

# Energy Balances and Numerical Methods Design Project

## Production of Maleic Anhydride

Maleic anhydride is a chemical intermediate that is used to produce resins, surface coatings, lubricant additives, and agricultural chemicals.

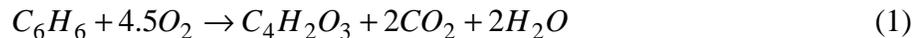
The purpose of this project is to continue a preliminary analysis to determine the feasibility of constructing a chemical plant to manufacture 40,000 tonne/y maleic anhydride.

A suggested process flow diagram (PFD) is attached. You should use this as a starting point only. Your primary task is to recommend operating conditions for the reactor that maximize the equivalent annual operating cost, or EAOC (This term is defined below). Process improvements that increase the EAOC are also required. Any change that you can justify, and that does not violate the laws of nature, is allowed. Your assignment is to develop a “best” case, where “best” is dependent upon economic considerations, i.e., EAOC. In reporting your best case, clearly indicate the modified process and state not only the operating conditions for the (modified) process but also the corresponding values for the single-pass conversion of benzene, the overall conversion of benzene, and EAOC. Also, state any recommendations you have for additional process improvements that you were not able to incorporate into the process calculations.

### Chemical Reaction

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

The chemical reactions are as follows:



### 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	BenzeneFeed	Feed Fired	Reactor Effluent	Maleic Anhydride	Dibutyl Phthalate	Maleic Anhydride	Maleic Anhydride	Maleic Tower	Maleic Tower
Compressor	Vaporizer	Heater	Cooler	Reactor	Mixing Vessel	Absorber	Distillation Column	Condenser	Reboiler/Fired
									Heater

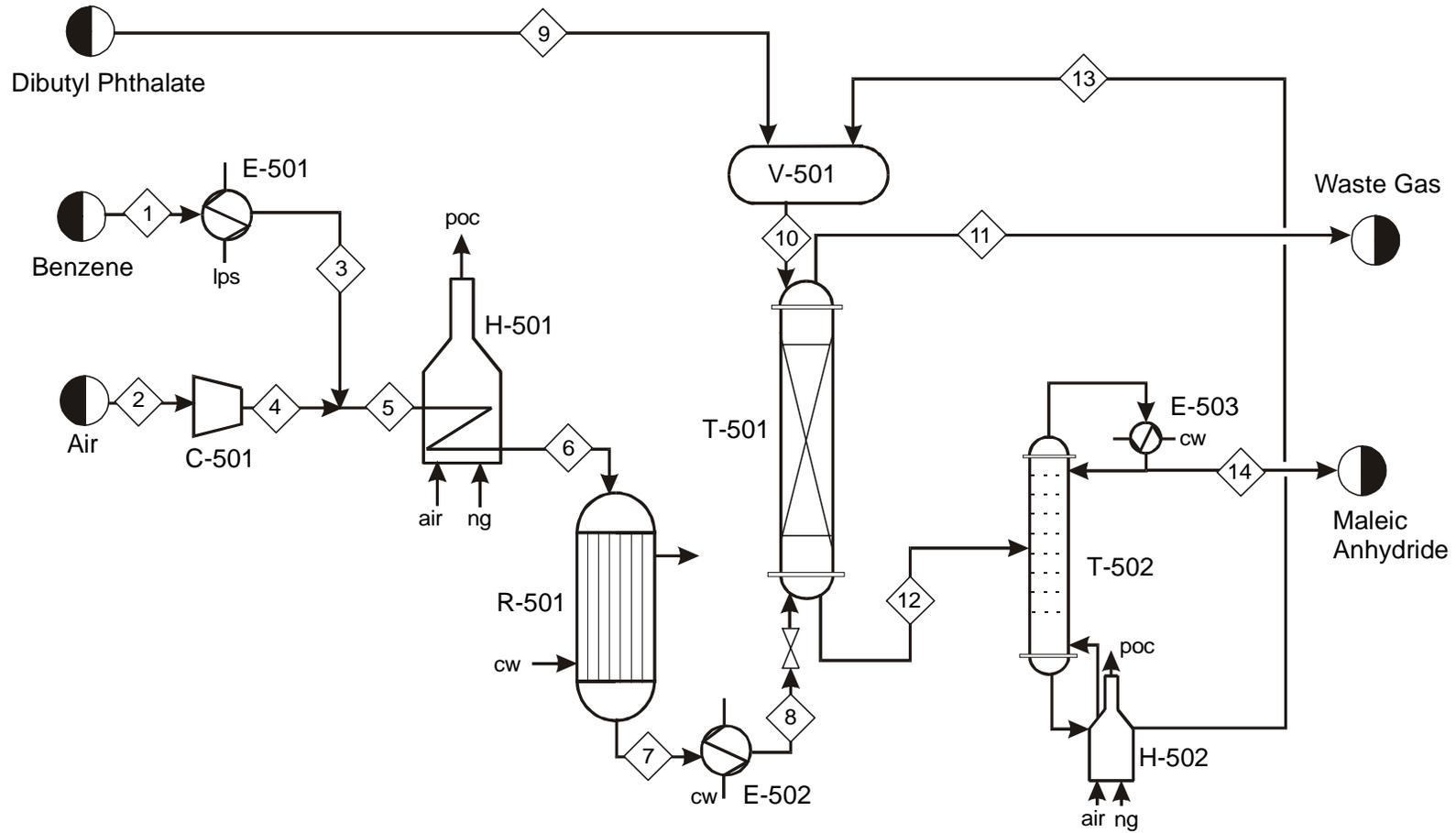


Figure 1: Maleic Anhydride Production Process

## 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<sub>2</sub>, 21 mol % O<sub>2</sub>. The cost for “pure” oxygen is \$0.20/100 std ft<sup>3</sup> (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<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, 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

$$W_s = 4.5R(T_{out} - T_{in}) \quad (4)$$

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:

$$T_{out} = T_{in} \left( \frac{P_{out}}{P_{in}} \right)^{0.286} \quad (5)$$

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.

## Economic Analysis

When evaluating alternative cases, the objective function to be used is the Equivalent Annual Operating Cost (EAOC), defined as

$$\text{EAOC} = -(\text{product value} - \text{feed cost} - \text{utility costs} - \text{waste treatment cost} - \text{capital cost annuity})$$

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.

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. A list of fixed capital costs on an installed basis (“installed cost”) for all pieces of equipment will be provided by mid-March.

The capital cost annuity is defined as follows:

$$\text{capital cost annuity} = FCI \frac{i(1+i)^n}{(1+i)^n - 1} \quad (6)$$

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  $n = 10$ .

## Optimization

You will learn optimization methods in ChE 230. The objective function (EAOC) is defined above. You should consider both topological and parametric optimization.

Topological optimization involves considering different process configurations (such as air vs. pure oxygen, adiabatic vs. isothermal reactor). Recall that you may alter the process configuration in any way that improves the economic performance, as long as it does not violate the laws of nature.

Parametric optimization involves determining the best operating parameters for the chosen process topology. It is your responsibility to define appropriate decision variables. If there are too many decision variables to do a reasonable parametric optimization, it is your responsibility to determine, with appropriate justification, which ones most significantly affect the objective function. Then you should focus on only those decision variables.

### Reactor Information

The reaction conditions are as follows. Limit the temperature to between 450°C and 650°C. The pressure is 2.5 atm. Table 1 gives conversion ( $X$ ) and selectivity information for the reactor for this range of conditions. Here the selectivity of maleic anhydride,  $S$ , is defined as follows:

$$S = \text{moles of maleic anhydride} / \text{moles CO}_2 \quad (7)$$

It should be observed that CO<sub>2</sub>, the undesired product, is also formed in the desired reaction. Therefore, from Equations (1) – (3), the maximum possible value of  $S$  is 0.5.

**Table 1: Reactor Conversions and Selectivities**

$T$ (°C)	$X$ Conversion of benzene	$S$ Selectivity of maleic anhydride
450	17.5	0.257
460	21.6	0.252
480	31.8	0.238
500	44.5	0.229
520	58.8	0.219
540	63.0	0.208
560	85.0	0.197
580	93.3	0.185
600	97.7	0.175
620	99.47	0.163
640	99.92	0.152
650	99.97	0.147

It is suggested that you regress or curve-fit these data to obtain accurate interpolated values for the conversion and selectivity.

## Utility Costs

Low-Pressure Steam (618 kPa, saturated, cost or credit)	\$7.78/1000 kg
Medium-Pressure Steam (1135 kPa, saturated, cost or credit)	\$8.22/1000 kg
High-Pressure Steam (4237 kPa, saturated, cost or credit)	\$9.83/1000 kg
Natural Gas or Fuel Gas (446 kPa, 25°C)	
cost	\$6.00/GJ
credit	\$5.00/GJ
Electricity	\$0.06/kWh
Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg
(There is a cost for boiler feed water only if the steam produced enters process streams. If, on the other hand, the steam produced is subsequently condensed, it can be made into steam again. In that case, there would be no net cost for boiler feed water.)	
Cooling Water	\$0.354/GJ
available at 516 kPa and 30°C	
return pressure $\geq$ 308 kPa	
return temperature should be no more than 15°C above the inlet temperature	
Refrigerated Water	\$4.43/GJ
available at 516 kPa and 5°C	
return pressure $\geq$ 308 kPa	
return temperature should be no higher than 15°C	
Process Water	\$0.067/1000 kg
available at 300 kPa and 25°C	
Waste Water Treatment	\$56/1000 m <sup>3</sup>

**Data**

Data for benzene, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O are available in your textbook.<sup>1</sup> The following data are provided for the other components.

**Heat of Formation at 25°C, [kJ/kg] – all in gas phase**

maleic anhydride	dibutyl phthalate
-4062	-2698

**Heat of Vaporization [kJ/kmol] at normal boiling point,  $T_b$  [°C]**

	maleic anhydride	dibutyl phthalate
$\Delta H_v$	47191	80922
$T_b$	202	340

**Vapor Phase Heat Capacity – use the following equation**

$$C_p = A + B \left[ \frac{C/T}{\sinh(C/T)} \right]^2 + D \left[ \frac{E/T}{\cosh(E/T)} \right]^2, \text{ where } T \text{ is in [K] and } C_p \text{ is in [J/kmol/K]}$$

	maleic anhydride	dibutyl phthalate
$A$	165140	237300
$B$	68030	771600
$C$	1459.6	1950.7
$D$	$-6.732 \times 10^{-7}$	632900
$E$	8.4765	848.5

**Liquid Phase Heat Capacity – use the following equation**

$$C_p = A + BT + CT^2, \text{ where } T \text{ is in [K] and } C_p \text{ is in [J/kmol/K]}$$

	maleic anhydride	dibutyl phthalate
$A$	93670	461790
$B$	188.9	-616.04
$C$	0	2.2101

**Vapor Pressure Equation Constants – use the following equation**

$$\ln [P^*] = A - (B/T), \text{ where } P^* \text{ is in [mm Hg] and } T \text{ is in [K]}$$

	maleic anhydride	dibutyl phthalate
$A$	19.5146	21.2221
$B$	6094.8928	8924.6934

## Other Information

You should assume that a year equals 8000 hours. This is about 330 days, which allows for periodic shutdown and maintenance.

You may receive a credit for steam produced in excess of any steam needed. You may burn the waste gas and receive a credit at its LHV. The cost of steam assumes that it is returned to the steam generation plant as condensate. The cost of cooling water assumes that it is returned to the cooling-water plant within the specified temperature range.

## Deliverables

Each group must deliver a word-processed report. It should be clear and concise. The format is explained in a separate document. When presenting results for different cases, graphs are superior to tables. The body of the report should be short, emphasizing only the results and briefly summarizing computational strategies. The report appendix should contain details of calculations that are easy to follow. Calculations that cannot be followed easily will lose credit.

The project is due April 26, 2004, at the beginning of class. There will be oral presentations of project results on that day. Oral presentation guidelines will be provided in a separate document.

Anyone not participating in this project will automatically receive an F for ChE 230, regardless of other grades earned in this class.

## Groups

You will work on this project in groups of 4. More details of group formation and peer evaluation will be discussed in class.

## Revisions

As with any open-ended problem; i.e., a problem with no single correct answer, the problem statement above is deliberately vague. The possibility exists that, as you work on this problem, your questions will require revisions and/or clarifications. You should be aware that these revisions/clarifications may be forthcoming.

## References

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