DESIGN OF A PHTHALIC ANHYDRIDE PRODUCTION PROCESS FROM O-XYLENE

(Courtesy of the Department of Chemical Engineering at West Virginia University, USA)
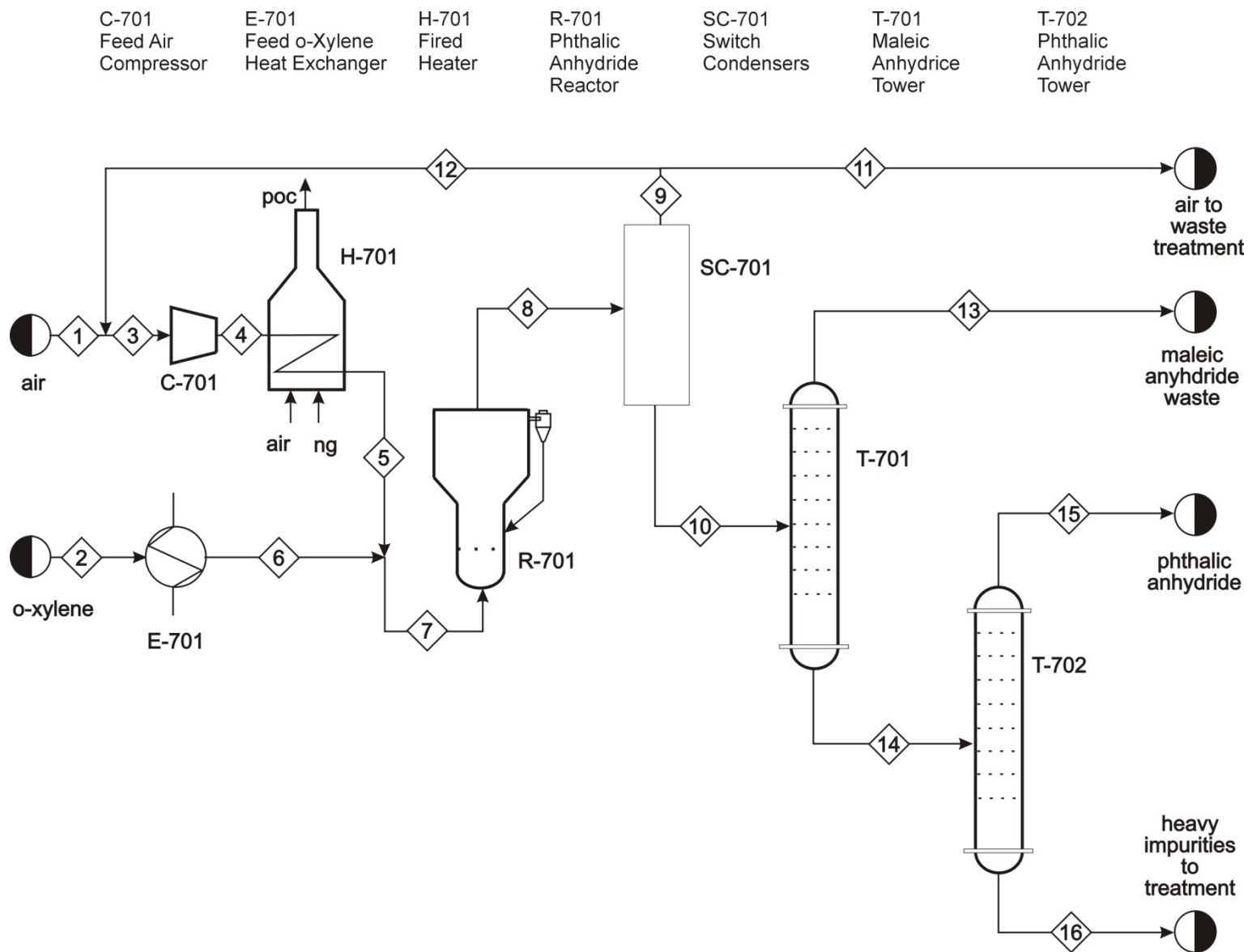
Introduction

Phthalic anhydride is used in the manufacture of plasticizers (additives to polymers to give them more flexibility) and polyesters, among other applications. The compound's chemical formula is $C_6H_4(CO)_2O$ and is the acid anhydride of phthalic acid. The most common method for production of phthalic anhydride is by oxidation of o-xylene. In 2002, approximately 4.6 billion kilograms were produced.
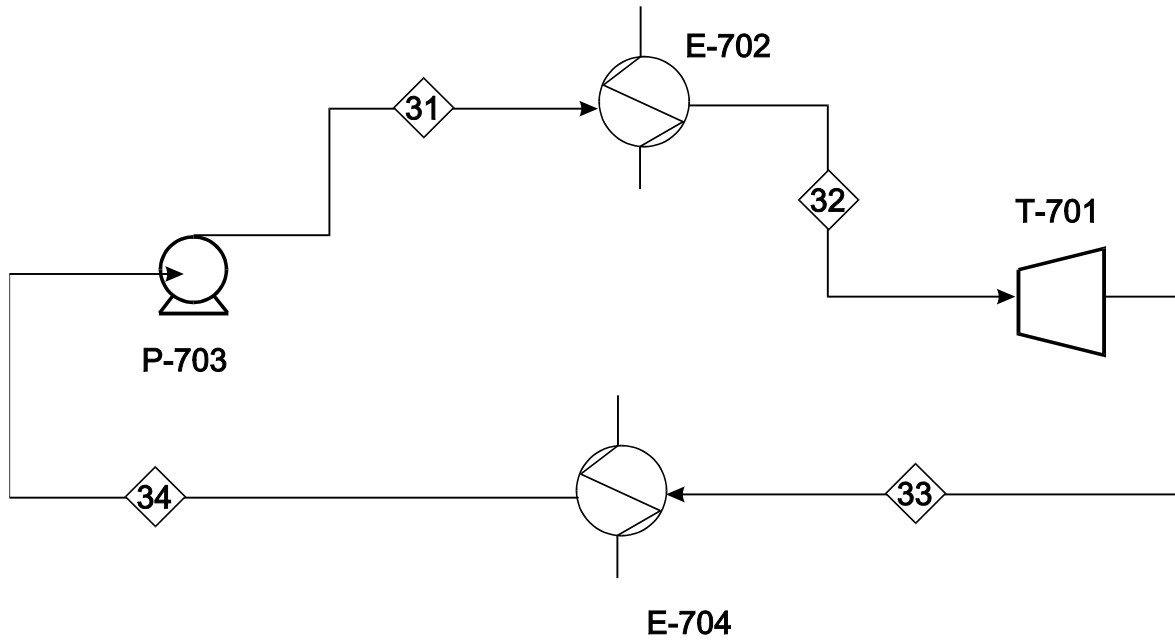
A suggested process flow diagram is in Figure 1. You should use this as a starting point. However, any change that you can justify that does not violate the laws of nature is allowed. Your job is to analyze the simplified phthalic anhydride production process, to suggest profitable operating conditions, and to write a final report summarizing your findings. Note that optimization is NOT required in this design project.

Process Description

The raw materials are air and o-xylene. The o-xylene feed, which contains 5 wt% inert impurities is vaporized in unit V-701. Air, which may be assumed to contain only O_2 and N_2, is mixed with recycle, if there is any recycle, and heated. The hot air and vaporized o-xylene are mixed and sent to a fluidized bed reactor. The contents of Stream 7 must be below the LFL of o-xylene, which is 1 mole%. In this reactor, essentially 100% of the o-xylene is reacted. Most goes to form phthalic anhydride, but some complete and incomplete combustion of o-xylene occurs, some maleic anhydride is formed, and a heavy impurity is also formed. The selectivities are given later. The reactor effluent enters a complex series of devices known as switch condensers. The net result is that all light gases and water leave in Stream 9, with small amounts of both anhydrides, and the phthalic anhydride, maleic anhydride, inerts, and heavy impurity leave in Stream 10. The "dirty air" in Stream 9 must be treated before it can be vented, and this is an additional expense. It is also possible to recycle some of the "dirty air." Any "dirty air" not recycled must be sent to a scrubber, in which the anhydrides are scrubbed into water. The water is then sent to an on-site waste water treatment plant, and an operating charge is assessed. The contents of Stream 10 are sent to a series of two distillation columns which produce liquid waste (Streams 13 and 16) which is burned for fuel. No economic credit is allowed. The product in Stream 15 must be 99.9 mass % phthalic anhydride. This process must produce 75,000 metric tons/year of phthalic anhydride.

C-701	E-701	H-701	R-701	SC-701	T-701	T-702
Feed Air	Feed o-Xylene	Fired	Phthalic	Switch	Maleic	Phthalic
Compressor	Heat Exchanger	Heater	Anhydride	Condensers	Anhydrice	Anhydride
			Reactor		Tower	Tower

air to waste treatment

poc

H-701

air

C-701

air   ng

o-xylene

E-701

R-701

SC-701

maleic anyhdride waste

T-701

phthalic anhydride

T-702

heavy impurities to treatment

Unit 700 - Phthalic Anhydride from o-Xylene

E-702

31

32

T-701

P-703

34

33

E-704

Power Cycle Section

Process Details

Feed Streams

Stream 1: air, consisting of 79% N_2 and 21% O_2 - free

Stream 2: o-xylene with 5 wt % inert impurity

Equipment

Compressor (C-701): increases pressure of air feed from 1 atm to 3 atm
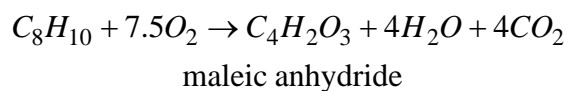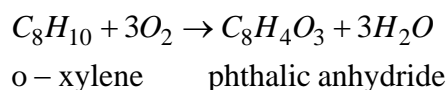
Vaporizer (E-701): vaporizes o-xylene feed which is already above 3 atm

Fired Heater (H-701): heats air to reaction temperature

Reactor (R-701):
The reactor feed may be no lower than 300°C. The catalyst is only active to produce phthalic anhydride between 300°C and 420°C.

The following reactions occur:

$$C_8H_{10} + 3O_2 \rightarrow C_8H_4O_3 + 3H_2O$$
$$\text{o} - \text{xylene} \qquad \text{phthalic anhydride}$$

$$C_8H_{10} + 7.5O_2 \rightarrow C_4H_2O_3 + 4H_2O + 4CO_2$$
$$\text{maleic anhydride}$$

The complete combustion of o-xylene also occurs.

Selectivity data are in Table 1. These data are approximate and are to be used only for the initial mass and energy balance calculations, not for more complex versions to be completed later based on the kinetic data given in the Appendix.

Table 1			
Fractional Conversion of o-Xylene into (Yield of) Indicated Product			
T(°C)	**maleic anhydride**	**CO₂**	**phthalic anhydride**
300	1.00	0.00	0.00
320	0.536	0.0339	0.425
340	0.215	0.102	0.683
360	0.100	0.200	0.700
380	0.0463	0.356	0.598
400	0.0215	0.602	0.377
420	0.00	1.00	0.00

Switch Condensers (SC-701): These are a complex set of condensers. Phthalic anhydride is first condensed as a solid (desublimated) and then melted. There are three condensers, one in the desublimation mode, one in the melting mode, and one in stand-by mode.

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

o-Xylene	1.00
Oxygen	1.00
Nitrogen	1.00
Water	1.00
Carbon Dioxide	1.00
Carbon Monoxide	1.00
Phthalic Anhydride	0.010
Maleic Anhydride	0.89
Heavy Impurity	0.00

Distillation Column (T-701): Here, 99% of the phthalic anhydride and all of the heavy impurity goes to Stream 14. All of the inert and enough of the maleic anhydride to allow Stream 15 to satisfy its purity requirement go to Stream 13.

Distillation Column (T-702): Here, 99.9% of the phthalic anhydride, and any remaining maleic anhydride go to Stream 15, and all of the heavy impurity goes to Stream 16.

Molten Salt Loop: Streams 21-24 contain molten salt. Its properties may be found in Reference [1]. The molten salt removes the heat generated by the exothermic heat of reaction in the reactor.

Power Cycle Section: The energy removed from the molten salt in E-702 is to be used as the energy source in a power cycle. Steam is to be the fluid in the cycle. The turbine generates electricity which can be sold to the power company for 90% of the price of electricity given below, or it can be used internally in the plant. The heat sink in E-704 may be cooling water or refrigerated water. You must evaluate the economics of the power cycle.

Separation Section

This section may be simulated on Aspen Plus with a series of component separators. The installed cost of the separation section, in millions of dollars, may be taken as

$$\$2.25 + 0.5n$$

where n is the number of separation devices needed, not including the one which removes the dirty air. The utility costs associated with the separation section may be assumed to be 50% of the utility costs associated with the process through Stream 10.

Design of Heat Exchanger, E-701

A detailed design of E-701 is required for base-case conditions. It should be assumed that cooling water is available at the conditions specified in the Appendix of this problem statement. For this heat exchanger design, the following information should be provided:

- Diameter of shell
- Number of tube and shell passes
- Number of tubes per pass
- Tube pitch and arrangement (triangular/square/..)
- Number of shell-side baffles, if any, and their arrangement (spacing, pitch, type)
- Diameter, tube-wall thickness, shell-wall thickness, and length of tubes
- Calculation of both shell- and tube-side film heat transfer coefficients
- Calculation of overall heat transfer coefficient (you may assume that there is no fouling on either side of the exchanger)
- Heat transfer area of the exchanger
- Shell-side and tube-side pressure drops (calculated, not estimated)
- Materials of construction
- Approximate cost of the exchanger

A detailed sketch of the exchanger should be included along with a set of comprehensive calculations in an appendix for the design of the heat exchangers. You should use ASPEN Exchanger Design & Rating (EDR) in the ASPEN Plus simulator to carry out the detailed design.

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 (e.g. RADFRAC in Aspen Plus)

Economic Analysis

When evaluating alternative cases, you should carry out an economic evaluation and profitability analysis based on a number of economic criteria such as payback period, internal rate of return, and cash flow analysis. In addition, the following objective function should be used. It is the equivalent annual operating cost (EAOC), and is defined as

EAOC = – (product value – feed cost – other operating costs – 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, although you are **not** being asked to carry out optimization.

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.

The capital cost annuity is defined as follows:

$$capital\ cost\ annuity = FCI \frac{i(1+i)^n}{(1+i)^n - 1} \tag{12}$$

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 $n = 10$.

For detailed sizing, costing, and economic evaluation including profitability analysis, you may use the Aspen Process Economic Analyzer (formerly Aspen Icarus Process Evaluator) in Aspen Plus Version 8. However, it is also a good idea to independently verify the final numbers based on other sources such as cost data given below.

Other Information

You should assume that a year equals 8,000 hours. This is about 330 days, which allows for periodic shut-down and maintenance.

Final Comments

As with any open-ended problem; i.e., a problem with no single correct answer, the problem statement above is deliberately vague. You may need to fill in some missing data by doing a literature search, Internets search, or making assumptions. 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 may be forthcoming.

Moreover, in some areas (e.g. sizing/costing) you are given more data and information than what is needed. You must exercise engineering judgment and decide what data to use. Also you should also seek additional data from the literature or Internet to verify some of the data, e.g. the prices of products and raw materials.

Reference

1. Perry, R.H. and D. Green, eds., *Perry's Chemical Engineering Handbook (6th ed.)*, McGraw-Hill, New York, 1984, p. 9-74.

Appendix 1
Economic Data

Utility Costs

Low-Pressure Steam (446 kPa, saturated) $3.00/1000 kg

Medium-Pressure Steam (1135 kPa, saturated) $6.50/1000 kg

High-Pressure Steam (4237 kPa, saturated) $8.00/1000 kg

Natural Gas (446 kPa, 25°C) $3.00/$10^6$ kJ

Electricity $0.05/kW hr

Boiler Feed Water (at 549 kPa, 90°C) $300.00/1000 m^3

Cooling Water $20.00/1000 m^3
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, otherwise
there is an additional cost of $0.35/$10^6$ kJ

Refrigerated Water $200.00/1000 m^3
available at 516 kPa and 10°C
return pressure $\geq$ 308 kPa
return temperature is no higher than 20°C
if return temperature is above 20°C, there is an additional cost of $7.00/$10^6$ kJ

Equipment Costs (Purchased)

Piping $/m = 0.7 (dia, in) + 1

Valves $100 (flow diameter, in)$^{0.8}$
for control valve with orifice plate, double the price

Pumps $630 (power, kW)$^{0.4}$

Heat Exchangers $1030 (area, m^2)$^{0.6}$
If extended surfaces are used, area is that for same size tubing without
fins. Then add a 25% surcharge for fins.

Compressors $770 (power, kW)$^{0.96}$ + 400 (power, kW)$^{0.6}$

Steam Turbine 2.18\times10^5$ (power output, MW)$^{0.67}$
assume 75% efficiency

Fired Heater $635 (duty, kW)$^{0.8}$

assume 80% thermal efficiency

Storage Tank $1000V^{0.6}$
               V = volume, m^3

Equipment Cost Factors

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

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

Carbon Steel   0.0
Stainless Steel   4.0

Appendix 2
Other Design Data

Other Data

Pressure drops for heat exchangers other than E-703 may be estimated as 30 kPa for the tube side and 20 kPa for the shell side.

Individual heat transfer coefficients for all heat exchange devices other than E-703 may be estimated as follows:

situation	h (W/m^2°C)
condensing steam	6000
condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60

Air treatment is accomplished by absorption of the organic matter into water, with the light gases vented to the atmosphere. The water is then sent to a waste-water treatment plant. The annual cost is based upon the volume of vapor sent to the treatment plant and the mole fraction of organic matter (phthalic and maleic anhydrides) in Stream 11 or 15. The cost is:

$$\$/h \ air \ treated = 10^{-4}V_{tot}(0.5 + 1000x_{or})$$

V_{tot} = total volume of "dirty air" to be treated, m^3
x_{or} = mole fraction of organics (CO_2 is not an organic!) in "dirty air" stream

Appendix 3

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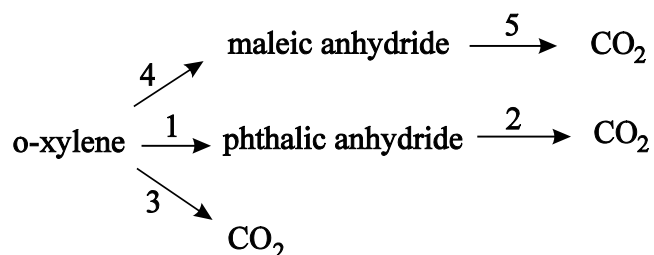
The catalyst must operate between 300°C and 400°C, and at pressures between 1 atm and 3 atm. In this range, the kinetics are as follows: (partial pressures in atmospheres, r_i in kmole hr^{-1} (kg catalyst)$^{-1}$, k_0 = 1 kmole hr^{-1}(kg catalyst)$^{-1}$atm^{-2}, R = 1.987 cal/K mole, and T is in K)

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

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

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

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

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

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 $d_p = 300$ μm
catalyst particle density $\rho_{cat} = 1600$ kg/m^3
void fraction at minimum fluidization $\varepsilon_{mf} = 0.50$
heat transfer coefficient from fluidized bed to tube wall h = 300 W/m^2°C
reactor should operate between $2u_{mf}$ and $5u_{mf}$

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

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

where

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

where ρ_g is the density of the gas in the fluidized bed (at average conditions) and ρ_s is the solid catalyst particle density (called ρ_{cat} above).

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

catalyst particle diameter $d_p = 3$ mm
catalyst particle density $\rho_{cat} = 1600$ kg/m^3
void fraction $\varepsilon = 0.50$
heat transfer coefficient from packed bed to tube wall h = 60 W/m^2°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 4

Equations for Pump Curves

P-701

$$\Delta P \text{ (kPa)} = 500 - 4.662 \times 10^{-3}\dot{m} - 1.805 \times 10^{-6}\dot{m}^2 \qquad \dot{m} \text{ in kg/h}$$

P-702

for $\dot{m} > 670 \text{ Mg/h}$
$$\Delta P \text{ (kPa)} = 196.2 + 0.2972\dot{m} - 2.692 \times 10^{-4}\dot{m}^2 + 4.899 \times 10^{-8}\dot{m}^3 \qquad \dot{m} \text{ in Mg/h}$$

for $\dot{m} < 670 \text{ Mg/h}$
$$\Delta P \text{ (kPa)} = 289.0$$

C-701

for 3500 rpm
$$P_{\text{out}}/P_{\text{in}} = 5.201 + 2.662\dot{m} - 1.358 \times 10^{-4}\dot{m}^2 + 4.506 \times 10^{-8}\dot{m}^3 \qquad \dot{m} \text{ in Mg/h}$$

for 2200 rpm
$$P_{\text{out}}/P_{\text{in}} = 4.015 + 5.263 \times 10^{-3}\dot{m} - 1.838 \times 10^{-4}\dot{m}^2 \qquad \dot{m} \text{ in Mg/h}$$

Appendix 5

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^3
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^3
Condensate Return (credit)			$ 2.54/ m^3
Cooling Water*	5 bar	30°C	$ 6.70/ 1000 m^3
Cooling Water Return	3 bar	40°C	
Refrig. Water*	5 bar	5°C	$10.00/ 100 m^3
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?

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

Cost of Air Treatment: $\$/$m^3 air treated $= 10^{-4}(0.5 + 1000 x_{or})$
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^{9}J