Design Project
Energy Balances and Numerical Methods

Production of Phthalic Anhydride from o-Xylene

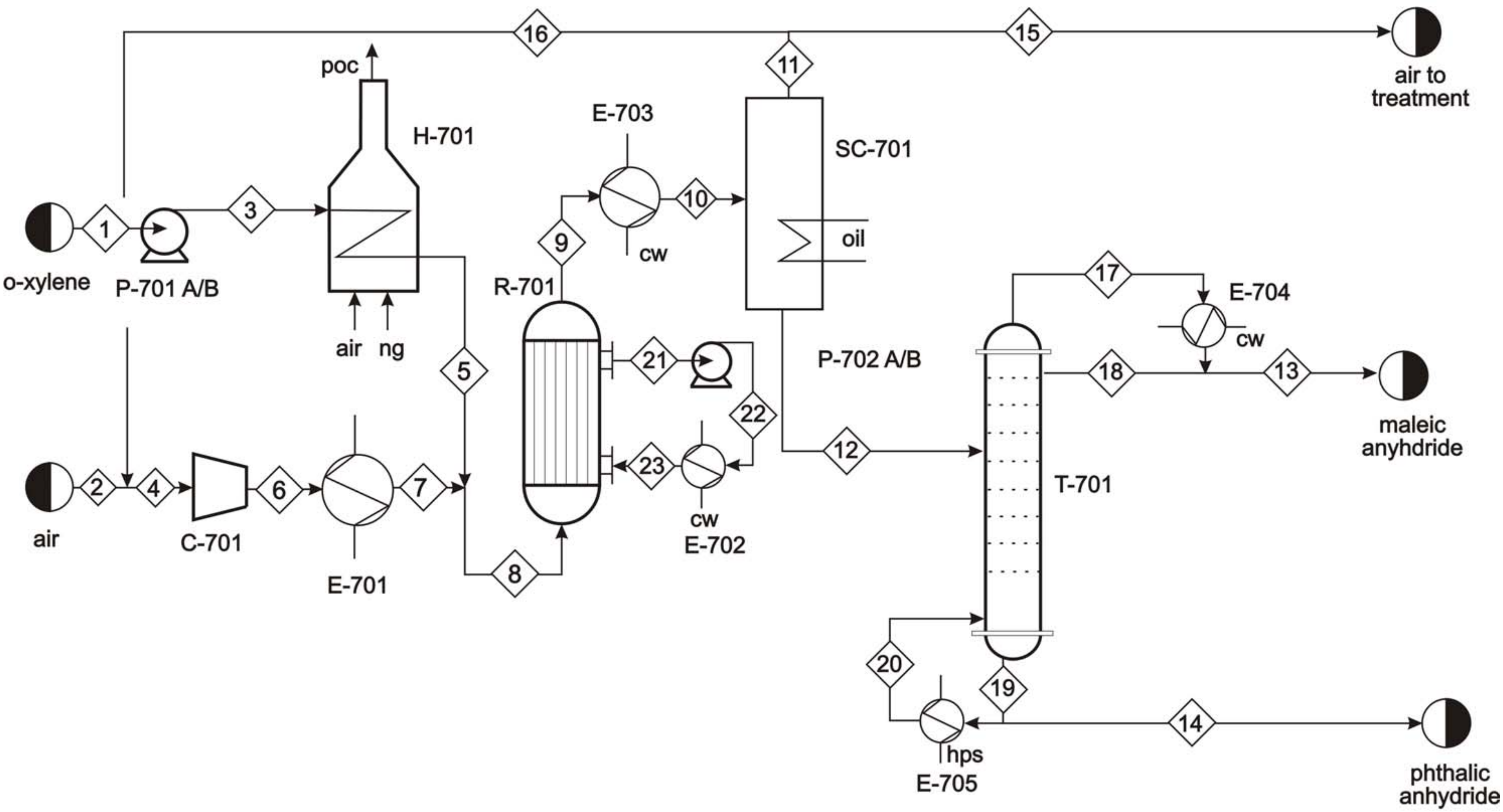
The subject of this project is a process for manufacturing 75,000 metric tons/year of a liquid containing 99.9% phthalic anhydride, subject to constraints which will be defined later in this document. The project is a continuation (of sorts) of the project you completed last semester for material balances. However, there are important differences in the two, including assumptions and products.

A suggested process flow diagram (PFD) is attached (Figure 1). You should use this as a starting point. However, any change that you can justify (and that does not violate the laws of nature) is allowed. Your assignment is to develop an optimum case based upon an objective function defined later. It is your job to define the decision variables, and to choose and implement a method to arrive at an optimum design.

Process Description

See Figure 1. The raw materials are air and o-xylene. The o-xylene feed, which may be considered pure and at 0.75 atm, is pumped to 3 atm and then vaporized in a fired heater, H-701. Air, which may be assumed to contain only O_2 and N_2, is mixed with recycle, if any, compressed to 3 atm, and heated in E-701. The hot air and vaporized o-xylene are mixed and sent to a packed-bed reactor, R-701. The o-xylene content of Stream 8 must be either below the lower flammability limit (LFL) of o-xylene (1 mole %) or above the upper flammability limit (UFL) of o-xylene (6 mole %). For the purposes of the present preliminary design only, assume that the o-xylene mole fraction into R-701 must be less than 5 mol %. (This avoids heat-transfer gradients in the reactor design.) Under these conditions, assume that 100% of the o-xylene is reacted in R-701. Most of the o-xylene reacts to form phthalic anhydride, some complete combustion of o-xylene occurs, and some maleic anhydride is formed. The yields depend upon the reactor temperature, as indicated later. The reactor temperature is controlled by a molten-salt loop, Streams 21-23. Stream 9, the reactor effluent, which is at 2 atm, enters a complex series of devices known as a switch condenser set (SC-701). The feed to the switch condensers may be no higher than 180°C; hence, the reactor effluent must be cooled before entering SC-701. The net result of the switch condensers is that all of the phthalic anhydride and maleic anhydride leaves in Stream 12, while Stream 11 contains all light gases and water. The mixture of gases in Stream 11 is termed “dirty air.” It may be recycled (Stream 16) but at least some of it must be vented in a purge stream (Stream 15). The “dirty air” must be treated before it can be vented, and this is an expense. Treatment (not shown in the PFD) consists of scrubbing the anhydrides into water, which is then sent to a waste-water plant. The contents of Stream 12 are sent to a distillation tower, T-701, which produces liquid waste (Stream 13) that is burned for fuel. The product in Stream 14 must be 99.9 wt % phthalic anhydride. This process must produce 75,000 metric tons/year of phthalic anhydride.

P-701 A/B	C-701	H-701	E-701	R-701	E-702	E-703	P-702 A/B	SC-701	T-701	E-704	E-705
o-xylene feed pump	feed compressor	o-xylene feed heater	feed air cooler	phthalic anhydride reactor	molten salt cooler	product cooler	molten salt pump	switch condensers	phthalic anhydride tower	phthalic tower condenser	phthalic tower reboiler



Unit 700 - Phthalic Anhydride from o-Xylene

Process Details

Feed Streams

Stream 1: air, consisting of 79% N_2 and 21% O_2. No charge.

Stream 2: o-xylene at 0.75 atm and 100°C. Cost provided in Table 5.

Switch-Condenser Streams

Stream 10: Reactor outlet composition, vapor phase, pressure ≤ 2 atm, temperature ≤ 180°C.

Stream 11: "Dirty Gas," vapor phase, 1 atm, 130°C.

Stream 12: Mixture of phthalic anhydride and maleic anhydride, liquid phase, 1 atm, 150°C.

Effluent Streams

Stream 13: Waste organic material, may be burned in fired heater H-701 for credit. Assume that the energy content of this stream is its lower heating value.

Stream 14: Phthalic anhydride product, 75,000 metric tons/yr, 99.9 wt % pure.

Stream 15: Air to waste treatment (scrubber and waste-water plant). The appropriate cost is charged, see below.

Equipment

Compressor C-701:

The compressor increases pressure of the air feed from 1 atm to 3 atm at the valve outlet. The compressor may be assumed to be adiabatic. In that case, the compressor power may be calculated as:

$$\dot{W}_s\,[\text{kW}] = 20{,}000\,\dot{m}[\text{kmol/s}]\left\{\left(\frac{P_{out}}{P_{in}}\right)^{0.286} - 1\right\} \tag{1}$$

where $\dot{m}$ [kmol/s] is the total molar flow rate of the inlet stream. Equation 1 includes the compressor efficiency.

In general, the ratio of outlet to inlet pressure (compression ratio) in a compressor is between 3 and 5. If a compression ratio greater than 5 is needed, compressors are usually staged, with cooling between the compressor stages ("intercooling"), but not after the last stage. If you choose to do this, the compression ratio for each stage should be identical, and the intercooling should be to 50°C. The PFD that you draw should accurately represent the chosen compressor configuration.

The compressor increases the temperature of the stream being compressed according to:

$$\frac{T_{out}}{T_{in}} = \left(\frac{P_{out}}{P_{in}} \right)^{0.286} \tag{2}$$

where T is absolute temperature.

The cost of electricity to run the compressor is a utility cost and is given below.

Pumps:

Pump P-701 increases pressure of the o-xylene feed from 0.75 atm to 3 atm at the valve outlet.

For all pumps, the cost of energy may be neglected.

Fired Heater H-701:

The fired heater vaporizes the o-xylene feed and heats the vapor to any temperature. H-701 is fueled with natural gas (ng) and/or Stream 13.

Heat Exchangers:

Heat exchanger E-701 heats the air feed, Stream 6. The air temperature of the exit stream, Stream 7, may not exceed a value which is 5°C lower than the inlet temperature of the appropriate type of steam used for heating.

Temperature constraints of heat exchangers associated with other pieces of equipment are provided separately below.

Reactor (R-701):

The reactor feed may be no lower than 300°C. The catalyst is active to produce phthalic anhydride only between 300°C and 420°C. The reactor temperature and the temperature of the reactor outlet stream are to be controlled by the molten-salt loop, described below.

The following reactions occur:

$$\begin{array}{ccc} C_8H_{10} + 3O_2 & \rightarrow & C_8H_4O_3 + 3H_2O \\ \text{o} - \text{xylene} & & \text{phthalic anhydride} \end{array} \tag{3}$$

$$\begin{array}{c} C_8H_{10} + 7.5O_2 \rightarrow C_4H_2O_3 + 4H_2O + 4CO_2 \\ \text{maleic anhydride} \end{array} \tag{4}$$

The complete combustion of o-xylene also occurs:

$$C_8H_{10} + 10.5O_2 \rightarrow 5H_2O + 8CO_2 \tag{5}$$

Yield data are in Table 1. These data are approximate and are to be used only for this design project this semester, not for more complex versions to be completed in subsequent semesters.

Table 1
Yields of Products from Oxidation of o-Xylene

T(°C)	maleic anhydride	CO_2	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

Molten-Salt Loop:

Streams 21 - 23 contain the proprietary molten salt HiTec. Its properties may be found in Reference [1]. The molten salt removes the heat generated by the exothermic heat of reaction in Reactor R-701. The heat removed is then used to make high-pressure steam (in E-702) from boiler feed water (bfw), with an appropriate credit being taken for the steam made. The pressure of the bfw into E-702 may be assumed to be the pressure of high-pressure steam. The temperature of Stream 21 may not exceed a value which is 10°C lower than Stream 9, and the temperature of Stream 23 must exceed a value which is 10°C higher than that of the high-pressure steam formed in E-702.

Switch Condensers (SC-701):

These are a complex set of three condensers that operate in a semi-continuous mode. The inlet stream is first cooled by cold oil so that the anhydrides are desublimated (condensed as solids). Then hot oil is passed through the same condenser so that the solids are melted. At any given time, one condenser operates to desublimate, one to melt, the third as standby, and the feed is switched between the three. We will not consider the details of this operation here.

The feed to SC-701 may not exceed 180°C, so E-703 removes the necessary heat. The pressure must be less than or equal to 2 atm. For the purpose of this project, specifications for Streams 11 and 12 are given above. The heat load for SC-701 must be assumed to be the equivalent of <u>three times</u> the total amount needed to cool Stream 10 to Stream 12 and Stream 11. This is the heat load necessary to heat and cool the oil heat-transfer medium. The oil is in a closed loop, hence the cost of the oil may be neglected.

Distillation Column (T-701):

Here 99% of the phthalic anhydride in Stream 12 goes to Stream 14. Of the maleic anhydride in Stream 12, 99% goes to Stream 13. Stream 17, which goes to Condenser E-704, must be a saturated vapor. The molar flow rate of Stream 17 must be 10 times that of Stream 13. Stream 18 re-enters the distillation column as a saturated liquid. Stream 19 must be a saturated liquid and Stream 20 must be a saturated vapor. The molar flow rate of Stream 20 must be one-third that of Stream 14. T-701 must operate at a pressure low enough to make Stream 20 vaporize at a temperature that has a value no higher than 5°C lower than the temperature of the high-pressure steam used as the heat source for E-705.

Recycle

It is possible to recycle some of the "dirty" air from Stream 11 to mix with Stream 2, as long as there is sufficient purge (Stream 15). It is your job to determine the optimal recycle-to-purge ratio. The purge stream must go to the waste treatment unit with the appropriate charge taken.

Physical Property Data

Use data from Reference [2] or from any handbook. The following data are not readily available in these references. You may use these for this project only.

Some vapor heat capacities are given in Table 2.

Table 2. Heat Capacities of Organics

C_p[cal/mole/ K] $= a + bT + cT^2 + dT^3$, T in [K], range 150°C - 450°C

	a	$10 \times$ b	$10^5 \times$ c	$10^7 \times$ d
o-xylene	-3.786	1.424	-8.224	1.798
phthalic anhydride	-1.064	1.562	-1.023	2.411
maleic anhydride	-3.123	0.8323	-5.217	1.156

Liquid heat capacity for any organic compound is given by Equation (6).

$$C_p[\text{cal/mole/°C}] = 41.69 + 7.773 X 10^{-2} T \text{ , T in [°C], range 125°C - 200°C} \qquad (6)$$

Some data on vapor pressures are given in Table 3.

Table 3. Vapor Pressure Data

$$\ln P^{*}[\text{mmHg}] = A - \frac{B}{T - C}, \quad \text{T in [K], range 100°C - 300°C}$$

	A	B	C
o-xylene	16.1156	3395.57	59.46
phthalic anhydride	15.9984	4467.01	83.15
maleic anhydride	16.2747	3765.65	82.15

Data on normal heats of vaporization and the corresponding normal boiling points are given in Table 4.

Table 4. Heats of Vaporization at Normal Boiling Point

	$\Delta \hat{H}_V$ [cal/mole]	T_b [°C]
o-xylene	8,800	144.4
phthalic anhydride	11,850	284.5
maleic anhydride	5,850	202.0

Economic Analysis

Objective Function

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

EAOC = -(product value - feed cost - capital cost annuity - other operating costs) (7)

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 value of phthalic anhydride (the product) and the cost of o-xylene (the feed) are provided below in Table 5.

The capital cost annuity is an <u>annual</u> cost associated with the <u>one-time</u> costs for plant construction (like a car payment). A list of capital costs for each piece of equipment is provided below in Table 6. These can be added to obtain the total installed cost (FCI). The capital cost annuity is related to FCI as follows:

$$capital\ cost\ annuity = FCI \frac{i(1+i)^n}{(1+i)^n - 1} \tag{8}$$

where i is the interest rate (as a fraction) and n is the plant life, in [y]. For the purposes of this project, take $i = 0.15$ and $n = 10$.

The other operating costs are for compression and for waste treatment. The power needed for compression is provided in Equation (1). The cost of electricity to furnish this power is provided below.

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 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:

$$Cost\,[\$/y] = 10^{-4}\dot{V}_{tot}(0.5 + 1000x_{or}) \tag{9}$$

where

$\dot{V}_{tot}$ = total volume of "dirty air" to be treated [m^3 STP/y]
x_{or} = mole fraction of organics in "dirty air" stream. Note that CO_2 is not an organic!

Raw Material Costs/Product Value

These are provided in Table 5 below. When using these numbers, you should be aware that they may be modified later, so write programs, spreadsheets, etc. with this in mind.

Table 5. Material Prices

Material	Price [$/kg]
phthalic anhydride	1.25
o-xylene	0.80

Utility Costs/Credits

Low-Pressure Steam (618 kPa, saturated, cost or credit)	$13.28/GJ
Medium-Pressure Steam (1135 kPa, saturated, cost or credit)	$14.19/GJ
High-Pressure Steam (4237 kPa, saturated, cost or credit)	$17.70/GJ
Natural Gas (446 kPa, 25°C, cost)	$11.00/GJ
Waste Stream 13 used as a fuel source (credit)	$9.00/GJ
Electricity	$0.06/kW-h
Boiler Feed Water (at 549 kPa, 90°C)	$2.45/1000 kg

There is a cost for boiler feed water only if the steam produced enters process streams. If, on the other hand, the steam produced does not enter a process stream and is subsequently condensed, then it can be made into steam again. In that case, there is no net cost for boiler feed water.

Cooling Water $0.354/GJ

Available at 516 kPa and 30°C
Return pressure ≥ 308 kPa
Return temperature should be no more than 15°C above the inlet temperature

Refrigerated Water $4.43/GJ

Available at 516 kPa and 5°C
Return pressure ≥ 308 kPa
Return temperature should be no higher than 15°C

Equipment Costs

Preliminary equipment costs for the plant are given in Table 6. More up-to-date costs will be provided by early March. Each cost is for an individual piece of equipment, including installation.

Table 6. Equipment Costs

Equipment	Installed Cost [in thousands of dollars]
Isothermal packed-bed reactor	5,000
Adiabatic packed-bed reactor, per stage	100
Vessel	100
Distillation column	500
Heat exchanger	300
Pump	40
Compressor	Larger of {4,000 and 0.0189 $(\dot{W}_S\ [\mathrm{W}])^{0.8}$}
Fired Heater	11×10^{A} where $A = 0.8 \log_{10}[Q] - 0.5$ and Q is the heat duty [kW]

Optimization

You will learn optimization methods in ChE 230. The objective function (EAOC) is defined above. You should consider both topological and parametric optimization.

Topological optimization involves considering different process configurations (such as location of process equipment, whether or not to add or remove equipment). You may alter the process configuration in any way that improves the economic performance as long as it does not violate the laws of nature. Determining the optimum number of staged compressors with intercooling is an example of a topological optimization.

Parametric optimization involves determining the best operating parameters for the chosen process topology. It is your responsibility to define appropriate decision variables. It is suggested that you look carefully at the efficient use of raw materials and the purge/recycle ratio for Stream 11, and correlate the reactor temperature with separation costs. If there are too many decision variables to do a reasonable parametric optimization, it is your responsibility to determine, with appropriate justification, which ones most significantly affect the objective function. Then you should focus on only those decision variables. This is called a Pareto analysis.

Other Information

You should assume that a year equals 8000 hours. This is about 330 days, which allows for periodic shut-down and maintenance.

You should assume that two streams that mix must be at identical pressures.

Groups

You will work on this project in groups of 3 or 4. More details of group formation and peer evaluation will be discussed in class.

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 may be forthcoming.

Deliverables

Written Report

Each group must deliver a word-processed report. It should be clear and concise and should adhere to the prescribed format. The format is explained in the Written Report Guidelines, provided as a separate document. Reports not adhering to the prescribed format will receive significant deductions and will have to be rewritten. The body of the report should be short, emphasizing only the results and explaining why the results presented are optimal. When presenting results for different cases, graphs are often superior to tables (but see discussion in the Guidelines). The report appendix should contain details of calculations. These calculations should be annotated so that they are easy to follow; calculations that cannot be followed easily will lose credit. Computer output without detailed explanations is not appropriate; neatly hand-written calculations are best.

The written report is due on Friday, April 23, 2010 by 3:00 pm.

Oral Report

There will be oral presentations of project results in the ChE 202 class on Tuesday, April 27, 2010. Oral presentations will continue on April 28, 2010, since we will probably be unable to complete all presentations on April 27, 2010.

Oral Presentation Guidelines are also provided. These should be followed in your presentations.

Project Review

There will be a project review in the ChE 230 class on Thursday, April 29, 2010.

Grading

Anyone not participating in this project will be subject to actions as noted in the syllabi for ChE 202 and ChE 230.

The grades for the oral presentation and written report will be composite grades for the entire team. Therefore, group preparation and feedback are recommended.

The report grade for each course will be based on the technical content pertinent to that course (including the response to questions during the oral presentation), the overall technical content (including that pertinent to the other class), the oral presentation, and the written report. The grades for the oral presentation and written report will take into account the quality of the writing or the oral presentation and the adherence to the prescribed format.

The documents on the following web site provide an indication of the expected attributes of a written design report and an oral presentation.

http://www.che.cemr.wvu.edu/ugrad/outcomes/rubrics/index.php

References

1. http://www.coastalchem.com/PDFs/HITECSALT/HITEC%20Heat%20Transfer%20Salt.pdf

2. Felder, R.M. and R.W. Rousseau, *Elementary Principles of Chemical Processes (3rd ed. 9th printing)*, Wiley, New York, 2005.