Separations and Reaction Engineering
Design Project

Production of Maleic Anhydride from Benzene

Problem Statement

We are now prepared for you to complete a final design of a production facility for maleic acid from benzene. You are to design a facility to produce 40,000 tonne/y of maleic anhydride.

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:

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

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

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

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

where

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

and

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

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

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

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

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.

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 (either TOWR or SCDS in Chemcad). Failure to use rigorous algorithms in the final case will result in a loss of credit. Preliminary screening using short-cut methods is acceptable.
- The ideal vapor pressure *K*-value and latent heat enthalpy options should be used for the Chemcad simulation.

Hints

In performing your study, you may wish to consider the following suggestions regarding the optimization.

- It is suggested that your first step be to synthesize a base-case process flowsheet.
- The air feed section should consist of a two-stage centrifugal compressor with inter-cooler that cools the air to a temperature of 45°C prior to entering the second compression stage.
- For the maleic anhydride process to have any chance of being profitable, the integration of process energy must be carefully planned.
- Dibutyl phthalate is used to absorb maleic anhydride from the cooled reactor effluent. This solvent absorbs the maleic anhydride, quinone, and small amounts of water. Any water in the solvent leaving the bottom of the absorber reacts with the maleic anhydride to form maleic acid, which must be removed and purified from the maleic anhydride. One possible separation scenario is as follows. The bottom product from the absorber is sent to a separation tower where the dibutyl phthalate is recovered as the bottom product

and recycled back to the absorber. A small amount of fresh solvent is added to account for losses. It should be noted that to obtain the desired separation in the absorber, a reboiler and condenser are required. Therefore, the absorber behaves like a distillation column with one of the feeds on the top tray and the other on the bottom tray. The overhead product from the dibutyl phthalate recovery column is sent to the maleic acid column, where 95 mol% maleic acid is removed as the bottom product. The overhead stream is taken to the quinone column, where 99 mol% quinone is taken as the top product and 99.9 mol% maleic anhydride is removed as the bottom product. It is this last column that must be designed in detail.

- In order to limit excessive reboiler and condenser duties on towers, the recycle flowrate of dibutylphthalate solvent should be limited. In addition, recovery and purification specifications of this solvent should be carefully evaluated.
- For the by-products (quinone and maleic acid), the option of not purifying them but using them for fuel credit should be considered. A comparison between the cost of separation and the loss in revenue from pure by-products should be used to determine the optimum strategy.

Specific Assignments

ChE 312

You are to determine the number of distillation columns required, their locations, their sequence, and enough information for each column to determine their costs. The distillation column that purifies the maleic anhydride should be designed in detail. A detailed design of a tray tower includes number of trays, tray spacing, diameter, reflux ratio, active area, weir height, top and bottom pressure specifications, and design of auxiliary equipment (heat exchangers, pump, reflux drum, if present). A detailed design of a packed tower includes height, packing size and type, and the same other specifications as in a tray tower. For all columns in this project, you may assume that HETP = 0.6 m. For the distillation column, the better economical choice between a packed and tray tower should be determined. For either a packed or a tray distillation column, the optimum reflux ratio should be determined.

Note that a tower consists of a vessel with internals (trays or packing). The constraints on a vessel are typically a height-to-diameter ratio less than 20. However, it is possible to extend this ratio to 30 as long as the tower is less than about 3 ft (1 m) in diameter. For larger-diameter towers, stresses caused by wind limit the actual height. Extra supports are needed for a height-to-diameter ratio above 20, even for smaller diameter columns. Therefore, there is a capital cost "penalty" of an additional 25% (only on the vessel) up to a ratio of 25, and a "penalty" of an additional 100% up to a ratio of 30.

You must choose the operating pressures for each column subject to constraints of operating temperature and available utilities. If vacuum columns are needed, pressure drop becomes a significant concern. As an alternative to tray towers, packed towers with a low-pressure-drop structured packing may be used. The packing factor as defined in Wankat[1], p. 424, is that for Koch Flexipac #2. Assume the HETP for the structured packing to be 0.6 m (see the definition of HETP in Wankat[1], p. 418, and the relationship between HETP and H_{OG} in Equation 19.36 in Wankat[1].), and that the pressure drop is 0.2 kPa/m (0.245 inch water/ft).

ChE 325

Several reactor types may be considered for use in this design. They are an adiabatic, packed bed reactor (a series of these with interstage cooling, if needed), an "isothermal," packed bed reactor, and a packed bed reactor with heat exchange. An "isothermal" reactor is defined here as one with a specified outlet temperature, not necessarily the inlet temperature, and some form of heat exchange is needed to add or remove the heat of reaction to maintain constant temperature. Chemcad will model the entire reactor as "isothermal" at that temperature. It must be understood that this situation is not physically realistic. In a reactor with heat exchange, the temperature along the length of the packed-bed reactor is not constant. The temperature can be controlled by varying the temperature and flowrate of the heat-transfer fluid, heat-transfer area, and the catalyst/inert ratio. The suggested heat-transfer fluid is molten salt, which is a mixture of 40 wt % sodium nitrite and 60 wt % sodium nitrate. If a heat-transfer fluid is used, it is circulated in a closed loop through the reactor where its temperature is increased (if the reaction is endothermic) or decreased (if the reaction is exothermic). Then, heat is added (removed) from the fluid in a heat exchanger (or fired heater, if needed). The heat-transfer fluid is then pumped back to the reactor. Properties of the molten salt mixture can be obtained from Chemcad from a stream with the appropriate composition.

For your best case, you should include a discussion of the temperature, pressure, and concentration profiles obtained from Chemcad.

General

The entire maleic anhydride process should be optimized using decision variables of your choosing. Decision variables should be chosen as the design variables most strongly affecting the objective function. There are topological optimization and parametric optimization. In topological optimization, which is usually done first, the best process configuration is chosen. Parametric optimization involves varying operating variables and should be done after topological optimization is complete. Some examples of parameters that can be used as decision variables are reactor temperature, pressure, and conversion; absorber temperature and pressure; and distillation column reflux ratio.

Economic Analysis

When evaluating alternative cases, the equivalent annual operating cost (EAOC) objective function should be used. The EAOC is defined as

EAOC = -(product value - feed cost – utility costs – waste treatment cost - capital cost annuity)

A negative EAOC means there is a profit. It is desirable to minimize the EAOC; i.e., a large negative EAOC is very desirable.

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

The capital cost annuity is defined as follows:

$$capital\ cost\ annuity = FCI \frac{i(1+i)^n}{(1+i)^n - 1} \tag{10}$$

where *FCI* is the installed cost of all equipment; *i* is the interest rate (take $i = 0.15$) and *n* is the plant life for accounting purposes (take $n = 10$).

Report Format

This report should conform to the Department 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 sample calculations. These calculations should be easy to follow.

The written report is a very important part of the assignment. Poorly written and/or organized written reports may require re-writing. Be sure to follow the format outlined in the guidelines for written reports. Failure to follow the prescribed format may be grounds for a re-write.

The following information, at a minimum, must appear in the main body of the final report:

1. a computer-generated PFD (not a Chemcad PFD) for the recommended optimum case,

2. a stream table containing the usual items,

3. a list of new equipment for the process, costs, plus equipment specifications (presented with a reasonable number of significant figures),

4. a summary table of all utilities used,

5. a clear summary of alternatives considered and a discussion, supported with figures, of why the chosen alternative is superior,

6. a clear economic analysis which justifies the recommended case

7. a discussion section pertinent to each class plus a general discussion section for optimization of the entire process

8. a Chemcad report only for your optimized case (in the Appendix). This must contain the equipment connectivity, thermodynamics, and overall material balance cover pages; stream flows; equipment summaries; tower profiles; and tray (packing) design specifications (if you use Chemcad to design the trays (packing)). It should not contain

stream properties. Missing Chemcad output will not be requested; credit will be deducted as if the information is missing.

Other Information

Unless specifically stated in class, the information in this document is valid for this project only. Any information in the sophomore projects not specifically stated in this document is not valid for this project.

Deliverables

Each group must deliver a report (two identical copies, one for each professor) written using a word processor. The report should be clear and concise. The format is explained in the document *Written Design Reports*. Any report not containing a labeled PFD and a stream table, each in the appropriate format, will be considered unacceptable. PFDs from Chemcad are generally unsuitable unless you modify them significantly. When presenting results for different cases, graphs are superior to tables. For the optimum case, the report appendix should contain details of calculations that are easy to follow. There should be separate appendices for each class, ChE 312 and ChE 325, each containing calculations appropriate for the respective class. These may be handwritten if done so neatly. Calculations that cannot be easily followed will lose credit.

Each group will give an oral report in which the results of this project will be presented in a concise manner. The oral report should be between 15-20 minutes, and each group member must speak once. Reports exceeding this time limit will be stopped. A 5-10 minute question-and-answer session will follow. Instructions for presentation of oral reports are provided in a separate document entitled *Oral Reports*. The oral presentations will be Wednesday, April 20, 2005, starting at 11:00 a.m. and running until approximately 3:00 p.m. Attendance is required of all students during their classmates' presentations (this means in the room, not in the hall or the computer room). Failure to attend any of the above-required sessions will result in a decrease of one letter grade (per occurrence) from your project grade in ChE 312 and ChE 325.

The written project report is due by 11:00 a.m. Wednesday, April 20, 2005. Late projects will receive a minimum deduction of one letter grade.

In order to evaluate each team members writing skills, the results and discussion sections for each specific assignment should be written by a different team member. The authorship of each of these specific assignments should be clearly specified in the report. If a team has four members, the member not authoring a specific assignment should author the cover memorandum, abstract, introduction, and conclusion.

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 of the problem statement. You should be aware that these revisions/clarifications might be forthcoming.

References

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

Appendix 1
Chemcad Hints

In order to simulate the temperature profile in a packed bed reactor, the reactor is simulated as a co-current, packed bed kinetic reactor, with a molten salt stream as the utility.

Any water absorbed into the dibutyl phthalate will react completely in the absorber with maleic anhydride to produce maleic acid. Simulation of this reaction should be done by adding a stoichiometric reactor after the absorber. However, this bogus piece of equipment should not appear on your process flow diagram

Appendix 2
Raw Material Costs

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

Appendix 3
Cost Information

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.

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, 3000) 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)
Catalyst	$2.25/kg
Packed Tower	Cost as vessel plus cost of packing

Packing	$\log_{10}(\text{purchased cost}) = 3 + 0.97\log_{10} V + 0.0055[\log_{10} V]^2$ V = packing volume (m^3, 0.03, 628)
Tray Tower	Cost as vessel plus cost of trays
Trays	$\log_{10}(\text{purchased cost}) = 3.3 + 0.46\log_{10} A + 0.37[\log_{10} A]^2$ A = tray area (m^2, 0.07, 12.3)
Storage Tank	$\log_{10}(\text{purchased cost}) = 5.0 - 0.5\log_{10} V + 0.16[\log_{10} V]^2$ V = volume (m^3, 90, 30,000)
Reactors	For this project, the reactor is considered to be a vessel.

It may be assumed that pipes and valves are included in the equipment cost factors. Location of key valves should be specified on the PFD.

Equipment Cost Factors

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

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

Carbon Steel MF = 0.0
Stainless Steel MF = 4.0

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

Any fuel gas purge may be assumed to be burned elsewhere in the plant at a credit of \$2.50/GJ. Steam produced cannot be returned to the steam supply system for the appropriate credit. Steam produced in excess of that required in this process is purged with no credit.

Appendix 4
Other Design Data

Heat Exchangers

For heat exchangers, use the following approximations for heat-transfer coefficients to allow you to determine the heat transfer area:

situation	**h (W/m²°C)**
condensing steam	6000
condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60