ChE 455
Fall 2003
Major 1

Production of Maleic Anhydride from Benzene

Problem Statement

You are a new process engineer at TSC, Inc., a company specializing in the design and construction of chemical plants worldwide. TSC, Inc., provides a variety of functions related to the design of chemical facilities from conceptual and feasibility studies through the detailed design and sometimes construction of entire plants. As a new engineer, you have been assigned to the process design group. Your boss has been working on several designs, one of which is a preliminary design of a 20,000 tonne/yr maleic anhydride plant using benzene as the feedstock. This project is for a client in the Far East, who has access to a significant amount of benzene. Currently, the preferred route to maleic anhydride in the U.S. is via isobutane in fluidized bed reactors. However, the route via benzene is usually carried out using a shell-and-tube reactor with catalyst in the tubes and a cooling medium being circulated through the shell.

Due to unforeseen circumstances, your boss must leave for a period of three weeks to present a series of reports at TSC's head office in Dusseldorf, Germany, and will be unavailable for consultation. Upon her return, she (and you) must make a presentation to the client from the Far East on the progress of the maleic anhydride project. The responsibility for this work is now in your hands.

As a starting point, your supervisor has left you a converged simulation for the flowsheet along with a preliminary PFD, Figure 1, and a process description given below. Your boss has also included a list of comments and some concerns regarding the converged solution and has suggested some areas that you should concentrate on during her three week absence.

Process Description

A process flow diagram for the reactor section of the maleic anhydride process is shown in Figure 1 and a stream summary table is given in Table 1. Benzene is vaporized in E-501, mixed with air, and then heated in a fired heater, H-501, prior to being sent to a packed bed catalytic reactor, R-501, where the following reactions take place:

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

V-501	C-501	P-501A/B	E-501	H-501	P-502 A/B	E-502	R-501	P-503A/B	E-503	T-501	T-502	E-504	V-502	P-504 A/B	E-505
Benzene Feed Drum	Inlet Air Compressor	Benzene Feed Pumps	Benzene Feed Vaporizer	Feed Heater	Molten Salt Circ. Pumps	Molten Salt Cooler	Reactor	Dibutyl make-up Pumps	Reactor Effluent Cooler	MA Scrubber	Dibutyl Tower	Dibutyl Tower Condenser	Dibutyl Reflux Drum	Dibutyl Reflux Pumps	Dibutyl Reboiler

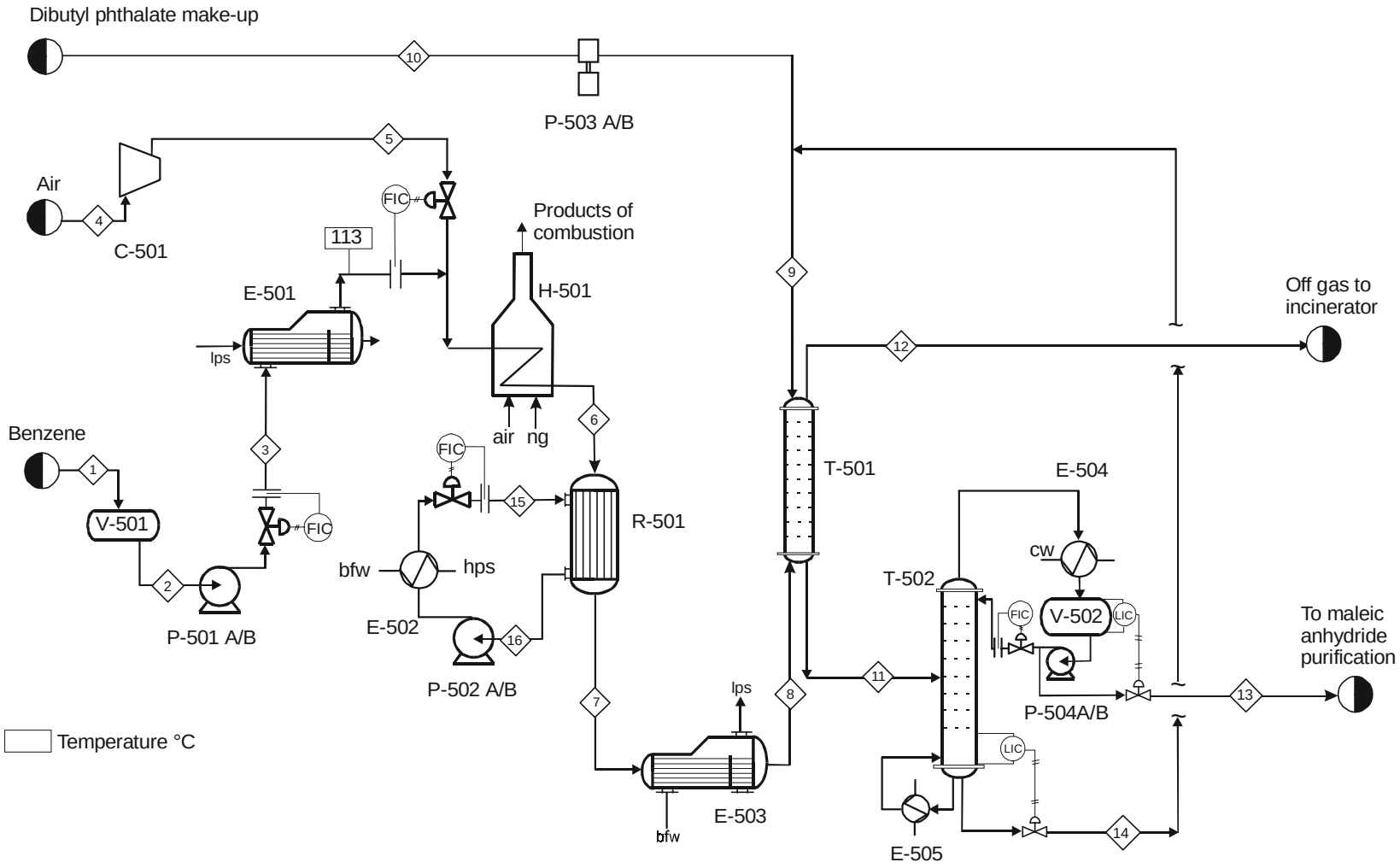

Figure 1: Preliminary PFD for Reactor loop of Maleic Anhydride Production Process

Table 1: Flow Stream Summary for Maleic Anhydride Process

Stream No.	1	2	3	4	5	6	7	8
Temp °C	30	30	30	30	145	460	608	260
Pres kPa	101	101	280	101	250	235	220	215
Total kmol/h	42.3	42.3	42.3	2790.0	2790.0	2832.3	2825.2	2825.3
Total kg/h	3304	3304	3304	80490	80490	83794	83794	83794
Flowrates in kmol/h								
Maleic Anhydride							26.3	26.3
Dibutyl Phthalate								
Nitrogen				2205.0	2205.0	2205.0	2205.0	2205.0
Water							91.5	91.5
Oxygen				585.0	585.0	585.0	370.2	370.2
Benzene	42.3	42.3	42.3			42.3	2.6	2.6
Quinone							0.7	0.7
Carbon Dioxide							129.0	129.0
Maleic Acid								
Sodium Nitrite								
Sodium Nitrate								

Stream No.	9	10	11	12	13	14	15	16
Temp °C	329	320	194	84	189	329	419	561
Pres kPa	80	100	82	75	70	80	200	200
Total kmol/h	500.1	0.1	526.2	2797.9	26.2	500.0	5000.0	5000.0
Total kg/h	139191.6	30.6	141866	81225	2597	139269	391925	391925
Flowrates in kmol/h								
Maleic Anhydride			24.8	0.5	24.8			
Dibutyl Phthalate	500.5	0.1	500.4	0.1		500.4		
Nitrogen				2205.0				
Water				90.5				
Oxygen				370.2				
Benzene				2.6				
Quinone			0.4	0.4	0.4			
Carbon Dioxide				129.0				
Maleic Acid			1.0		1.0			
Sodium Nitrite							2065.6	2065.6
Sodium Nitrate							2934.4	2934.4

$$C_6H_6 + 7.5O_2 \xrightarrow{k_2} 6CO_2 + 3H_2O \quad (2)$$
benzene

$$C_4H_2O_3 + 3O_2 \xrightarrow{k_3} 4CO_2 + H_2O \quad (3)$$
maleic anhydride

$$C_6H_6 + 1.5O_2 \xrightarrow{k_4} C_6H_4O_2 + H_2O \quad (4)$$
benzene *quinone*

All the reactions are highly exothermic. For this reason, the ratio of air to benzene entering the reactor is kept very high. A typical inlet concentration (Stream 6) of approximately 1.5 vol% of benzene in air is used. Cooling is achieved by circulating molten salt (a mixture of sodium nitrite and sodium nitrate) co-currently through the shell of the reactor and across the tubes containing the catalyst and reactant gases. This molten salt is cooled in an external exchanger, E-502, prior to returning to the reactor.

The reactor effluent, Stream 7, containing small amounts of unreacted benzene, maleic anhydride, quinone, and combustion products is cooled in E-502 and then sent to an absorber where it is contacted with a heavy organic solvent (dibutyl phthalate). This solvent absorbs the maleic anhydride, quinone, and small amounts of water. Any water in the solvent leaving the bottom of the absorber, T-501, reacts with the maleic anhydride to form maleic acid, which must be removed and purified from the maleic anhydride. The bottom product from the absorber is sent to a separation tower, T-502, where the dibutyl phthalate is recovered as the bottom product, Stream 14, and recycled back to the absorber. A small amount of fresh solvent, Stream 10, is added to account for losses. It should be noted that to obtain the desired separation in T-501, a reboiler and condenser are required (not shown in Figure 1). The overhead product from T-502, Stream 13, is sent for further purification.

Comments and Background Information on Simulation and Areas for Study for Upcoming Client Meeting

- The simulation that resulted in the stream flows in Table 1 used a packed bed reactor with 22,000 catalyst-filled tubes (each tube has an inside diameter of 0.025 m and is 3.2 m long). The catalyst sinters (degrades) rapidly above 650°C.
- Laboratory tests using the same catalyst in a single tube (same dimensions as above) have been used to verify the temperature sensitivity of the catalyst. It has been noticed that a hot spot develops in the tube in the laboratory experiments. In the plant, the location and magnitude of the hot spot must be controlled so that the activity of the catalyst can be maintained. This can be achieved by adjusting the flow of cooling medium, by adjusting the inlet reactor temperature, or by a combination of both
- Long-term studies in the laboratory have shown that even when the temperature is kept below 650°C, the catalyst does loose some of its activity. After 1 year of operation, the rate of the desired reaction (reaction 1) drops to about 80% of its initial rate. This can be

simulated by reducing the pre-exponential constant in reaction 1 by 20% (see Appendix 1).

- Although, the preferred reactor is the shell-and-tube design, it has been suggested by our client that a fluidized bed may be considered if the shell-and-tube design turns out to be unworkable.
- The recycle loop for the dibutyl phthalate, Stream 14, in the simulation is very large, requiring very large towers, T-501 and T-502. The cost of recycling this solvent should be investigated carefully.

The specific issues that should be addressed before the client meeting are as follows:

Using the given simulation as a base case:

1. Determine the operating conditions necessary to operate the plant at the end of 1 year to produce the same amount of maleic anhydride when the catalyst activity has dropped to 80% of its initial value for the main reaction. This should be a comprehensive account of how the equipment should be operated to give the same desired product, with the same equipment, under the constraint of reduced catalyst activity. A Chemcad (or other process simulator) simulation for the operation with reduced catalyst activity must be included in your report.
2. Determine the additional cost of operation at this reduced catalyst activity. It should be noted that increasing the rate of benzene feed to compensate for the reduced catalyst activity is highly undesirable due to the additional cost, and should only be suggested if no other solution can be found.
3. Determine the additional cost (if any) of using a fluidized bed instead of a packed bed to produce the maleic anhydride product.
4. For the fluidized bed option, consider also the operation of the unit at the end of 1 year when the catalyst activity has decreased. Again, you should give a comprehensive account of how the equipment must be operated to give the same desired product, with the same equipment, under the constraint of reduced catalyst activity. A Chemcad (or other process simulator) simulation for the operation with reduced catalyst activity must be included in your report.
5. Determine the additional cost of operation at this reduced catalyst activity for the fluidized bed reactor.
6. Investigate the dibutyl phthalate recycle loop and recommend ways in which the recycle flow can be reduced. Quantify your analysis using an incremental net present value (INPV). You should use the base case as a starting point and consider changes to the recycle separately. In other words, this optimization may be done separately and independently of the reactor issues outlined above.

For all economic comparisons, use a 10%, before-tax rate of return and a 10-year lifetime.

Deliverables

Specifically, you are to prepare the following by 9:00 am, Monday, November 10, 2003:

1. an analysis, for the process with a packed bed reactor, for the change in catalyst activity.

2. an analysis, for the process with a fluidized bed reactor, for the change in catalyst activity.

3. an analysis of the dibutylphthalate recycle loop.

4. process flow diagrams, relevant Chemcad (or other process simulator) output, and stream tables for all recommended cases.

5. a written report, conforming to the guidelines, detailing the information in items 1 - 3, above.

6. a legible, organized set of calculations justifying your recommendations, including any assumptions made.

7. a signed copy of the attached confidentiality statement.

Report Format

This report should be brief and should conform to the guidelines. It should be bound in a folder that is not oversized relative to the number of pages in the report. Figures and tables should be included as appropriate. An appendix should be attached that includes items such as the requested calculations. These calculations should be easy to follow. The confidentiality statement should be the very last page of the report.

The written report is a very important part of the assignment. Reports that do not conform to the guidelines will receive severe deductions and will have to be rewritten to receive credit. Poorly written and/or organized written reports may also require re-writing. Be sure to follow the format outlined in the guidelines for written reports.

Oral Presentation

You will be expected to present and defend your results some time between November 10, 2003, and November 14, 2003. Your presentation should be 10-15 minutes, followed by about a 30 minute question and answer period. Make certain that you prepare for this presentation since it is an important part of your assignment. You should bring at least one hard copy of your slides to the presentation and hand it out before beginning the presentation.

Other Rules

You may not discuss this major with anyone other than the instructors. Discussion, collaboration, or any other interaction with anyone other than the instructors is prohibited.

Violators will be subject to the penalties and procedures outlined in the University Procedures for Handling Academic Dishonesty Cases (begins on p. 48 of 2001-03 Undergraduate Catalog or p. 47 of the 2003-05 Undergraduate Catalog).

Consulting is available from the instructors. Chemcad consulting, *i.e.*, questions on how to use Chemcad, not how to interpret results, is unlimited and free, but only from the instructors. Each individual may receive five free minutes of consulting from the instructors. After five minutes of consulting, the rate is 2.5 points deducted for 15 minutes or any fraction of 15 minutes, on a cumulative basis. The initial 15-minute period includes the 5 minutes of free consulting.

Late Reports

Late reports are unacceptable. The following severe penalties will apply:

- late report on due date before noon: one letter grade (10 points)
- late report after noon on due date: two letter grades (20 points)
- late report one day late: three letter grades (30 points)
- each additional day late: 10 additional points per day

Appendix 1
Reaction Kinetics

The reactions and reaction kinetics are as follows:

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

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

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

$$\underset{\text{benzene}}{C_6H_6(g)} + 1.5O_2(g) \xrightarrow{k_4} \underset{\text{quinone}}{C_6H_4O_2(g)} + H_2O(g) \tag{A.4}$$

where

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

and

$$k_1 = 7.7\times10^6 \exp(-25{,}143/RT) \tag{A.6}$$

$$k_2 = 6.31\times10^7 \exp(-29{,}850/RT) \tag{A.7}$$

$$k_3 = 2.33\times10^4 \exp(-21{,}429/RT) \tag{A.8}$$

$$k_4 = 7.20\times10^5 \exp(-27{,}149/RT) \tag{A.9}$$

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 catalyst is placed in 25 mm diameter tubes that are 3.2 m long. The catalyst pellet diameter is 5 mm. The maximum temperature that the catalyst can be exposed to without causing irreversible damage (sintering) is 650°C.

For the fluidized bed reactor you should use the same catalyst size and assume a particle density of 1200 kg/m^3.

Appendix 2
Chemcad Hints

The Chemcad simulation used as a base case has several simplifications that you may assume are valid for this system. The removal of trace amounts of non-condensables is achieved after the absorber using a component separator, which avoids problems with column convergence downstream. The formation of maleic acid in Stream 11 is simulated by using a stoichiometric reactor and setting the conversion of water to 1.

Tower T-501, the maleic anhydride scrubber, is simulated using the rigorous tower simulator. Tower T-502, the dibutyl phthalate tower, is simulated using the ***shortcut column*** module. Currently, we do not have any experimental vapor pressure data for the components in this simulation. It appears that the vapor pressures of the components differ widely and no azeotropes are known of at this time. For this reason, the ideal vapor pressure *K*-value option and the latent heat enthalpy option should be used.

In order to simulate the temperature spike in the reactor, the reactor is simulated as a co-current, packed bed kinetic reactor, with a molten salt stream as the utility. The kinetics given in Appendix A are used in the simulation. Dimensions of the reactor are given in the main problem statement. The number of tubes may be changed in the simulation, but the length and diameter of each tube should remain the same.

For the simulation of the reactor as a fluidized bed, the reactor should be modeled as an isothermal plug flow reactor with 10% of the feed bypassing the reactor. This simulation is necessary to capture the isothermal nature of the fluidized bed but also to take into account the fact that the reactor feed bypasses the catalyst in the form of bubbles. Other data on the reactor design are given in Appendix 4.

Appendix 3
Raw Material Costs

Chemical	Price/Cost, $/kg
Dibutylphthalate	1.72
Benzene	0.45
Maleic Anhydride	0.93
Maleic Acid	0.90
Quinone	0.70

For utility costs, use the values in Chapter 6 of *Analysis, Synthesis, and Design of Chemical Processes*, R. Turton, R.C. Bailie, W.B. Whiting, and J.A. Shaeiwitz, 2nd ed., Prentice-Hall, 2003.

Appendix 4
Reactor Design Information

Packed Bed Reactor

The packed bed reactor should be costed as a shell-and-tube exchanger. The heat transfer area should be calculated based on the total external area of the catalyst-filled tubes required from the simulation. Because of the high temperatures involved, the shell-and-tube material should both be stainless steel. An overall heat transfer coefficient for the reactor should be set as 100 $W/m^2°C$ (This is the value specified in the simulation.)

Fluidized Bed Reactor

For the simulation of the reactor as a fluidized bed, the reactor should be modeled as an isothermal plug flow reactor with 10% of the feed bypassing the reactor. This simulation is necessary to capture the isothermal nature of the fluidized bed but also to take into account the fact that the reactor feed bypasses the catalyst in the form of bubbles. The overall heat transfer coefficient between the fluidized bed (comprising the catalyst) and the heat transfer medium circulating through tubes in the reactor should be taken as 250 $W/m^2°C$. The fluidized bed reactor may also be costed as a shell-and-tube exchanger made of stainless steel. Again, the heat transfer area should be based on (five times) the external surface area of the tubes through which the coolant flows. Because the fluidized bed reactor is more complicated than the packed bed shell-and-tube reactor, the fluidized bed reactor should be costed based on a heat exchanger area 5 times greater than that required for the heat transfer.