ChE 456
Spring 2010
Major 2

Phthalic Anhydride Production

Background

The results from your recent scale-up study indicated that only an additional 2% of product could be produced from the current phthalic anhydride (PA) production facility. Despite the current downturn in the economy, our management feels that the future for PA-based products continues to be strong and that investment in future PA production facilities is warranted. With this in mind, you are being asked to prepare a study to investigate the feasibility of a new production facility to produce 50,000 tonne/y of 99.9 mol% purity PA.

Design Criteria

The new production facility is being planned for construction at the same facility as the existing plant. A review of utility requirements and usage at the existing plant indicate that there is extra capacity in the cooling water, process water, and instrument air services. However, the steam at the facility is in balance and the new PA process will not be tied into the existing steam headers. This means that all steam for the new unit should be generated from within the process, and that excess steam can neither be sold nor can credit be taken for it. If steam is required for this unit, then packaged boilers should be priced and included in the new design.

The Net Present Value (NPV) should be the objective function used to optimize the configuration and operating conditions in the new process. The following economic parameters should be used in your design:

Land Cost = $0
Salvage Value = $0
Construction period = 2 yrs.
Working Capital = 6 months supply of raw materials
Fixed Capital Investment = 65% in year 1 and 35% in year 2
Internal hurdle rate = 7% after taxes
Taxation rate = 45%
Depreciation method – MACRS 5 year

For this study, you should assume the following raw material and utility costs:

o-xylene = $0.80/kg
phthalic anhydride = $1.25/kg
Fuel gas = $ 11.00/GJ
Cooling water = $0.354/GJ based on heating duty in exchangers
Process water = $0.07/1000kg
Electricity = $0.06/kWh

Assignment

The aim of the current assignment is to design the most profitable configuration for the proposed plant using the NPV as the objective function for profitability. You may wish to take a scaled down version of the existing process as your base case or starting point for the new design. However, because of the different design constraints for the new plant, this base-case is unlikely to be optimal. Hints on using Chemcad for this project are given in Appendix 1. The same reactions (and catalyst) as used in the existing plant will be used here, and information on the reaction pathways and rates is repeated in Appendix 2. In addition to considering a packed bed reactor, you should investigate the use of a fluidized bed reactor. Design information for fluidized beds is given in Appendix 3.

In anticipating future demand of PA beyond the 50,000 tonne/y design management would also like to have the PA/MA separation tower designed to accommodate a 20% increase in throughput. Your tower design must be able to handle the design flow and a 1.2 times scale up.

Deliverables

Specifically, the following is to be completed by 9:00 a.m., Monday, February 22, 2010:

1. Prepare a written report, conforming to the guidelines, detailing the information requested in the assignment. Your discussion of the optimal design and tower scale-up should explain clearly the methodology and logic used to determine your final design.

2. Include a legible, organized set of calculations justifying your recommendations, including any assumptions made. These should be placed in a well-indexed appendix to the main report.

3. Provide a PFD, stream table, and equipment summary table for the optimized design.

4. Attach a signed copy of the attached confidentiality statement.

Report Format

This report should be brief and should conform to the guidelines, which are available at the end of the following web page: http://www.che.cemr.wvu.edu/publications/projects/index.php. It should be bound in a 3-ring binder/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 and a converged Chemcad simulation for your recommended case. Stream properties **are not** to be included in the Chemcad report. The calculations in the appendix 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 rewriting. 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 February 22, 2010 and February 26, 2010. Your presentation should be 15-20 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 interaction with anyone other than the instructor is prohibited. This means that any cross talk among students about anything relating to this assignment, no matter how insignificant it may seem to you, is a violation of the rules and is considered academic dishonesty. Violators will be subject to the penalties and procedures outlined in the University Procedures for Handling Academic Dishonesty Cases (see p. 45 of 2009-11 Undergraduate Catalog (http://coursecatalog.wvu.edu/fullcatalogs/09-11catalog.pdf) or follow the link http://www.arc.wvu.edu/rightsa.html).

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
Chemcad Hints

A converged simulation for the plant at current operating conditions was included with your previous assignment and may be used as a starting point for this project.

The kinetic equations for all the reactions are given in Appendix 2 and are the same reactions used in the previous study.

The thermodynamics and enthalpy models are UNIFAC and latent heat and have shown to be accurate for the portions of the plant that are modeled in the flowsheet.

A warning message will appear when running Chemcad stating that heat of formation data are missing for Dowtherm. Ignore this warning, since it makes no difference to the simulation because Dowtherm is not involved in any reactions.

The recovery of phthalic anhydride is done using a set of switch condensers that desublimate the PA using cooled oil. This unit operation has been modeled as a component separator with the following fractions leaving in the off gas.

o-xylene	1.0000
Oxygen	1.0000
Nitrogen	1.0000
Water	1.0000
Carbon Dioxide	1.0000
Phthalandione	0.0100 (phthalic anhydride)
Maleic Anhydride	0.8900
Benzoic Acid	0.9500

The maleic anhydride is purified from the off-gas and mixed with the maleic anhydride (MA) from the PA purification tower, and sold. The switch condenser and maleic anhydride purification and recovery equipment is not covered in the current design and will be designed by an outside contractor. The remainder of the off-gas is incinerated

The PA/MA separation tower should be included in the design and be simulated using the SDCS unit operation. Tower sizing calculations using sieve trays and the Fair flooding correlation, O'Connell tray efficiency, and other pertinent tray and column data can be performed by Chemcad using the "tower sizing" tab. Use of other tray types is also allowed and should be considered in the design.

Note the constraint in the assignment about sizing the tower to accommodate a 20% increase in throughput.

Appendix 2
Reaction Chemistry and Kinetics

The oxidation reactions that take place are highly exothermic, and the temperature everywhere in the reactor must be very carefully controlled. The catalyst, vanadium pentoxide (V_2O_5), sinters above a temperature of 400°C. The reactions taking place are:

$$C_6H_4(CH_3)_2 + 3O_2 \rightarrow C_6H_4(CO)_2O + 3H_2O \quad (1)$$

o-xylene phthalic anhydride

$$C_6H_4(CO)_2O + \frac{15}{2}O_2 \rightarrow 8CO_2 + 2H_2O \quad (2)$$

phthalic anhydride

$$C_6H_4(CH_3)_2 + \frac{21}{2}O_2 \rightarrow 8CO_2 + 5H_2O \quad (3)$$

o-xylene

$$C_6H_4(CH_3)_2 + \frac{15}{2}O_2 \rightarrow C_2H_2(CO)_2O + 4CO_2 + 4H_2O \quad (4)$$

o-xylene maleic anhydride

$$C_2H_2(CO)_2O + 3O_2 \rightarrow 4CO_2 + H_2O \quad (5)$$

maleic anhydride

$$C_6H_4(CH_3)_2 + 3O_2 \rightarrow C_6H_5(COOH) + CO_2 + 2H_2O \quad (6)$$

o-xylene benzoic acid

$$C_6H_5(COOH) + \frac{15}{2}O_2 \rightarrow 7CO_2 + 3H_2O \quad (7)$$

benzoic acid

The kinetic expressions for these reactions all have the form:

$$-r_A = k_o e^{-\frac{E_a}{RT}} p_1 p_2 \quad (8)$$

where k_o has units of kmol/m^3-reactor/h, E_a has units of kcal/kmol, and p_i are partial pressures in atm. The constants for these reactions are given in Table 4:

Table 4: Kinetic Constants used for Reactions (Equations 1-7)

Reaction Number	k_o	E_a	1	2
1	4.12×10^{11}	27,000	o-xylene	oxygen
2	1.15×10^{12}	31,000	phthalic anhydride	oxygen
3	1.73×10^{11}	28,600	o-xylene	oxygen
4	2.25×10^{11}	27,900	o-xylene	oxygen
5	7.76×10^{11}	30,400	maleic anhydride	oxygen
6	5.00×10^{09}	27,000	o-xylene	oxygen
7	5.00×10^{11}	29,500	benzoic acid	oxygen

Appendix 3
Reactor Design

In order to operate safely, the reaction mixture must be kept below the lower explosive limit of 1 mol% of o-xylene in air. The oxidation of o-xylene can take place in a packed-bed reactor with catalyst-filled tubes that are cooled using a circulating stream of Dowtherm A, as in the current plant that was the focus of the previous study. This configuration is technically feasible and should be considered in your design, but it may not be optimal.

An alternative reactor design for these highly exothermic reactions is a turbulent fluidized bed with heat transfer tubes located in the reactor. A review of some pertinent design criteria for a fluidized bed reactor is given in the following section.

Operating flow should range from 20-30 times the minimum fluidizing velocity, u_{mf}.

Catalyst particle size (d_p) = 400 μm (400×10^{-6} m)
Catalyst particle density, ρ_p = 2,400 kg/m^3
Catalyst bulk density, ρ_{bulk} = 1,350 kg/m^3
Catalyst sinters above a temperature of 400°C

Minimum fluidizing velocity can be calculated from the correlation of Wen and Yu[2]

$$\frac{d_p u_{mf} \rho_f}{\mu} = \mathrm{Re}_{\mathrm{p,mf}} = \left[(28.7)^2 + 0.0494\mathrm{Ar}\right]^{0.5} - 28.7$$

where Ar is the Archimedes number and is given by

$$\mathrm{Ar} = \frac{(|\rho_p - \rho_f|)\rho_f d_p^3 g}{\mu^2}$$

and ρ, μ, and g have their normal meaning and subscripts p and f refer to particle and fluid, respectively.

The pressure drop through the fluidized bed is given by:

$$\Delta P_{bed} = L(1-\varepsilon)(\rho_p - \rho_f)g$$

Where L is the height of the bed and ε is the bed voidage. For a turbulent fluidized bed operating at 20-30 times u_{mf}, you should assume that ε = 0.55.

Pressure drop through distributor plate and exit cyclones = 25% of bed pressure drop

Heat transfer coefficient between tube wall and turbulent fluid bed = 300 W/m^{2}K

For modeling a fluidized bed, you should assume that the bed operates isothermally, *i.e*., the bed of solids is well mixed. However, the gas flow through the solids bed is a mixture of plug flow and by-passing. For this design, you should assume that 90% of the gas entering the bed passes through in plug flow while the other 10% bypasses the catalyst, *i.e*., does not react. The flow model for the reactor is shown below in Figure A3.1

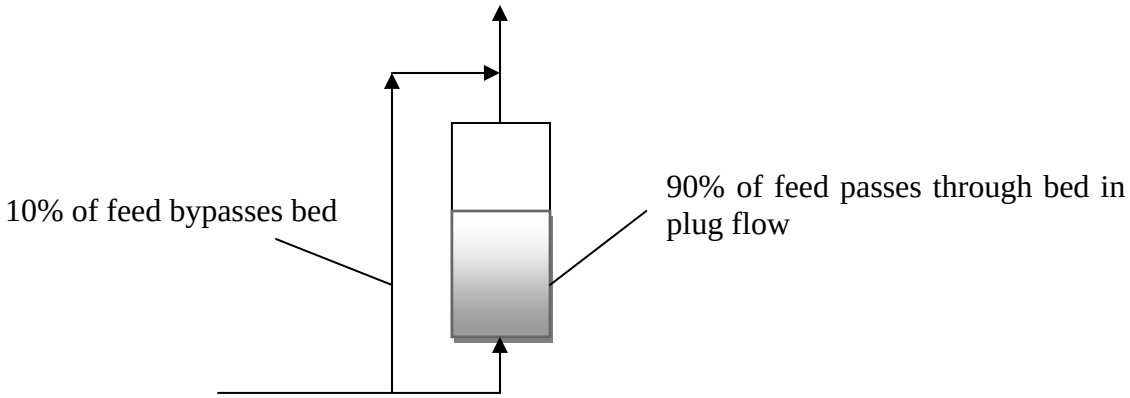

Figure A3.1: Flow model of turbulent fluidized bed (bed temperature = constant), heat transfer tubes not shown but should be included in design

For all surfaces in contact with phthalic anhydride, the recommended material of construction is 304 stainless steel.

The cost of the packed bed reactor can be estimated by adding the cost of a shell-and-tube heat exchanger to the cost of the process vessel required to house the catalyst tubes.

The cost of the fluidized bed reactor should be taken to be twice the cost of the sum of a shell-and-tube heat exchanger and the process vessel required to house the heat transfer tubes.