Separations and Reaction Engineering
Design Project

Production of Formalin

Your assignment is to continue evaluating the details of a process to produce 50,000 tonne/y of formalin. Formalin is 37wt% formaldehyde in water. Formaldehyde and urea are used to make urea-formaldehyde resins that subsequently are used as adhesives and binders for particle board and plywood.

A suggested process is described below. You should use this as a starting point. You are free (and expected) to alter it in any feasible way that does not violate the laws of nature. Be sure to justify any changes you make. Your assignment is to complete the overall design and the mini-designs described later in this document.

General Description

Unit 800 produces formalin (37 wt% formaldehyde in water) from methanol using a silver catalyst process. Figure 1 is the base case and is described below.

Air is mixed with recycled off-gas, compressed and preheated; methanol is pumped and preheated, and these two streams are mixed to provide reactor feed. The feed mixture should be below the lower flammability limit for methanol. (For methanol, UFL = 36 mole %; LFL = 6 mole %.)

In the reactor, the following two reactions occur (using a catalyst described below):

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O \tag{1}$$

$$CH_3OH \rightarrow HCHO + H_2 \tag{2}$$

Reaction (1) is exothermic while reaction (2) is endothermic. Reaction (1) is desired and the reactor is generally run so that the overall reaction is slightly exothermic. Kinetic and other data that you should use for these catalytic reactions can be found in Appendix 1 and are loosely based on published data [1,2].

The reactor effluent is cooled before entering an absorber. This unit is operated counter-currently so that the vapor enters from the bottom while water enters from the top. The inlet water flow rate can be adjusted so that the liquid leaving the absorber at the bottom contains 37 wt% formaldehyde, or additional water can be added to the liquid exit stream to achieve this level of dilution. The off gas, *i.e.*, the vapor stream exiting the top of the absorber, may be purged and combusted (for heat economy or for environmental reasons) and/or may be recycled to mix with the fresh air stream.

Process Details

Feed Stream and Effluent Streams

For uniformity among groups, these are characterized below and should be numbered as shown.

Stream 1:	air feed at 25°C and atmospheric pressure
Stream 2:	methanol feed at 25°C and atmospheric pressure, pure liquid
Streams 12:	deionized water. If a second stream of deionized water is needed, it should be labeled as Stream 17.
Stream 15:	off-gas stream to be purged or combusted
Stream 18:	37 wt% formaldehyde in water, less than 1 wt% methanol allowed – This is the stream that must be at a flowrate equivalent to 50,000 tonne/y.

Equipment

For uniformity among groups, these should be labeled as shown (if needed). Process parameters represent base-case values and may be changed if justified.

Air Compressor (C-801) -- increases the pressure of the feed air to 300 kPa. The compressor may be assumed to be adiabatic with an efficiency of 70%.

Methanol Feed Pump (P-801 A/B) -- increases pressure of methanol fed to 300 kPa, efficiency 80%

Heat Exchangers (E-801 and E-802):
E-801 heats (or cools) methanol feed to 150°C.
E-802 heats (or cools) air to 200°C.
Pressure drop of 25 kPa on the process side for each heat exchanger.

Reactor(s) (R-801, *etc.*) – convert(s) reactants optimally to products using kinetics and other properties as supplied in Appendix 1. Catalyst must be replaced regularly. The reactor temperature may not exceed 650°C. See details of the reactor(s) in the Assignment.

Heat Exchanger (E-803) -- cools and partially condenses reactor effluent, pressure drop 25 kPa

Absorber(s) (T-801, *etc.*) – separate(s) formaldehyde (and some methanol) from reactor outlet stream by countercurrent flow of water. The off gas leaving from the top of the absorber contains all of the unreacted oxygen, nitrogen and hydrogen, and some of the water (as vapor). See details in Assignment.

Heat Exchanger (E-804) – cools product to between 35°C and 45°C, pressure drop 25 kPa

Pump (P-802 A/B) – provides pressure to pump formalin to storage tank

Tank (Tk-801) – storage tank for formalin, stores three days of product – not shown on PFD.

Equipment, feed and catalyst costs and product value are provided in Appendices 2 and 3.

Assignment

The assignment consists of the overall process optimization (overall design) and two "mini-designs."

1. Overall Process Optimization

The entire process should be optimized using decision variables of your choosing. Decision variables should be chosen as those most strongly affecting the objective function. There are two types of optimization: topological and parametric.

In topological optimization, which is usually done first, the best process configuration is chosen. In this case, your choices for the reactor are limited, in that you will use an ideal plug-flow (packed-bed) reactor (PFR/PBR) operated adiabatically, followed by a heat exchanger. Your choices for separation are also limited, in that you will use a single packed-column absorber. For all packed columns in this project, you may assume that HETP = 0.6 m.

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; and flowrate of water to the absorber.

In evaluating various cases in this portion of the work, you will use the equivalent annual operating cost (EAOC) as defined in the **General** section. You will calculate the EAOC for the entire plant.

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

1. a computer-generated PFD (not a Chemcad PFD) for the recommended optimum case, including equipment and the location of key valves,

2. a stream table containing the usual items,

3. a list of all 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 summary table of the raw materials used, including the catalyst,

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

7. a clear economic analysis which justifies the recommended case,

8. a discussion section,

9. a Chemcad report only for your optimized case (in the Appendix). This must contain the equipment connectivity, thermodynamics, unit operations, and overall material balance cover pages; stream flows; equipment summaries; tower profiles; and tray (or packing) design specifications if you use Chemcad to design the trays (or packing). The Chemcad report <u>should not contain</u> stream properties. Missing Chemcad output will not be requested; credit will be deducted as if the information is missing.

2. Mini-Design – Chemical Reaction Engineering

You are to consider various alternatives to the adiabatic PFR and the heat exchanger. Chemcad may not be used for any portion of this design. Only software for the solution of differential equations and/or algebraic equations may be used.

First (Case I), you are to replicate your Chemcad findings without using Chemcad. Specifically, using the other software, you are to obtain the process conditions of the outlet stream from the heat exchanger after the reactor. In this case, the inlet stream to the reactor and the properties of the reactor and heat exchanger are to be those obtained in the overall process optimization above (with Chemcad). (It is possible that an exact match to the composition of the exit stream may not be obtainable. In that case, the composition of methanol, *i.e.*, the overall conversion in the reactor, should be the same.) Discuss any changes in the outlet stream from the heat exchanger obtained here, relative to the values obtained in the overall process optimization, with Chemcad. Obtain the EAOC for the sub-system consisting of the reactor and heat exchanger.

Second (Case II), you are to design a single fluid-bed reactor (treat as a constant-flow stirred-tank reactor [CFSTR] with heat transfer) required to convert the inlet stream to the reactor above to the exit stream from the heat exchanger above. If necessary, a heat exchanger may be added to the reactor exit. Again, the exit compositions for Case I and Case II may differ, but the overall conversions should be the same. Discuss changes in the composition and other properties of the exti streams for Case I and Case II. Calculate the EAOC for this sub-system and compare it to that for Case I. Discuss any differences.

In Case III, you are to repeat Case II except that you are to use two optimized equal-sized fluid-bed reactors in series, again with a heat exchanger at the end if necessary. Discuss as before.

In Case IV, use three optimized equal-sized fluid-bed reactors in series, again with a heat exchanger at the end if necessary. Discuss as before.

This section of the report should contain items 1 through 8 as mentioned above for the Overall Process Optimization subsection above. Printouts and solutions from the software should be in the Appendix.

3. Mini-Design -- Separations

You are to consider various alternatives to the single packed-bed absorber.

First, for a tray tower, you should determine the absorption efficiency by evaluating the average relative volatility and viscosity of the liquid phase between the top and bottom. This absorption efficiency will be used to convert the number of equilibrium stages to the actual number of stages.

Second, for the absorption column, the more-economical choice between a single packed tower and a single tray tower should be determined.

Third, you are to come up with a detailed design of your choice above, and a design of auxiliary equipment (heat exchangers and pump, if present). A detailed design of a tray tower includes the number of trays, tray spacing, diameter, weir height, and top and bottom pressure specifications. A detailed design of a packed tower includes height, packing size and type, and the same other specifications as in a tray tower.

Finally, determine the number of absorbers required and their locations. For this case only, modify the cost data in Appendix 2 to apply only to 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 that about 3 ft 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 columns of smaller diameter. 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. Use this “penalty” to determine if more and smaller towers may be more economical.

General

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:

$$capital\ cost\ annuity = FCI\,\frac{i(1+i)^n}{(1+i)^n - 1} \tag{3}$$

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

The written report is a very important part of the assignment. This report should conform to the Department guidelines. The report should be clear and concise. It should be bound in a folder that is not oversized or undersized relative to the number of pages in the report. Figures and tables should be included as appropriate. Any report not containing labeled PFDs and stream tables, 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 generally superior to tables. A episodic account of what each member of the group did is neither required nor wanted. Results and explanations should be those needed to justify your choices, not a litany of everything that was tried. An appendix should be attached that includes sample calculations. These calculations should be easy to follow.

For the optimum case, the report appendix should contain details of calculations that are easy to follow. There should be separate sections for each class, ChE 312 and ChE 325, each containing information appropriate for the respective class. Each of these two sections should stand alone, *i.e.*, it should not be necesssary to read (or obtain information on) the section on Reaction Engineering to be able to understand the section on Separations, and *vice versa*. Calculations that cannot be easily followed will lose credit.

Poorly written and/or disorganized written reports may require re-writing. Failure to follow the format outlined in the guidelines for written reports may be grounds for a re-write.

Other Information

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

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

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.

Deliverables

Each group must deliver a report (two identical copies, one for each professor) written using a word processor. The format is explained above and in the document *Written Design Reports*.

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.

The written project report is due by 11 am Tuesday, April 22, 2008. Late projects will receive a minimum deduction of one letter grade.

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 Tuesday, April 22, 2008, starting at 11 am and running until approximately 2:00 p.m. Note that this is one day earlier than the date specified originally in the schedules for ChE 312 and ChE 325. 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.

References

1. Huang, X., N.W. Cant, M.S. Wainright and L. Ma, Chemical Engg. Proc. **44**(3) 393-402 (2005).
2. Kirk-Othmer Encyclopedia of Chemical Technology Vol. 12, John Wiley and Sons, New York (2005) p. 107.

Appendix 1

The reaction engineering group headed by I.M. (Shirley) Wright has obtained the following kinetic information for the methanol oxidation reaction:

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O \tag{A-1}$$

The rate expression is:

$$-r_{m1}[mole/gcatalyst/hr] = \frac{k_1 p_m}{1 + k_2 p_m} \tag{A-2}$$

where *p* is a partial pressure in atm, and *m* refers to methanol. The rate expression in Eq. (A-2) is only valid when oxygen is present in excess. The constants in Eq. (A-2) are defined as:

$$\ln k_1 = 12.50 - \frac{8774}{T} \tag{A-3}$$

$$\ln k_2 = -17.29 + \frac{7439}{T} \tag{A-4}$$

where *T* is in Kelvin.

Based on these data, the statistical mechanics group headed by Marge Inovera estimates rate data as follows for the side reaction:

$$CH_3OH \rightarrow HCHO + H_2 \tag{A-5}$$

The rate expression is:

$$-r_{m2}[mole/gcatalyst/hr] = \frac{k_1^{'}\ p_m^{0.5}}{1 + k_2^{'}\ p_m^{0.5}} \tag{A-6}$$

The constants in Eq. (A-6) are defined as:

$$\ln k_1^{'} = 16.9 - \frac{12500}{T} \tag{A-7}$$

$$\ln k_2^{'} = 25.0 - \frac{15724}{T} \tag{A-8}$$

To convert rate data from a catalyst-mass basis to a volume-of-reactor basis, take the catalyst bulk density to be 1500 kg catalyst/m^3 of reactor volume (void fraction is 0.5). The catalyst particles are spherical, with a 1 mm diameter.

Standard enthalpies of reaction (298 K, 1 atm) for the two reactions are given as:

$$\Delta H_1^o = -\ 156 \text{ kJ/mol methanol} \tag{A-9}$$

$$\Delta H_2^o = +\ 85 \text{ kJ/mol methanol} \tag{A-10}$$

Appendix 2
Economic Data

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. To err on the side of caution, use the price for multiple, identical smaller pieces of equipment.

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, 20, 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)

Packed Tower — Cost as vessel plus cost of packing. Assume that HETP = 0.6 m.

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)
Reactor, Adiabatic	Cost as 2 x (Cost of vessel based on volume)
Reactor with Heat Exchange	Cost as 2 x (Cost of vessel based on volume + cost of heat exchanger based on area)

It may be assumed that pipes and valves are included in the equipment cost factors. The 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 Factors:

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

Material Factors:

Carbon Steel	MF = 0.0
Stainless Steel	MF = 4.0

Utility Costs

Low Pressure Steam (618 kPa saturated)	\$7.78/GJ
Medium Pressure Steam (1135 kPa saturated)	\$8.22/GJ
High Pressure Steam (4237 kPa saturated)	\$9.83/GJ
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 can be returned to the steam supply system for the appropriate credit.

Catalyst, Feed and Product Prices

Methanol	\$0.64 / kg
Formaldehyde	\$0.99 / kg
Catalyst	\$2.25 / kg / year

Appendix 3
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