

# Reactors and Separations Design Project

## Phthalic Anhydride Production

We are continuing our evaluation of process alternatives for the production of Phthalic Anhydride via the catalytic oxidation of o-xylene. In this regard we are requesting JrDes Co., Inc. to participate in a study to evaluate several more process alternatives in the separation and reactor sections of the process.

The specific details of your assignment are outlined in the following pages. However, the main goal of this project is to prepare an optimized preliminary design of a plant which will produce 80,000 metric tons/yr of Phthalic Anhydride (99.5 wt %) using essentially pure o-xylene feed. In order to “optimize” it is necessary to use an objective function. The value of  $C_{PH}$  in the following equation should be used as the objective function for this project:

$$\begin{aligned} & (\text{Phthalic Anhydride Produced per year [ kg ]}) ( C_{PH} [ \$ / \text{ kg } ] ) = \\ & (0.3) (4) \{ \sum \text{ Purchased Equipment Cost [\$]} \} + \text{ Annual Utility Cost [\$]} + \\ & \text{ Annual Cost of Raw Materials [\$]} - \text{ Annual Revenue from By - Products [\$]} - \\ & - \text{ Annual Credit from Fuel Gas and Steam [\$]} \end{aligned}$$

where  $C_{PH}$  is the break - even price for Phthalic Anhydride[ \$ / kg ]

The above equation for estimating the cost of phthalic anhydride,  $C_{PH}$  [\$/kg], is based on the price that phthalic anhydride would have to be sold for in order for the process to “break-even”, clearly your design should try to minimize this “break-even price.” You will notice that the first term on the right hand side contains two constants, 0.3 and 4. The second constant (4) is used to convert the total purchased equipment cost to the total installed equipment cost or the cost of building the plant. The first constant (0.3) converts the one time cost of building the plant into an equivalent annual operating cost. The conversion of a one time cost to an equivalent yearly cost is sometimes called amortization (these economic details will be covered in detail in ChE 182/3).

Detailed equipment estimates are required only for the reactor and separation sections of the process.

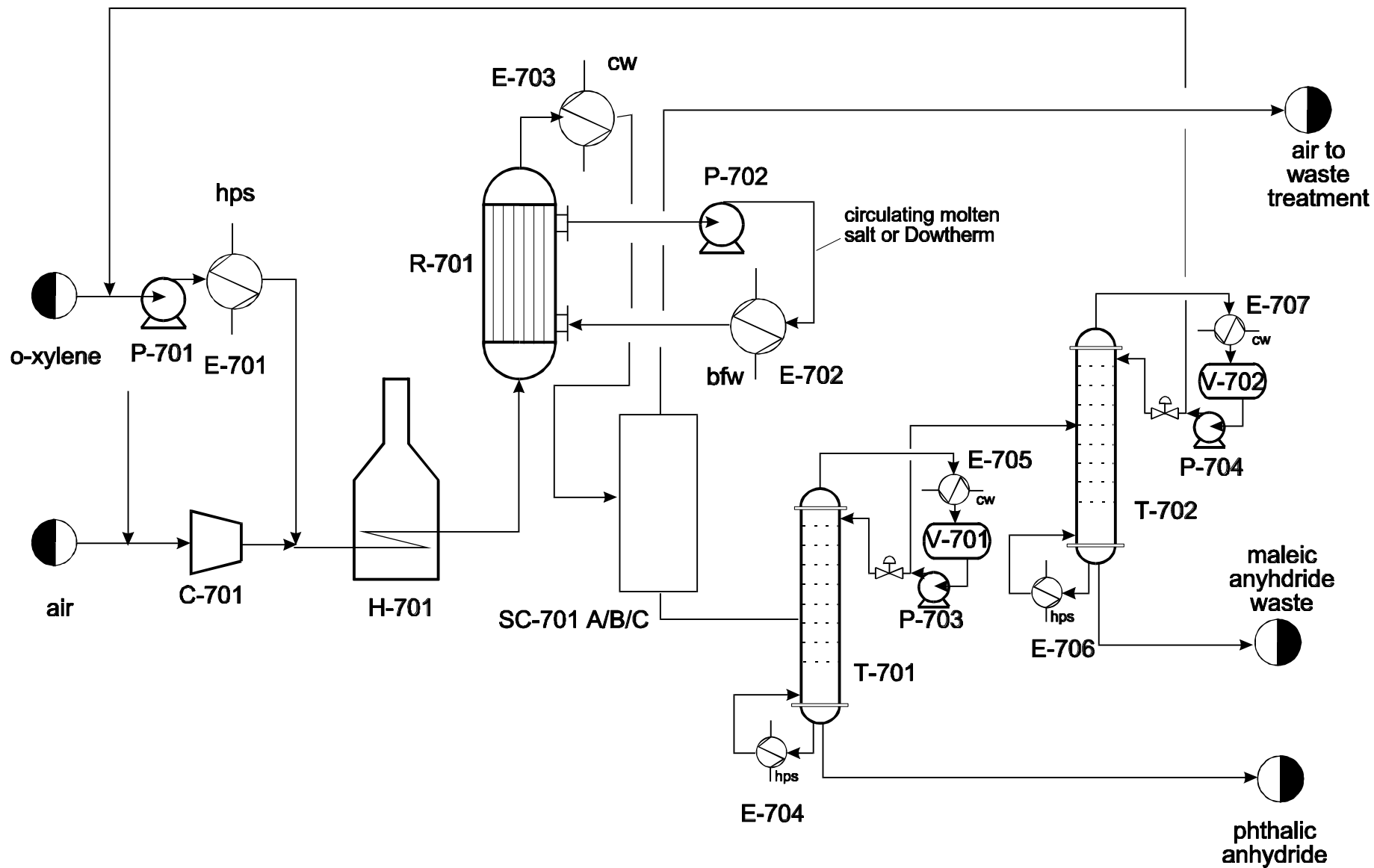
All other equipment may be sized roughly and design criteria and cost estimates are provided in Appendix I and II of this memorandum. The costs of utilities, raw materials, waste treatment, by-product, fuel and steam credits are given in Appendix III. Detailed explanations of the reactor and separation sections are provided below. A preliminary process flow diagram (PFD) for this process, Figure 1, is provided for reference purposes. This flow diagram serves only as a starting point and to aid discussions about process strategy. The optimized PFD (namely the one corresponding to a minimum price for phthalic anhydride) will most likely be different from the one shown here.

## **Process Description**

The basic process consists of mixing a stream of vaporized ortho-xylene with compressed air and then feeding this stream into a fired heater and then into a catalytic reactor. The reactor operates in the temperature range of 300 to 400°C and in the pressure range of 1 to 3 bar. The reaction is highly exothermic and the reacting gas stream must be cooled in the reactor to avoid excessive temperatures and a run away reaction. This cooling can be achieved by placing the catalyst in tubes and passing a cooling medium (molten salt) on the outside of the tubes with the reacting gases passing on the inside of the tubes over the catalyst. This configuration is similar to a shell and tube heat exchanger. An alternative scheme is to operate the reactor as a fluidized bed where the bed comprises the catalyst and heat transfer tubes, with coolant flowing inside the tubes, pass through the bed to remove the heat of reaction. The process stream containing the xylene and air pass upward through the bed and cause the solids to fluidize. Due to the potential for an explosion it is common to adjust the inlet concentration in the reactor to be outside the explosive limits, information on this and the reactor configuration is given in Appendix V. The stream leaving the reactor is cooled quickly in one or more heat exchangers prior to being sent to the switch condensers. These condensers use a cyclic process to separate the condenseable organics (99% recovery) from the non-condenseable gases and are discussed in more detail in Appendix VI. The organic material, containing phthalic and maleic anhydrides and any unreacted xylene are fed to two distillation columns to recover the products, which are then sent to storage. Any unreacted xylene may be recycled to the front end of the process.

### **(i) Separations Section**

Due to the high boiling points of the products, the separation section is often run under vacuum. This is necessary to avoid the use of a fired heater to reboil the towers (and to avoid possible cracking reactions at the higher temperatures). When specifying the separations section you should provide the following information:



Unit 700 - Phthalic Anhydride from o-Xylene

**Operating Pressure** (which determines operating temperatures)

**Reflux Ratio** (which affects the size of the condenser, reboiler, utility costs for both and the diameter of the tower)

**Type of Internals** (trays or packing)

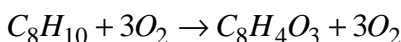
**Number of Theoretical and Actual Stages**

**Tray Spacing** (if trays are used)

**Height and Diameter of Column**

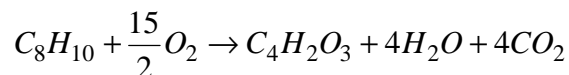
## (ii) Reaction Section

The main reaction of interest is the partial oxidation of cumene to produce phthalic anhydride:



This reaction can be carried out heterogeneously (using a solid catalyst). We have information on a new proprietary catalyst that we would like you to use (see Appendix V). The reactor types that you should consider are a **packed bed** and a **fluidized bed**. For a Fluidized Bed design the bed/reactor temperature may be assumed to be isothermal (i.e. the solids are well mixed).

No matter what reactor configuration is used the formation of by-products cannot be helped. Using the catalyst mentioned above we eliminate most by-products the most notable exception is maleic anhydride. Maleic anhydride is produced by the following reaction:



In addition, o-xylene and both anhydrides can be further oxidized to give carbon dioxide and water. A complete description of the reaction kinetics including rate data are given in Appendix V.

## Written Reports

### Due Date

All written reports (one for each design group) will be due on Friday the 19th of April by 5:00 pm in Dr. Turton's Mailbox in Room 401.

### Penalty for Late Reports

All late written reports will receive a one letter grade penalty - No Exceptions!

### **Hints on Solving the Problem**

Having read the problem statement it should be clear that there are many process options available to you. It is tempting to just jump right in and start optimizing things but this is a mistake! It is recommended that the first thing that you do is to establish a “base case.” This should consist of the simplest process which is technically feasible and a good base case would be one based on the PFD supplied. Using this case you should establish material and energy balances using ChemCad and do the necessary calculations in order to estimate the size of all major equipment and the costs of all raw materials, utilities and credits. Using all this information you can calculate the break-even price for phthalic anhydride for this base case. Once the base case has been established you can focus on the optimization of the process. The purpose of the optimization is to reduce (minimize) the break-even price for phthalic anhydride. Using the economics from the base case, you should be able to focus on the important areas for optimization and establish the important decision variables. Remember, slick process tricks are only slick if they save us money and only an economic analysis will give you this information.

**Good Luck with Your Assignment !**

## APPENDIX I

### Design Criteria for all Equipment

#### Heat Exchangers

Use the following overall heat transfer coefficients

	BTU/hr.ft <sup>2</sup> .°F	W/m <sup>2</sup> .K
condensing vapor to boiling liquid	250	1420
condensing vapor to flowing liquid	150	850
condensing vapor to flowing gas	20	115
flowing liquid to boiling liquid	150	850
flowing liquid to flowing liquid	50	280
flowing liquid to flowing liquid	20	115
flowing gas to flowing gas	10	58

Assume exchanger efficiencies of 100% i.e.  $F=1.00$

#### Reactor Feed Preheater/Furnace

Assume an overall thermal efficiency of the furnace = 0.90 or 90%

example : if the duty required to heat the reactor feed is 500 kW then the required size of the furnace =  $500/0.9 = 556$  kW and the fuel required should be based on a duty of 556 kW.

#### Pumps

Assume an overall efficiency of 0.75 or 75%

Use electric drives.

Each pump must have a spare.

#### Compressors

All compressors are to use electric drives

Assume an overall efficiency of 0.70 or 70%

Maximum pressure ratio for a single stage is 3. For multiple stages with intercoolers the compression ratio for each stage should be equal.

## Tanks

No storage tanks should be sized. All flash drums and overhead reflux drums should be priced as vessels. Off site storage needs should not be considered for this design.

## Vessels (flash drums and reflux drums)

### Reflux Drums

1. Reflux drums should have a total capacity equivalent to 10 minutes of liquid flow from the drum.

example: if the total condensed liquid feed to a reflux drum is  $0.05 \text{ m}^3/\text{s}$  then the drum capacity should be  $(0.05)(60)(10) = 30 \text{ m}^3$

2. For reflux drums use horizontal vessels with an L/D (length to diameter ratio) equal to 3.0

### Flash or Liquid/Vapor Separators

1. Use vertical vessels with L/D of 2.5 to 5.0
2. Use a liquid hold up of 10 minutes i.e. same volume as for reflux drums.
3. Gas velocity in the separator =  $v$  where

$$v = 0.1 \sqrt{\frac{r_l}{r_g} - 1} \quad \text{m/s}$$

note: the size of the vessel must be based on the limiting value from either 2 or 3 above.

## Piping and Valves

The costs of piping and valves are included in the factor 4 used to convert purchased costs to installed costs. You do not need to size any valves or pipes.

## Distillation Towers

See Appendix IV

## Reactors

See Appendix V

## APPENDIX II

## Purchased Cost of Equipment

All equipment prices are for carbon steel or the appropriate material of construction.

Purchased Cost		Pressure Factors for All Equipment (unless stated otherwise)
Heat Exchangers	\$ 1,600 [m <sup>2</sup> ] <sup>0.7</sup>	<10 atm = 1.0
Furnaces	\$ 70,000 [MW] <sup>0.8</sup>	10 - 20 atm = 1.6
Pumps	\$ 750 [kW] <sup>0.7</sup>	20 - 40 atm = 3.0
Compressors	\$ 1900 [kW] <sup>0.8</sup>	>40 atm = 5.0

**Vessels (vertical and horizontal)**

$$\text{Purchased Cost} = A \times 10^B$$

where

$$A = 0.75 + 0.42(0.96 + 0.041P - 8.3 \times 10^{-6} P^2)$$

$$B = 3.17 + 0.2D + 0.5 \log L + 0.2 \log(L^2)$$

the range of applicability for the above equation is

$$D < 4.0 \text{ m}, L/D < 20, 1 \text{ atm} < P < 400 \text{ atm}$$

example : What is the purchased cost for a vessel that has a diameter of 2 m, height of 10 m and operates at 50 atm.

$$A = 0.75 + 0.42(0.96 + 0.041(50) - 8.3 \cdot 10^{-6}(50)^2) = 2.01$$

$$B = 3.17 + 0.2(2) + 0.5 \log(10) + 0.2 \log(100) = 4.47$$

$$\text{purchased cost} = A \cdot 10^B = 2.01 \times 10^{4.47} = \$ 59,300$$

**Vessel Internals**

$$\text{Cost of trays (sieve or valve)} = \$ 200 + 30D + 71D^2 \text{ for } D < 4.0 \text{ m}$$

example : what is the cost of 1 tray 3 m in diameter ?

$$C = 200 + 30(3) + 71(9) = \$929$$

$$\text{Cost of packing} = 10^{\{1.88 + 0.91D - 0.099D^2\}} [L_p^{0.89}] \text{ for } D < 4.0 \text{ m}$$

example : what is the cost of packing for a 1.5 m diameter column with a packed section 20 m high ?

$$\begin{aligned} C &= 10^{\{1.88 + 0.91(1.5) - 0.099(2.25)\}} [20^{0.89}] \\ &= \$ 15,140 \end{aligned}$$

## Reactor

For all reactors containing heat transfer surfaces the cost of the heat transfer surface (taken to be the same as that given for heat exchangers in this appendix) should be added to the vessel costs given below.

### Packed Bed Reactor

For a packed bed reactor use 1.25 times the cost of a heat exchanger with the same surface area for heat transfer as the reactor. The 1.25 factor will take account of the added cost for internals, instrumentation and sample ports etc.

### Fluidized Bed

For a fluidized bed reactor use 1.7 times the cost of a vessel with the same dimensions as the reactor. The 1.7 factor reflects the more complicated nature of fluidized beds.

The volume of the reactor is equal to 1.25 times the volume of solids (catalyst and filler material). This extra volume is provided to allow for disengaging of gas and solids above the bed.

The cost and physical properties of the filler material (if required) are the same as the catalyst. In fact, this material is simply the support solid on to which the catalytic metals are deposited.

## APPENDIX III

**Costs of Raw Materials**

	Composition	Pressure	Temp	Price/Cost
Feed O-Xylene	~100 %	1.0 bar	25°C	\$ 0.35/kg

**Cost of Utilities**

	Available Pressure	Available Temperature	Price/Cost
Natural Gas	4 bar	25°C	\$ 0.085/ std m <sup>3</sup>
Low Pressure Steam	4 bar	sat vap	\$ 6.62/ 1000 kg
Med. Pressure Steam	11 bar	sat vap	\$ 7.31/ 1000 kg
High Pressure Steam	41 bar	sat vap	\$ 8.65/ 1000 kg
Electricity			\$ 0.06/ kWh
Boiler Feed Water	4 bar	100°C	\$ 2.54/ m <sup>3</sup>
Condensate Return (credit)			\$ 2.54/ m <sup>3</sup>
Cooling Water*	5 bar	30°C	\$ 6.70/ 1000 m <sup>3</sup>
Cooling Water Return	3 bar	40°C	
Refrig. Water*	5 bar	5°C	\$10.00/ 100 m <sup>3</sup>
Refrig. Water Return	3 bar	15°C	

\* Cooling water and refrigerated water costs reflect the fact that a 10°C temperature rise is assumed for the stream. The following example illustrates the use of these costs:

example : what is the yearly operating cost for a heat exchanger with a duty of 50 kW using cooling water?

$$\begin{aligned}
 \text{mass of cooling water req'd} &= Q/C_p/\Delta T = 50000/4200/10 = 1.19 \text{ kg/s} \\
 \text{volume of cooling water} &= M/\rho = 1.19/1000 = 1.19 \cdot 10^{-3} \text{ m}^3/\text{s} \\
 \text{cost for cooling water} &= (1.19 \cdot 10^{-3})(3600)(24)(350)(6.70)/(1000) \\
 &= \$ 241 \text{ per year}
 \end{aligned}$$

**Cost of Air Treatment:**  $\$/\text{m}^3 \text{ air treated} = 10^{-4}(0.5 + 1000x_{or})$   
 $x_{or}$  = mole fraction of organics in “dirty air” stream

**By-Product Credits**

Maleic Anhydride (99.5 wt%)		\$ 0.95/kg
Steam produced in excess of internal requirements	(4 and 11 bar)	\$ 3.00/1000k
	(41 bar)	\$ 5.00/1000kg
Fuel Gas or Liquid in excess of internal requirements		\$ 1.50/10 <sup>9</sup> J

## APPENDIX IV

### Design Guidelines for Distillation Columns

#### Tray Columns (sieve or valve trays)

**Overall Column Efficiency, E :** This can be calculated using the attached graph.

note: the x coordinate on the graph is the product of the liquid viscosity and the relative volatility of the key components. The conditions at the top and bottom of the column should be checked and an average value of these two efficiencies should be used.

**Tray Spacing and Flooding Criteria :** You should use established methods to calculate the flooding conditions for a given tray spacing. You should design the column based on a gas velocity equal to 80% of that required for flooding.

#### Packed Columns

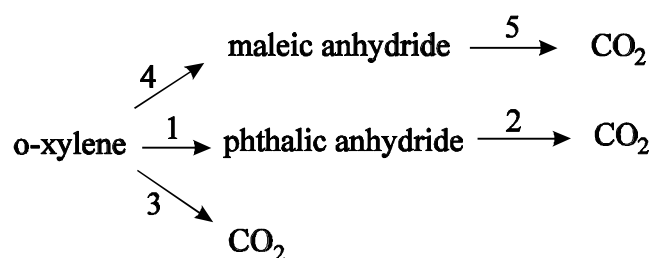
**Height Equivalent of a Theoretical Plate, HETP :** You may assume an HETP value of 2 ft for this design.

**Flooding Criteria :** You should assume a vapor velocity equivalent to 70 % of that at flooding. You should specify the type of packing you use (e.g. 1" rashig rings or 2" Berl saddles etc.) and use the appropriate packing factor.

## APPENDIX V

**Reactor Design Data**

The catalysis and reaction engineering group has obtained kinetic information regarding the o-xylene to phthalic anhydride reaction. In addition, the complete combustion reaction for each organic component occurs. The reaction network is given below. As you can see, a major advantage of our catalyst is that CO formation is essentially eliminated and no heavy impurity is made.



The catalyst must operate between 300°C and 400°C, and at pressures between 1 atm and 3 atm. In this range, the kinetics are as follows: (partial pressures in atmospheres,  $r_i$  in  $\text{kmole hr}^{-1} (\text{kg catalyst})^{-1}$ ,  $k_0 = 1 \text{ kmole hr}^{-1} (\text{kg catalyst})^{-1} \text{ atm}^{-2}$ ,  $R = 1.987 \text{ cal/K mole}$ , and  $T$  is in K)

$$r_1 = k_1 p_{xy} p_{o_2} \quad \ln \frac{k_1}{k_0} = -\frac{27,000}{RT} + 19.837$$

$$r_2 = k_2 p_{pa} p_{o_2} \quad \ln \frac{k_2}{k_0} = -\frac{31,000}{RT} + 20.86$$

$$r_3 = k_3 p_{xy} p_{o_2} \quad \ln \frac{k_3}{k_0} = -\frac{28,600}{RT} + 18.97$$

$$r_4 = k_4 p_{xy} p_{o_2} \quad \ln \frac{k_4}{k_0} = -\frac{27,900}{RT} + 19.23$$

$$r_5 = k_5 p_{ma} p_{o_2} \quad \ln \frac{k_5}{k_0} = -\frac{30,400}{RT} + 20.47$$

The lower flammability limit of o-xylene in air is 1 mole %, and the upper flammability limit is 6 mole%. For safety reasons, it is necessary that process conditions not be within these limits. It is also necessary that the o-xylene content of the reactor never exceed 10 mole %, because, if that limit is exceeded, the catalyst no longer operates at the desired selectivity, the reaction could become oxygen starved, forming significant amounts of CO and other undesired byproducts.

At this time, we are unsure as to whether a packed bed reactor (shell and tube type -- modeled as PFR) or a fluidized bed reactor (modeled as an isothermal packed bed) is the better choice. Please address this in your preliminary design. For the shell and tube packed bed, the catalyst would be in the tubes. We do believe, however, that tube diameters exceeding one inch in a shell and tube configuration would not allow for rapid enough heat removal, causing significant hot spots, and subsequent catalyst damage.

For a fluidized bed, the following data may be assumed:

spherical catalyst particle, diameter  $d_p = 300 \text{ } \mu\text{m}$

catalyst particle density  $\rho_{cat} = 1600 \text{ kg/m}^3$

void fraction at minimum fluidization  $\epsilon_{mf} = 0.50$

heat transfer coefficient from fluidized bed to tube wall  $h = 300 \text{ W/m}^2\text{ }^\circ\text{C}$

reactor should operate between  $2u_{mf}$  and  $5u_{mf}$

for  $u_{mf}$ , use the correlation of Wen & Yu:

$$\text{Re}_{mf} = \frac{d_p u_{mf} \rho_g}{\mu} = \left( \sqrt{33.7^2 + 0.0408 Ar} \right) - 33.7$$

where

$$Ar = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2}$$

where  $\rho_g$  is the density of the gas in the fluidized bed (at average conditions) and  $\rho_s$  is the solid catalyst particle density (called  $\rho_{cat}$  above).

For a shell and tube packed bed, the following data may be assumed:

catalyst particle diameter  $d_p = 3 \text{ mm}$

catalyst particle density  $\rho_{cat} = 1600 \text{ kg/m}^3$

void fraction  $\epsilon = 0.50$

heat transfer coefficient from packed bed to tube wall  $h = 60 \text{ W/m}^2\text{ }^\circ\text{C}$

use standard tube sheet layouts as for a heat exchanger

shell diameter is a function of heat transfer characteristics and frictional losses

The cost of catalyst (for any particle size) is \$1.00/kg.

It is anticipated that a heat transfer fluid will be used in a closed loop to remove the highly exothermic heat of reaction from either type of reactor. We anticipate that all surplus high pressure steam made can be sold elsewhere in the plant, for a credit of \$5.00/1000 kg.

## APPENDIX VI

### Miscellaneous Data

- (1) You may assume that the following pressure drops can be used for equipment in your design:

Heat Exchangers 0.3 bar for tube side and 0.14 bar for shell side

Process Vessels (Excluding Towers) 0.14 bar

Fired Heaters (Furnaces) 0.3 bar

Piping assume zero pressure drop between each piece of equipment

Towers to be calculated

Reactors to be calculated

- (2) You should assume that any fuel gas generated or used on site must be provided at a minimum pressure of 2 bar. This will provide adequate pressure to promote good mixing in burner nozzles etc. and to overcome frictional losses.

### Switch Condensers

These are a complex set of three condensers. Because of the low partial pressure of phthalic anhydride in the stream, it de-sublimates rather than condenses. Therefore, the process stream is cooled using a low temperature oil in tubes to promote de-sublimation. Then, after solid is loaded on the heat transfer surface, gas flow to this condenser is stopped, and higher temperature oil is circulated in the tubes to melt the solid. There are three such devices, one operating in de-sublimation mode, one operating in melting mode, and one on standby. The net result is a liquid stream containing the condensables and a vapor stream containing some maleic anhydride, some phthalic anhydride, and all of the non-condensables.

These condensers will be designed and maintained under contract by condensex<sup>®</sup>. They indicate that operation at any scale is possible as long as the pressure of the feed to the condensers is between 1.7 and 2.0 bar. You may assume that all light gases are neither condensed nor dissolved, and that 99% of the organics are de-sublimated and melted. Based on past experience, condensex<sup>®</sup> suggests that we may estimate the capital cost of these condensers as 15% of all other capital costs for the new process, and that the annual operating cost is 5 times the cost of an equivalent amount of cooling water needed to satisfy the cooling duty from the energy balance on the condenser unit modeled as a component separator.

## **Chemcad Hints**

Use SRK for the entire process.

For heat exchangers with multiple zones, it is recommended that you simulate each zone with a separate heat exchanger. For the reactor, you can use an adiabatic reactor followed by a heat exchanger; however, it is possible that this will not work. You can also use an isothermal reactor, but then Chemcad will not be able to do the heat exchanger calculation. For the switch condensers, use a component separator, which will calculate the heat duty.

When simulating a process using “fake” streams and equipment, it is absolutely necessary that the process flow sheet that you present not included any “fake” streams and equipment. It must represent the actual process.