ChE 455
Fall 2006
Major 1

Formalin Production

Background

You have recently joined a chemical company. Among the chemicals that this company produces is methanol, mostly for internal consumption. A major use of internal methanol is to produce formalin, which is a 37 wt% solution of 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.

We recently have received a memorandum from a customer who buys our formalin indicating that there are periodic problems, mostly in the summer, with the formalin they are receiving from us. They claim that the formalin contains unacceptably high amounts of formic acid relative to formaldehyde. It seems that this alters the urea-formaldehyde resin properties such that the particle board and plywood subsequently manufactured does not have the appropriate tensile and load strength. They are threatening legal action unless this problem is rectified immediately.

Formaldehyde Production

Unit 800 produces formalin (37 wt% formaldehyde in water) from methanol using the silver catalyst process. Figure 1 illustrates the current process. Tables 1 and 2 are the stream tables and utility summary, respectively. Table 3 is a partial equipment summary.

Air is compressed and preheated, fresh and recycled methanol is pumped and preheated, and these two streams are mixed to provide reactor feed. The feed mixture is about 39 mole % methanol in air, which is above the upper flammability limit for methanol. (For methanol, UFL = 36 mole %; LFL = 6 mole %.) In the reactor, the following two reactions occur:

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O \qquad \Delta H_{rxn} = -37.3 \text{ kcal/mole} \qquad (1)$$

$$CH_3OH \rightarrow HCHO + H_2 \qquad \Delta H_{rxn} = 20.3 \text{ kcal/mole} \qquad (2)$$

The reactor is a unique configuration, in which the silver catalyst is in the form of a wire gauze, suspended above a heat exchanger tube bank. Because the net reaction is very exothermic, the heat generated in the adiabatic reactor section must be removed quickly, hence the close proximity of the heat exchanger tubes. The heat exchanger resembles a pool boiler, with a pool of water on the shell side. If the temperature of the effluent is too high, the set point on a liquid level controller is adjusted. The level controller feeds back to the boiler feed water inlet that increases the boiler feed water rate entering the heat exchanger to increase the water

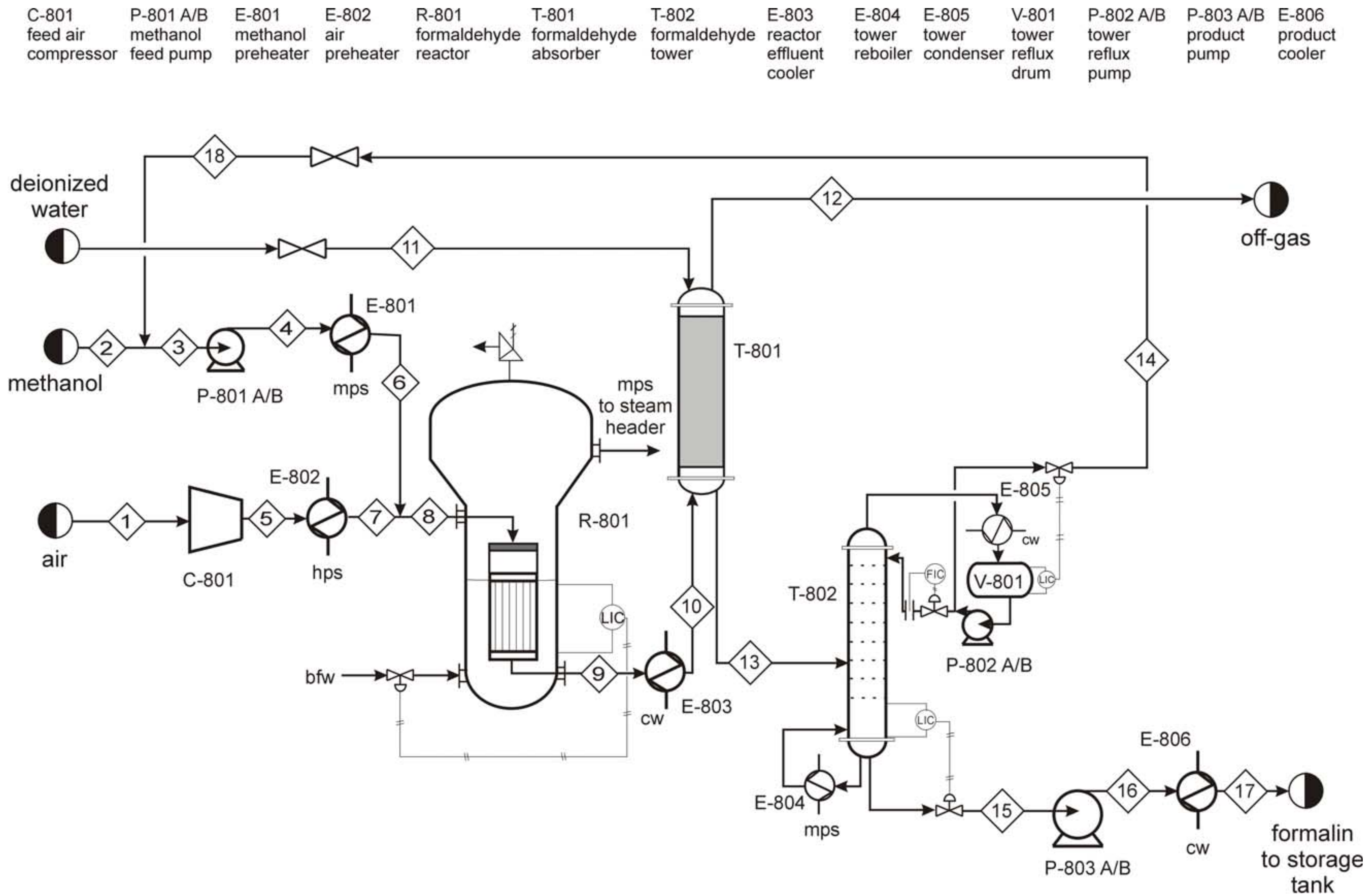


Figure 1: Unit 800 Formalin Production from Methanol

Table 1
Stream Tables for Unit 800

Stream No	1	2	3	4
Temp °C	25.00	30.00	40.66	40.78
Pres kPa	101.325	120.00	101.325	300.00
Vapor fraction	1.0	0.0	0.0	0.00
Total kg/h	4210.54	2464.75	3120.31	3120.31
Total kmol/h	145.94	76.92	99.92	99.92
Component kmol/h				
methanol		76.92	94.11	94.11
oxygen	30.66			
formaldehyde				
water			5.81	5.81
hydrogen				
nitrogen	115.28			

Stream No.	5	6	7	8
Temp °C	183.01	150.00	200.00	171.94
Pres kPa	300.00	265.00	265.00	255.00
Vapor fraction	1.0	1.0	1.0	1.0
Total kmol/h	145.94	99.92	145.94	245.86
Total kg/h	4210.54	3120.31	4210.54	7330.85
Component kmol/h				
methanol		94.12		94.12
oxygen	30.66		30.66	30.66
formaldehyde				
water		5.81		5.81
hydrogen				
nitrogen	115.28		115.28	115.28

Stream No.	9	10	11	12
Temp °C	200.00	100.00	30.00	84.57
Pres kPa	185.00	150.00	150.00	140.00
Vapor fraction	1.0	1.0	0.0	1.0
Total kg/h	7330.82	7330.82	2576.15	5354.21
Total kmol/h	278.03	278.03	143.00	224.16
Component kmol/h				
methanol	31.45	31.45		13.35
oxygen	0.15	0.15		0.15
formaldehyde	62.67	62.67		0.04
water	66.82	66.82	143.00	93.68
hydrogen	1.66	1.66		1.66
nitrogen	115.28	115.28		115.28

Table 1 (cont'd)
Stream Tables for Unit 800

Stream No.	13	14	15	16
Temp °C	89.85	75.46	106.64	106.71
Pres kPa	150.00	130.00	150.00	350.00
Vapor mole fraction	0.0	0.0	0.0	0.0
Total kg/h	4552.75	655.56	3897.06	3897.06
Total kmol/h	196.87	23.00	173.86	173.86
Component kmol/h				
methanol	18.10	17.19	0.90	0.90
oxygen				
formaldehyde	62.63		62.63	62.63
water	116.14	5.81	110.33	110.33
hydrogen				
nitrogen				

Stream No.	17	18
Temp °C	35.00	73.36
Pres kPa	315.00	120.00
Vapor mole fraction	0.0	0.0
Total kg/h	3897.06	655.56
Total kmol/h	173.86	23.00
Component kmol/h		
methanol	0.90	17.19
oxygen		
formaldehyde	62.63	
water	110.33	5.81
hydrogen		
nitrogen		

Table 2
Utility Stream Flow Summary for Unit 800

E-801	**E-802**	**E-803**	**E-804**
mps	hps	cw	mps
2063 kg/h	45.43 kg/h	23500 kg/h	18949 kg/h

E-805	**E-806**	**R-801**
cw	cw	bfw → mps
775,717 kg/h	27,957 kg/h	3723 kg/h

Table 3
Partial Equipment Summary

Heat Exchangers

E-801 A = 405 m^2 1-2 exchanger, floating head, carbon steel process stream in shell Q = 4111 MJ/h maximum pressure rating of 350 kPa	**E-804** A = 37.3 m^2 1-2 exchanger, kettle reboiler, stainless steel process stream in shell Q = 37,755 MJ/h maximum pressure rating of 250 kPa
E-802 A = 4.62 m^2 1-2 exchanger, floating head, carbon steel process stream in tubes Q = 76.75 MJ/h maximum pressure rating of 350 kPa	**E-805** A = 269 m^2 1-2 exchanger, floating head, stainless steel process stream in shell Q = 32,456 MJ/h maximum pressure rating of 250 kPa
E-803 A = 28.16 m^2 1-2 exchanger, floating head, carbon steel process stream in shell Q = 983.23 MJ/h maximum pressure rating of 350 kPa	**E-806** A = 41 m^2 1-2 exchanger, floating head, stainless steel process stream in tubes Q = 1169.7 MJ/h maximum pressure rating of 400 kPa

Reactors

R-801 – Heat Exchanger Portion A = 140.44 m^2 counterflow exchanger, floating head, carbon steel process stream in tubes Q = 8928 MJ/h maximum pressure rating of 350 kPa	**R-801 – Reactor Portion** thin layers of silver wire gauze suspended above heat exchanger tube bank

Pumps and Compressors

C-801 carbon steel power = 658 MJ/h 70% efficient	**P-801 A/B** carbon steel power = 1 MJ/h 80% efficient
P-803 A/B stainless steel power = 1.52 MJ/h 75% efficient	

Towers

T-801 carbon steel 10 m of packing 2 in ceramic Berl Saddles 20 theoretical stages 1.00 kPa/m pressure drop diameter = 0.86 m packing factor = 45 maximum pressure rating of 300 kPa	**T-802** carbon steel 31 sieve trays plus reboiler and partial condenser 70% efficient trays feed on tray 18 reflux ratio = 37.34 0.6096 m tray spacing, 0.091 m weirs column height 19 m diameter = 2.5 m maximum pressure rating of 200 kPa

vaporization rate to remove more heat. The reactor effluent enters an absorber in which most of the methanol and formaldehyde are absorbed into water, with most of the remaining light gases purged into the off-gas stream. The methanol, formaldehyde, and water enter a distillation column, in which the methanol overhead is recycled, and the bottom product is a formaldehyde/water mixture that contains ≤1 wt% methanol as an inhibitor. This mixture is cooled and sent to a storage tank, which is sized at four days capacity. This storage tank is essential, since some of the downstream processes are batch. The composition in the storage tank exceeds 37 wt % formaldehyde, so the appropriate amount of water is added when the downstream process draws from the storage tank. This is not shown on the PFD.

Storage of formaldehyde/water mixtures is tricky. At high temperatures, undesirable polymerization of formaldehyde is inhibited, but formic acid formation is favored. At low temperatures, acid formation is inhibited, but polymerization is favored. There are stabilizers which inhibit polymerization, but they are incompatible with resin formation. Methanol, at concentrations between 5 and 15 wt %, can also inhibit polymerizaton, but no separation equipment for methanol currently exists on site, and methanol above 1 wt % also causes defective resin production. With ≤1 wt% methanol, the storage tank contents must be maintained between 35°C and 45°C.

Observations

You have toured the plant, checked the log books, spoken to engineers and operators, and have gathered the following information:

- The catalyst is replaced once per year, and for about five days after start-up, a pressure relief valve in the reactor (R-801) releases.

- During the same time period, bfw consumption in R-801 was not seen to increase beyond normal, day-to-day fluctuations of ±1%, and the reactor outlet temperature was not seen to increase significantly.

- Excess acidity occurs mainly in the summer.

- All existing equipment is made of carbon steel.

- One year ago, an unscheduled, emergency shut down was required to replace a control system between the tower (T-802) and the subsequent pump (P-803 A/B). Due to availability and time constraints, 1" schedule 40 pipe was used in place of 1.5" schedule 40 pipe.

- During hot-weather periods, the inlet temperature of cooling water has been observed to increase by as much as 5°C.

- During these hot weather periods, the pressure in the distillation column has been observed to increase slightly, but operation over a long period of time shows no leakage or safety problems associated with this change in pressure.

- Pump 803 A/B is located a height of 5 m below the tower (T-802) exit. There is a total of 30 equivalent meters of pipe, elbows, and valves in the line.

- An inspection of the pressure relief valve on the reactor (R-801) indicates that it is rated at 1115 kPag, *i.e.*, it will open at or above that pressure.

- Over long periods of time after catalyst replacement, the pressure of medium-pressure steam leaving R-801 is 1110 kPag.

- During hot weather, the volume of off gas leaving the absorber increases by 1%. However, the increase in formaldehyde is about 22%, and the increase in water is about 3%.

- Pump (P-803 A/B) constantly makes noise, and each individual pump has been replaced within the last year.

Other Information

Other pertinent information is appended, including a memo from catalyst R&D, an equipment list, and utility and equipment costs.

Assignment

Your assignment is to provide recommendations as to the causes of the periodic acid formation problem and ways to remedy the situation. You should also recommend any other changes that you feel should be made to improve performance in Unit 800. Since our plant is due for annual shut-down in a few months, we want specific recommendations as to what should be done at that time, and the cost of these alterations and/or modifications.

Specifically, you are to prepare the following by 9:00 a.m., Monday, November 6, 2006:

1. a written report detailing your diagnosis, recommended actions, and costs associated with fixing Unit 800. This should include:

   a. a diagnosis of all problems observed in Unit 800.

   b. a methodology for maintaining the temperature entering the tank and in the tank between 35°C and 45°C all year.

   c. an incremental economic evaluation (before-tax EAOC at an interest rate of 15%, 10 year lifetime) of the required changes required.

   d. suggestions for any additional long-term modifications to the process that would provide a before-tax, incremental DCFROR of 15% (5 year lifetime).

   e. a PFD that illustrates any/all modifications recommended for the process.

2. a list of new equipment to be purchased, including size, cost, and materials of construction

Deliverables

Specifically, you are to prepare the following by 9:00 a.m., Monday, November 6, 2006:

1. Prepare a written report, conforming to the guidelines, detailing the information in items 1, 2, and 3, above.

2. Include a legible, organized set of calculations justifying your recommendations, including any assumptions made.

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

Report Format

This report should be brief and should conform to the guidelines. It should be bound in a 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. These calculations 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 re-writing. 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 November 6, 2006 and November 9, 2006. 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 other interaction with anyone other than the instructors is prohibited. Violators will be subject to the penalties and procedures outlined in the University Procedures for Handling Academic Dishonesty Cases (begins on p. 47 of 2005-07 Undergraduate Catalog).

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

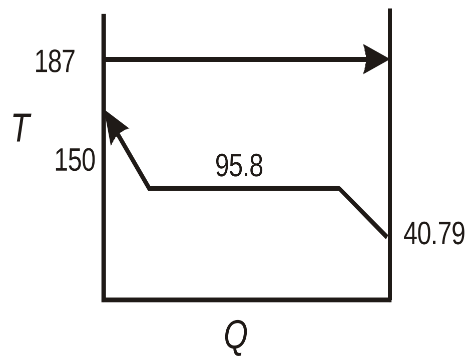
Solutions of formaldehyde and water are very non-ideal. Individually, the volatilities are, from most volatile to least volatile, formaldehyde, methanol, water. However, formaldehyde associates with water so that when this three-component mixture is distilled, methanol is the light key and water is the heavy key. The formaldehyde will "follow" the water. The ESDK *K*-value package in Chemcad simulates this appropriately. Latent heat should be used for enthalpy calculations. The expert system will recommend these choices.

When simulating an entire process, we recommend using the shortcut distillation column, within the process for the methanol-water/formaldehyde distillation. SCDS should then be used as a separate item to simulate the column based on the results obtained from the shortcut column. However, due to the non-ideality of the thermodynamics, the actual column simulation using SCDS will probably require many more stages than predicted by the shortcut simulation, possibly twice the number.

Appendix 2
Calculations and Other Pertinent Information

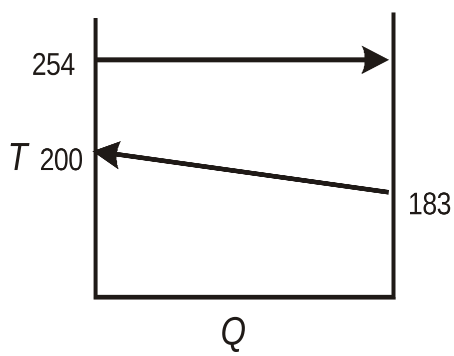
E-801

Q = 4111 MJ/h
process fluid in shell
mps condensing h_i = 6000 W/m^{2}K
desubcooling zone
ΔT_{lm} = 116.55°C
h_o = 500 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 461.5 W/m^{2}K
A = 21.2 m^2
boiling zone
ΔT_{lm} = 91.2°C
h_o = 6000 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 3000 W/m^{2}K
A = 4.17 m^2
superheating zone
ΔT_{lm} = 60.68°C
h_o = 50 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 49.6 W/m^{2}K
A = 379.4 m^2
A_{total} = 405 m^2
$Q = \dot{m}\lambda = \dot{m}$ (1992.5 kJ/kg)
lps flow in Table 2

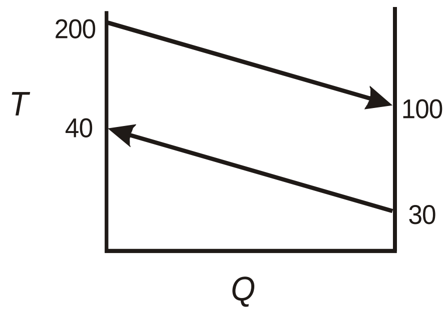


E-802

Q = 76.75 MJ/h
ΔT_{lm} = 62.11°C
process fluid h_i = 75 W/m^{2}K
hps condensing h_o = 7500 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 74.26 W/m^{2}K
A = 4.62 m^2
$\dot{m}_{hps} = Q / \lambda = Q / (1694 \text{ kJ/kg})$
hps flow in Table 2

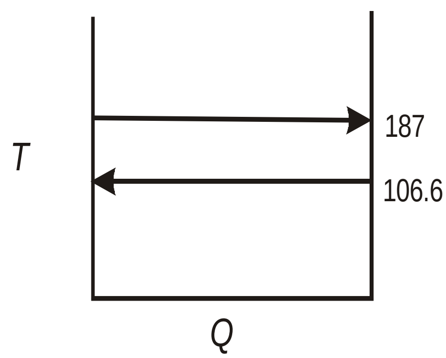


E-803



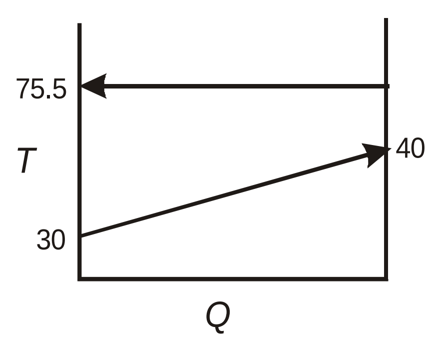
Q = 983.23 MJ/h
ΔT_{lm} = 108.87°C
cw h_i = 1000 W/m^{2}K
process stream h_o = 100 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 90.9 W/m^{2}K
F = 0.98
A = 28.16 m^2
$\dot{m}_{cw} = Q / C_p \Delta T = Q / [(4.184\,\text{kJ/kgK})(10\text{K})]$
cw flow in Table 2

E-804



Q = 37,755 MJ/h
ΔT_{lm} = 80.4°C
mps condensing h_i = 7000 W/m^{2}K
boiling process stream h_o = 7000 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 3500 W/m^{2}K
A = 37.3 m^2
$\dot{m}_{mps} = Q / \lambda = Q / (1990\,\text{kJ/kg})$
mps flow in Table 2

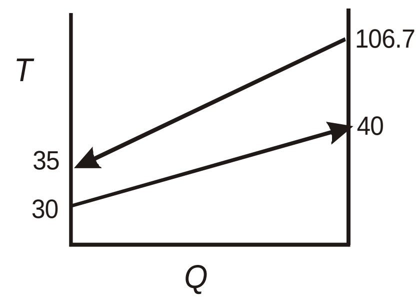
E-805



Q = 32,456 MJ/h
ΔT_{lm} = 40.24°C
cw h_i = 1200 W/m^{2}K
condensing organic process stream h_o = 2500 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 833.3 W/m^{2}K
A = 269 m^2
$\dot{m}_{cw} = Q / C_p \Delta T = Q / [(4.184\,\text{kJ/kgK})(10\text{K})]$
cw flow in Table 2

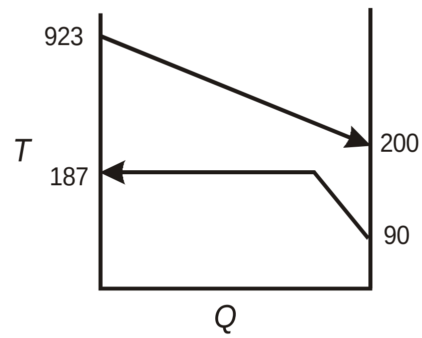
E-806

Q = 1169.7 MJ/h
ΔT_{lm} = 23.8°C
cw h_i = 1000 W/m^{2}K
process stream h_o = 500 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 333.3 W/m^{2}K
A = 41 m^2
$\dot{m}_{cw} = Q/C_p\Delta T = Q/[(4.184\,\text{kJ/kgK})(10\text{K})]$
cw flow in Table 2



R-801 heat exchanger

Q = 8928 MJ/h
adiabatic reaction temperature is 923°C
ΔT_{lm} = 179.1°C (based on 187°C "seen" by process fluid)
bfw to mps h_o = 7000 W/m^{2}K
process stream h_i = 100 W/m^{2}K
$U \approx (1/h_i + 1/h_o)^{-1}$ = 98.6 W/m^{2}K
A = 140.44 m^2
$\dot{m}_{cw} = Q/C_p\Delta T = Q/[1992 + (4.184\,\text{kJ/kgK})(187 - 90\text{K})]$
mps flow in Table 2



T-801

use packed bed
from Chemcad:
L = 3000 kg/h, G = 5750 kg/h
ρ_L = 925 kg/m^3
ρ_G = 1.15 kg/m^3
$(L/G)(\rho_G/\rho_L)^{0.5}$ = 0.018
2 in ceramic Berl Saddles
packing factor is 45
packing pressure drop is 1 kPa/m
from flooding (P. Wankat, *Equilibrium Staged Separations*, Prentice Hall, 1988, p. 421.)
parameter at flooding = 0.2
parameter at 75% flooding = 0.1125
G = 0.555 lb/ft^{2}s
A = (5750 kg/3600 s)/(0.555 lb/ft^{2}s)(2.2 lb/kg) = 6.32 ft^2
D = 2.84 ft = 0.86 m

T-802

from Chemcad, 22 ideal trays, plus partial reboiler and partial condenser

71.6% overall column efficiency (O'Connell correlation)
$\Rightarrow$ 22 trays (column is 19 m high with 18 in = 0.6096 m tray spacing)
$\Delta P = \rho g h N$
20,000 Pa = (725 kg/m^3)(9.8 m/s^2)(h_{weir})(31)
h_{weir} = 0.091 m ≈ 3.6 in

above feed:
L = 21,000 kg/h, G = 21,000 kg/h
ρ_L = 750 kg/m^3
ρ_G = 1 kg/m^3
$(L/G)(\rho_G/\rho_L)^{0.5}$ = 0.0.0365
from flooding graph for 18 in tray spacing (P. Wankat, *Equilibrium Staged Separations*, Prentice Hall, 1988, p. 387.)
C_{sb} = 0.29
u_{fl} = 7.93 ft/s
u_{act} = 1.81 m/s (75% of flooding)
if 75% active area
$A = (G/3600)/[(0.75)(\rho_G)(u_{act})]$ = 4.29 m^2
D = 2.34 m

below feed:
L = 27,000 kg/h, G = 23,000 kg/h
ρ_L = 690 kg/m^3
ρ_G = 1 kg/m^3
$(L/G)(\rho_G/\rho_L)^{0.5}$ = 0.0447
from flooding graph for 18 in tray spacing (P. Wankat, *Equilibrium Staged Separations*, Prentice Hall, 1988, p. 387.)
C_{sb} = 0.28
u_{fl} = 7.35 ft/s
u_{act} = 1.68 m/s (75% of flooding)
if 75% active area
$A = (G/3600)/[(0.75)(\rho_G)(u_{act})]$ = 5.07 m^2
D = 2.54 m

go with 2.5 m diameter

no information available for: P-801 A/B, P-802 A/B, C-801, V-801

prices: methanol \$0.29/lb, formalin \$0.40/lb