vessel, make-up dibutyl phthalate and recycled dibutyl phthalate streams are mixed.

Design of Heat Exchanger E-501

A detailed design of E-501 is required for base-case conditions. It should be assumed that cooling water and other utilities are available at the conditions specified in the Appendix of this problem statement. For this heat exchanger design, the following information should be provided:

- Diameter of shell
- Number of tube and shell passes
- Number of tubes per pass
- Tube pitch and arrangement (triangular/square/..)
- Number of shell-side baffles, if any, and their arrangement (spacing, pitch, type)
- Diameter, tube-wall thickness, shell-wall thickness, and length of tubes
- Calculation of both shell- and tube-side film heat transfer coefficients
- Calculation of overall heat transfer coefficient (you may assume that there is no fouling on either side of the exchanger)
- Heat transfer area of the exchanger
- Shell-side and tube-side pressure drops (calculated, not estimated)
- Materials of construction
- Approximate cost of the exchanger

A detailed sketch of the exchanger should be included along with a set of comprehensive calculations in an appendix for the design of the heat exchangers. You should use ASPEN Exchanger Design & Rating (EDR) in the ASPEN Plus simulator to carry out the detailed design.

Additional Constraints

- The LFL of benzene may not be exceeded in any stream
- No excess steam can be exported from the plant. Therefore, any steam generated within the process must be used within the process.
- The following specifications for products must be met if a product is to be sold:
  - ♦ Maleic Anhydride – purity > 99.8 mass%
  - ♦ Quinone – purity > 99 mass%
  - ♦ Maleic Acid – purity > 99.8 mass%
- Any liquid organic stream may be burned in a fired heater as fuel, and a credit may be taken for the fuel value (LHV) of the stream.
- All distillation columns must be simulated using rigorous unit operations (e.g. RADFRAC in Aspen Plus)

Economic Analysis

When evaluating alternative cases, you should carry out an economic evaluation and profitability analysis based on a number of economic criteria such as payback period, internal rate of return, and cash flow analysis. In addition, the following objective function should be used. It is the equivalent annual operating cost (EAOC), and is defined as

EAOC = – (product value – feed cost – other operating costs – capital cost annuity)

A negative value of EAOC means there is a profit. It is desirable to minimize EAOC; *i.e*., a large negative value of EAOC is very desirable, although you are **not** being asked to carry out optimization.

Utility costs are those for steam, cooling water, boiler-feed water, natural gas, and electricity.

The capital cost annuity is an ***annual*** cost (like a car payment) associated with the ***one-time***, fixed capital cost of plant construction and installation.

The capital cost annuity is defined as follows:

$$capital\ cost\ annuity = FCI\frac{i(1+i)^n}{(1+i)^n - 1} \tag{12}$$

where *FCI* is the installed cost of all equipment; i is the interest rate; and n is the plant life, in [y]. For accounting purposes, take $i = 0.15$ and $n = 10$.

For detailed sizing, costing, and economic evaluation including profitability analysis, you may use the Aspen Process Economic Analyzer (formerly Aspen Icarus Process Evaluator) in Aspen Plus Version 8. However, it is also a good idea to independently verify the final numbers based on other sources such as cost data given below.

Other Information

You should assume that a year equals 8,000 hours. This is about 330 days, which allows for periodic shut-down and maintenance.

Final Comments

As with any open-ended problem; i.e., a problem with no single correct answer, the problem statement above is deliberately vague. You may need to fill in some missing data by doing a literature search, Internets search, or making assumptions. The possibility exists that as you work on this problem, your questions will require revisions and/or clarifications of the problem statement. You should be aware that these revisions/clarifications may be forthcoming.

Moreover, in some areas (e.g. sizing/costing) you are given more data and information than what is needed. You must exercise engineering judgment and decide what data to use. Also you should also seek additional data from the literature or Internet to verify some of the data, e.g. the prices of products and raw materials.

References

1. Felder, R. M. and R. W. Rousseau, *Elementary Principles of Chemical Processes (3rd ed.)*, Wiley, New York, 2000.

2. Wankat, P., *Equilibrium Staged Separation Processes*, Prentice Hall, Upper Saddle River, NJ, 1988.

Appendix 1
Economic Data

Equipment Costs (Purchased)

Note: The numbers following the attribute are the minimum and maximum values for that attribute. For a piece of equipment with a lower attribute value, use the minimum attribute value to compute the cost. For a piece of equipment with a larger attribute value, extrapolation is possible, but inaccurate. To err on the side of caution, you should use the price for multiple, identical smaller pieces of equipment.

Pumps	$\log_{10}(\text{purchased cost}) = 3.4 + 0.05\log_{10} W + 0.15[\log_{10} W]^2$ W = power (kW, 1, 300) assume 80% efficiency
Heat Exchangers	$\log_{10}(\text{purchased cost}) = 4.6 - 0.8\log_{10} A + 0.3[\log_{10} A]^2$ A = heat exchange area (m^2, 10, 1000)
Compressors	$\log_{10}(\text{purchased cost}) = 2.3 + 1.4\log_{10} W - 0.1[\log_{10} W]^2$ W = power (kW, 450, no limit) assume 70% efficiency
Compressor Drive	$\log_{10}(\text{purchased cost}) = 2.5 + 1.4\log_{10} W - 0.18[\log_{10} W]^2$ W = power (kW, 75, 2600)
Turbine	$\log_{10}(\text{purchased cost}) = 2.5 + 1.45\log_{10} W - 0.17[\log_{10} W]^2$ W = power (kW, 100, 4000) assume 65% efficiency
Fired Heater	$\log_{10}(\text{purchased cost}) = 3.0 + 0.66\log_{10} Q + 0.02[\log_{10} Q]^2$ Q = duty (kW, 3000, 100,000) assume 80% thermal efficiency assume can be designed to use any organic compound as a fuel
Vertical Vessel	$\log_{10}(\text{purchased cost}) = 3.5 + 0.45\log_{10} V + 0.11[\log_{10} V]^2$ V = volume of vessel (m^3, 0.3, 520)
Horizontal Vessel	$\log_{10}(\text{purchased cost}) = 3.5 + 0.38\log_{10} V + 0.09[\log_{10} V]^2$ V = volume of vessel (m^3, 0.1, 628)

Additional Cost Information

Piping straight pipe $\$/\text{m} = 5.0\,(\text{nominal pipe diameter, in})(1+(\text{sch }\#)/20)^{0.25}$

sch = schedule number for pipe

use the same sch number for fittings and valves

fittings (except valves) $\$/\text{fitting} = 50.0\,(\text{nominal pipe diameter, in})(1+(\text{sch }\#)/20)^{0.25}$

Valves for gate (isolation) valves $\$100\,(\text{nominal pipe diameter, in})^{0.8}\,(1+(\text{sch }\#)/20)^{0.25}$

for control valve use $\$1000\,(\text{nominal pipe diameter, in})^{0.8}(1+(\text{sch }\#)/20)^{0.25}$

Equipment Bypasses

Bypasses around equipment should consist of a minimum of 20 ft of pipe, 2 standard elbows, and 1 gate valve. There will also be a tee at each point where the by-pass connects to the main pipe.

Utility Costs

Low-Pressure Steam (618 kPa saturated)	\$7.78/1000 kg
Medium-Pressure Steam (1135 kPa saturated)	\$8.22/1000 kg
High-Pressure Steam (4237 kPa saturated)	\$9.83/1000 kg
Natural Gas (446 kPa, 25°C)	\$6.00/GJ
Fuel Gas Credit	\$5.00/GJ
Electricity	\$0.06/kWh
Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg
Cooling Water available at 516 kPa and 30°C return pressure ≥ 308 kPa return temperature is no more than 15°C above the inlet temperature	\$0.354/GJ
Refrigerated Water available at 516 kPa and 10°C return pressure ≥ 308 kPa return temperature is no higher than 20°C	\$4.43/GJ
Deionized Water available at 5 bar and 30°C	\$1.00/1000 kg
Waste Treatment of Off-Gas	incinerated - take fuel credit
Refrigeration	\$7.89/GJ
Wastewater Treatment	\$56/1000 m^3

Equipment Cost Factors

Total Installed Cost = Purchased Cost (4 + material factor (MF) + pressure factor (PF))

Pressure (absolute)		
	< 10 atm, PF = 0.0	does not apply to turbines, compressors, vessels, packing, trays, or catalyst, since their cost equations include pressure effects
	10 - 20 atm, PF = 0.6	
	20 - 40 atm, PF = 3.0	
	40 - 50 atm, PR = 5.0	
	50 - 100 atm, PF = 10	

Carbon Steel MF = 0.0
Stainless Steel MF = 4.0

Appendix 2
Other Design Data

Heat Exchangers

For heat exchangers that are not designed in detail, use the following approximations for heat-transfer coefficients to allow you to determine the heat transfer area:

situation	***h*** **(W/m^2°C)**
condensing steam	6000
condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60