ChE 455
Fall 2010
Major 1

Styrene Production

Styrene is the monomer used to make polystyrene, which has a multitude of uses, the most common of which are in packaging and insulated, styrofoam beverage cups. Styrene is produced by the dehydrogenation of ethylbenzene. Ethylbenzene is formed by reacting ethylene and benzene, and one of the ways benzene is made is by the hydrodealkylation or transalkylation of toluene, which is obtained as a byproduct of gasoline manufacture. There is very little ethylbenzene sold commercially. Most ethylbenzene manufacturers convert it directly into styrene in the same plant.

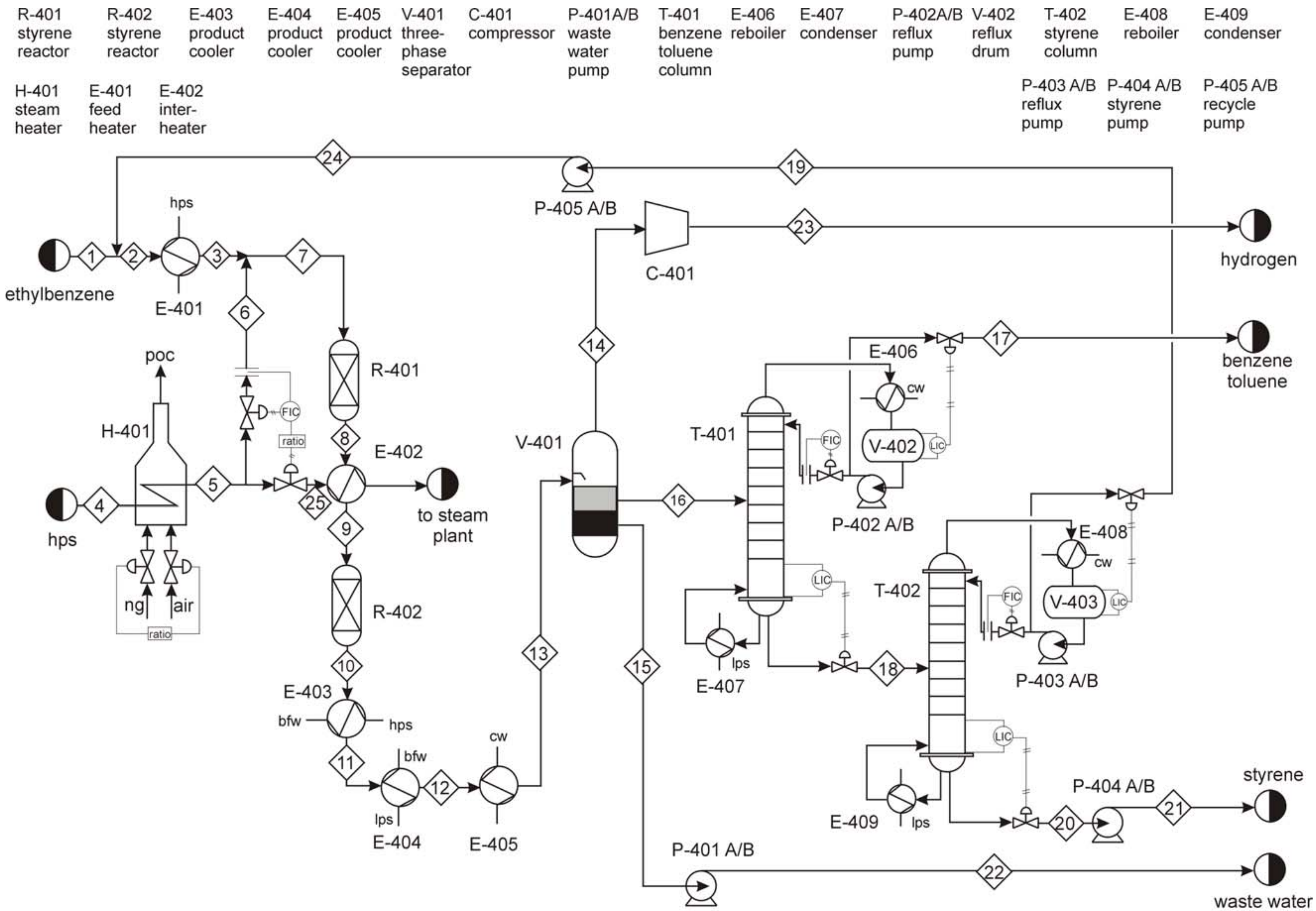
The plant at which you are employed currently manufactures ethylbenzene and styrene. This plant was recently acquired by your company in a takeover, and a team of engineers has been assigned to solve the problems observed in the process over the last few years. The unit to which you are assigned, Unit 400, converts the ethylbenzene into styrene, producing around 100,000 metric tons per year of 99.8 wt % styrene.

Process Description

The process flow diagram is shown in Figure 1. The reactions, the kinetics, and the equilibrium equations are detailed in Appendix 1. Ethylbenzene feed is mixed with recycled ethylbenzene, heated, and then mixed with high-temperature, superheated steam. Steam is an inert in the reaction, which drives the equilibrium (shown in Equation 1 in the Appendix 1) to the right by reducing the concentrations of all components. Since styrene formation is highly endothermic, the superheated steam also provides energy to drive the reaction to the right. The reactants then enter two adiabatic packed beds with interheating. The products are cooled, producing steam from the high-temperature reactor effluent. The cooled product stream is sent to a three-phase separator, in which light gases (hydrogen, methane, ethylene), organic liquid, and water each exit in separate streams. The hydrogen stream is further purified as a source of hydrogen elsewhere in the plant. The small amount of benzene and toluene is distilled and either incinerated for its fuel value or returned to the ethylbenzene process (since the benzene raw material always has some toluene impurity). The ethylbenzene and styrene stream is distilled to separate unreacted ethylbenzene for recycle from the styrene product.

The styrene product can spontaneously polymerize at higher temperatures. Since our product styrene is sent directly to the polymerization unit, experience suggests that as long its temperature is maintained below 125°C, there is no spontaneous polymerization problem. Since this is below styrene's normal boiling point, and since low pressure pushes the equilibrium to the right, much of this process is run at low pressures, with much of the separation section at vacuum.

Tables 1 and 2 show the design conditions for Unit 400. Table 3 contains an equipment list. Other pertinent information and calculations are contained in Appendix 2.



Unit 400: Production of Styrene from Ethylbenzene

Table 1
Stream Tables for Unit 400

Stream No.	**1**	**2**	**3**	**4**	**5**
Temperature (°C)	136.00	116.04	240.00	253.79	800.00
Pressure (kPa)	200.00	190.00	170.00	4237.00	4202.00
Vapor Mole Fraction	0.00	0.00	1.00	1.00	1.00
Total Flow (kg/h)	13,052.22	23,965.10	23,965.10	72,353.71	72,353.71
Total Flow (kmol/h)	123.42	226.21	226.21	4016.30	4016.30
Component Flows					
Water	0.00	0.00	0.00	4016.30	4016.30
Ethylbenzene	121.00	223.73	223.73	0.00	0.00
Styrene	0.00	0.06	0.06	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00
Benzene	1.21	1.21	1.21	0.00	0.00
Toluene	1.21	1.21	1.21	0.00	0.00
Ethylene	0.00	0.00	0.00	0.00	0.00
Methane	0.00	0.00	0.00	0.00	0.00

Stream No.	**6**	**7**	**8**	**9**	**10**
Temperature (°C)	722.03	566.57	504.27	550.00	530.07
Pressure (kPa)	170.00	160.00	150.00	135.00	125.00
Vapor Mole Fraction	1.00	1.00	1.00	1.00	1.00
Total Flow (kg/h)	54,045.00	78,010.10	78,010.18	78,010.18	78,010.19
Total Flow (kmol/h)	3000.00	3226.21	3317.28	3317.28	3346.41
Component Flows					
Water	3000.00	3000.00	3000.00	3000.00	3000.00
Ethylbenzene	0.00	223.73	132.35	132.35	102.88
Styrene	0.00	0.06	91.06	91.06	120.09
Hydrogen	0.00	0.00	90.69	90.69	119.38
Benzene	0.00	1.21	1.28	1.28	1.37
Toluene	0.00	1.21	1.52	1.52	1.86
Ethylene	0.00	0.00	0.07	0.07	0.16
Methane	0.00	0.00	0.31	0.31	0.65

Table 1
Stream Tables for Unit 400 (cont'd)

Stream No.	**11**	**12**	**13**	**14**	**15**
Temperature (°C)	267.00	180.00	65.00	65.00	65.00
Pressure (kPa)	110.00	95.00	80.00	65.00	65.00
Vapor Mole Fraction	1.00	1.00	0.15	1.00	0.00
Total Flow (kg/h)	78,010.19	78,010.19	78,010.19	255.64	54,045.00
Total Flow (kmol/h)	3346.41	3346.41	3346.41	120.20	3000.00
Component Flows					
Water	3000.00	3000.00	3000.00	0.00	3000.00
Ethylbenzene	102.88	102.88	102.88	0.00	0.00
Styrene	120.09	120.09	120.09	0.00	0.00
Hydrogen	119.38	119.38	119.38	119.38	0.00
Benzene	1.37	1.37	1.37	0.00	0.00
Toluene	1.86	1.86	1.86	0.00	0.00
Ethylene	0.16	0.16	0.16	0.16	0.00
Methane	0.65	0.65	0.65	0.65	0.00

Stream No.	**16**	**17**	**18**	**19**	**20**
Temperature (°C)	65.00	69.89	125.02	90.83	123.67
Pressure (kPa)	65.00	45.00	65.00	25.00	55.00
Vapor Mole Fraction	0.00	0.00	0.00	0.00	0.00
Total Flow (kg/h)	23,709.57	289.52	23,420.04	10,912.92	12,507.12
Total Flow (kmol/h)	226.21	3.34	222.88	102.79	120.08
Component Flows					
Water	0.00	0.00	0.00	0.00	0.00
Ethylbenzene	102.88	0.10	102.78	102.73	0.05
Styrene	120.09	0.00	120.09	0.06	120.03
Hydrogen	0.00	0.00	0.00	0.00	0.00
Benzene	1.37	1.37	0.00	0.00	0.00
Toluene	1.86	1.86	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00	0.00	0.00
Methane	0.00	0.00	0.00	0.00	0.00

Table 1
Stream Tables for Unit 400 (cont'd)

Stream No.	**21**	**22**	**23**	**24**	**25**
Temperature (°C)	123.78	65.04	202.21	90.96	800.00
Pressure (kPa)	200.00	200.00	140.00	200.00	4202.00
Vapor Mole Fraction	0.00	0.00	1.00	0.00	1.00
Total Flow (kg/h)	12,507.12	54,045.00	255.64	10,912.92	18,308.71
Total Flow (kmol/h)	120.08	3000.00	120.20	102.79	1016.30
Component Flows					
Water	0.00	3000.00	0.00	0.00	1016.30
Ethylbenzene	0.05	0.00	0.00	102.73	0.00
Styrene	120.03	0.00	0.00	0.06	0.00
Hydrogen	0.00	0.00	119.38	0.00	0.00
Benzene	0.00	0.00	0.00	0.00	0.00
Toluene	0.00	0.00	0.00	0.00	0.00
Ethylene	0.00	0.00	0.16	0.00	0.00
Methane	0.00	0.00	0.65	0.00	0.00

Table 2
Utility Summary for Unit 400
(all units of kg/h)

E-401	**E-403**	**E-404**	**E-405**
hps	bfw → hps	bfw → lps	cw
7982	18,451	5562	3,269,746

E-406	**E-407**	**E-408**	**E-409**
cw	lps	cw	lps
309,547	7,550	1,105,980	21,811

Table 3
Partial Equipment Summary

Heat Exchangers

H-401 fired heater – refractory-lined, stainless-steel tubes design Q = 23.63 MW max Q = 25.00 MW	**E-401** carbon steel A = 260 m^2 boiling in shell, condensing in tubes 1 shell – 2 tube passes Q = 13,530 MJ/h
E-402 316 stainless steel A = 226 m^2 steam in shell, process fluid in tubes 1 shell – 2 tube passes Q = 8322 MJ/h	**E-403** 316 stainless steel A = 1457 m^2 boiling in shell, process fluid in tubes 1 shell – 2 tube passes Q = 44,595 MJ/h
E-404 carbon steel A = 702 m^2 boiling in shell, process fluid in tubes 1 shell – 2 tube passes Q = 13,269 MJ/h	**E-405** 316 stainless steel A = 1446 m^2 cw in shell, process fluid in tubes 1 shell – 2 tube passes Q = 136,609 MJ/h
E-406 carbon steel A = 173 m^2 process fluid in shell, cooling water in tubes 1 shell – 2 tube passes Q = 12,951 MJ/h	**E-407** carbon steel A = 64 m^2 boiling in shell, steam condensing in tubes desuperheater – steam saturated at 150°C 1 shell – 2 tube passes Q = 15,742 MJ/h
E-408 carbon steel A = 385 m^2 process fluid in shell, cooling water in tubes 1 shell – 2 tube passes Q = 46,274 MJ/h	**E-409** carbon steel A = 176 m^2 boiling in shell, steam condensing in tubes desuperheater – steam saturated at 150°C 1 shell – 2 tube passes Q = 45,476 MJ/h

Reactors

R-401 316 stainless steel, packed bed cylindrical catalyst pellet (1.6 mm×3.2 mm) void fraction = 0.4 V = 25 m^3 9.26 m tall, 1.85 m diameter	**R-402** 316 stainless steel, packed bed cylindrical catalyst pellet (1.6 mm×3.2 mm) void fraction = 0.4 V = 25 m^3 9.26 m tall, 1.85 m diameter

Towers

T-401 carbon steel *D* = 3.0 m 61 sieve trays 54% efficient feed on tray 31 12 in tray spacing 1 in weirs column height = 61 ft = 18.6 m	**T-402** carbon steel *D* = 6.9 m 158 bubble cap trays 55% efficient feed on tray 78 6 in tray spacing 1 in weirs column height = 79 ft = 24.1 m

Other Equipment

C-401 carbon steel *W* = 134 kW 60% adiabatic efficiency	**V-401** carbon steel $V = 26.8\ m^3$
P-401 A/B stainless steel *W* = 2.59 kW (actual) 80% efficient	**P-404 A/B** carbon steel *W* = 0.775 kW (actual) 80% efficient
P-405 A/B carbon steel W = 0.825 kW (actual) 80% efficient	

Problem

Your company acquired this plant from another company through a take-over. Previously, this other company was having many problems meeting specifications and had lost customers because of these problems. Your company is in the process of diagnosing and fixing these problems to bring the plant back on-line at full capacity with product that meets specifications.

It is desired to bring the plant back on-line as soon as possible. However, there is a problem in the steam plant that will take much longer to fix. Therefore, the source of high-pressure steam that enters the process for which all condensate is not returned (Stream 4) will not be available. Because of excess capacity, it will be possible to use medium- or low-pressure steam as a process feed. The questions that must be answered are how this will affect the styrene production rate and how equipment performance will be affected. This is the primary assignment.

Additionally, current market conditions for styrene are very tight. Whatever we can do to improve the economic performance of Unit 400 will help the bottom line. Therefore, the second part of your assignment is to suggest process improvements that will enhance the profitability of Unit 400, especially ones that can reasonably be implemented during the upcoming shut down, such as changing operating conditions rather than purchasing new equipment. The cost and economic benefit of these suggested changes should be presented. The economic criterion to be used for analysis of process improvements is 15% before taxes over 7 years.

Deliverables

Specifically, the following is to be completed by 9:00 a.m., Monday, November 15, 2010:

1. Prepare a written report, conforming to the guidelines, detailing the solution to the problem.

2. Provide a list of suggested process improvements which can enhance the profitability of Unit 400.

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

4. Include an updated PFD and stream table for the modified process.

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

6. Include a signed copy of the attached confidentiality statement

Report Format

This report should be brief and should conform to the guidelines, which are available at the end of the following web page: http://www.che.cemr.wvu.edu/publications/projects/index.php. It should be bound in a 3-ring binder/folder that is not oversized relative to the number of pages in the report. Figures and tables should be included as appropriate. An appendix must be attached that includes items such as the requested calculations and a Chemcad consolidated report (required) of the converged simulation for your recommended case. Stream properties (viscosity, density, etc.) **are not** to be included in the Chemcad consolidated report but stream conditions and components must be included, and there will be a deduction if these rules are not followed. The calculations in the appendix 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 15, 2010 and November 19, 2010. 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 interaction with anyone other than the instructor is prohibited. This means that any cross talk among students about anything relating to this assignment, no matter how insignificant it may seem to you, is a violation of the rules and is considered academic dishonesty. Violators will be subject to the penalties and procedures outlined in the University Procedures for Handling Academic Dishonesty Cases (see p. 45 of 2009-11 Undergraduate Catalog (http://coursecatalog.wvu.edu/fullcatalogs/09-11catalog.pdf) or follow the link http://www.arc.wvu.edu/rightsa.html).

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
Reaction Kinetics and Equilibrium

The reactions for styrene production are as follows:

$$C_6H_5C_2H_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_6H_5C_2H_3 + H_2 \tag{1}$$

ethylbenzene styrene hydrogen

$$C_6H_5C_2H_5 \xrightarrow{k_3} C_6H_6 + C_2H_4 \tag{2}$$

ethylbenzene benzene ethylene

$$C_6H_5C_2H_5 + H_2 \xrightarrow{k_4} C_6H_5CH_3 + CH_4 \tag{3}$$

ethylbenzene hydrogen toluene methane

Kinetics (subscripts on r refer to reactions in Equation (1) – (3) (adapted from Snyder, J. D. and B. Subramaniam, *Chem. Engr. Sci.*, **49**, 5585-5601 (1994) – the positive activation energy can arise from non-elementary kinetics and/or from reversible reactions:

$$r_1 = 1.177 \times 10^8 \exp\left(-\frac{21708}{RT}\right) p_{eb} \tag{4}$$

$$r_2 = 20.965 \exp\left(\frac{7804}{RT}\right) p_{sty} p_{hyd} \tag{5}$$

$$r_3 = 7.206 \times 10^{11} \exp\left(-\frac{49675}{RT}\right) p_{eb} \tag{6}$$

$$r_4 = 1.724 \times 10^6 \exp\left(-\frac{21857}{RT}\right) p_{eb} p_{hyd} \tag{7}$$

where p is in bar, T is in K, R = 1.987 cal/mol K, and r_i is in mol/m^3 reactor s. When simulating this, or any, reactor in Chemcad, the units for the reactor may be set separately from the units for the rest of the simulation in the "more specifications" tab.

The styrene reaction may be equilibrium limited, and the equilibrium constant is

$$K = \left(\frac{y_{sty} y_{hyd} P}{y_{eb}}\right) \tag{8}$$

and

$$\ln K = 15.5408 - \frac{14852.6}{T} \tag{9}$$

where T is in K and P is in bar.

other data:

bulk catalyst density = 1282 kg/m^3
void fraction = 0.4

Appendix 2
Calculations and Other Pertinent Information

Vessel (V-401)

assume 10 min residence time based on total liquid flow, calculate volume and double it to provide space for vapor disengagement

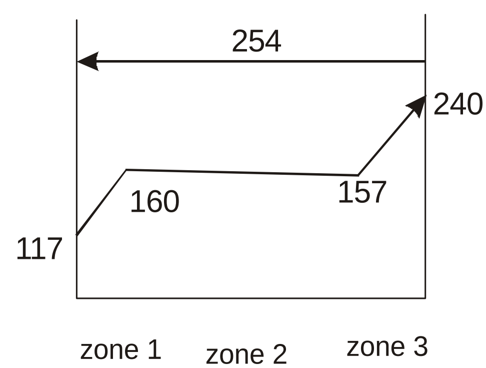
organic liquid at 26.6 m^3/h
water at 54.0 m^3/h
total liquid flow = 80.6 m^3/h = 1.34 m^3/min
total volume = 26.8 m^3

Heat Exchangers

key data:

latent heats
λ_{hps} = 1695 kJ/kg
λ_{mps} = 2002 kJ/kg
λ_{lps} = 2085 kJ/kg

E-401



zone 1
Q_1 = 2301.11 MJ/h
ΔT_{lm} = 113.96°C
liquid organic h = 600 W/m^{2}K
condensing steam h = 6000 W/m^{2}K
$U \approx 1/h_i + 1/h_o$ = 545.45 W/m^{2}K
A = 10.29 m^2

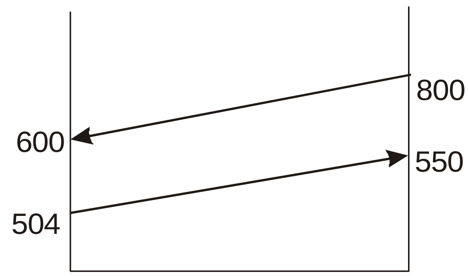
zone 2
Q_2 = 7546.36 MJ/h
ΔT_{lm} = 95.57°C
boiling organic h = 5000 W/m^{2}K
condensing steam h = 6000 W/m^{2}K
temperature drop in this zone due to pressure drop
$U \approx$2727.27 W/m^{2}K
A = 8.04 m^2

zone 3
Q_3 = 3681.13 MJ/h
ΔT_{lm} = 42.93°C
vapor organic h = 100 W/m^{2}K
condensing steam h = 6000 W/m^{2}K

$U \approx 98.36$ W/m^{2}K
$A = 242.13$ m^2

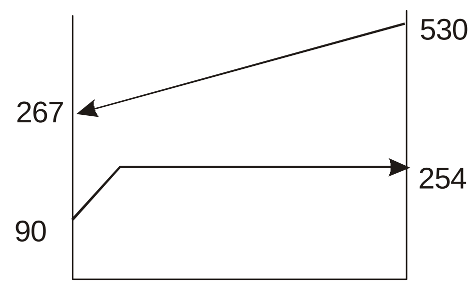
total $A = 260.46$ m^2
steam flowrate from Chemcad in Table 2

E-402



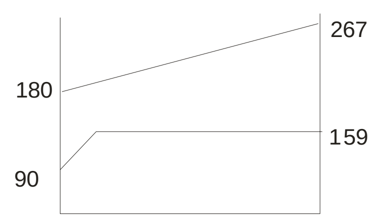
$Q = 8321.66$ MJ/h
$\Delta T_{lm} = 160.71$°C
hot desuperheating steam $h = 200$ W/m^{2}K
hot vapor organic $h = 100$ W/m^{2}K
$U \approx 66.67$ W/m^{2}K
LMTD corr factor – 1-2 exchanger = 0.9529
$A = 226.46$ m^2

E-403



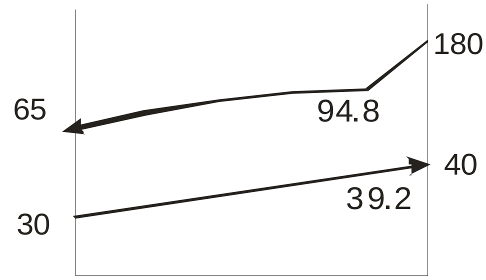
$Q = 44{,}594.43$ MJ/h
$\Delta T_{lm} = 86.09$°C
boiling water $h = 8000$ W/m^{2}K
hot vapor organic $h = 100$ W/m^{2}K
$U \approx 98.77$ W/m^{2}K
$A = 1456.85$ m^2
bfw flowrate from Chemcad in Table 2

E-404



$Q = 13{,}268.50$ MJ/h
$\Delta T_{lm} = 53.13$°C
boiling water $h = 8000$ W/m^{2}K
warm vapor organic $h = 100$ W/m^{2}K
$U \approx 98.77$ W/m^{2}K
$A = 702.43$ m^2
$m = Q/(2085 + 293) = 5579.97$ kg/h (denominator is $\lambda + C_p\Delta T$ in kJ/kg)
bfw flowrate from Chemcad in Table 2

E-405

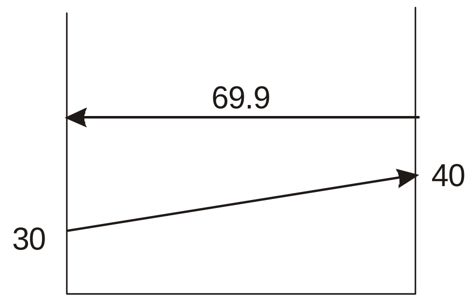


zone 1 - desuperheating
$Q_1 = 12{,}305.74$ MJ/h
$\Delta T_{lm} = 91.37$°C
vapor organic $h = 100$ W/m^{2}K
cooling water $h = 1000$ W/m^{2}K
$U \approx 1/h_i + 1/h_o = 90.91$ W/m^{2}K
$A = 411.53$ m^2

zone 2 – partial condensing – treat like cooling is straight line
Q_2 = 124,303.29 MJ/h
ΔT_{lm} = 44.49°C
partial condensation organic h = 3000 W/m^{2}K
cooling water h = 1000 W/m^{2}K
$U \approx$ 750 W/m^{2}K
A = 1034.781 m^2

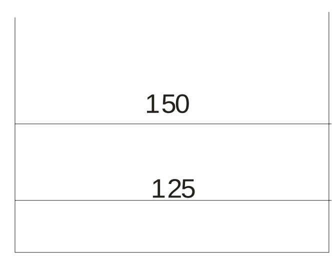
total A = 1446.31
cw flowrate from Chemcad in Table 2

E-406



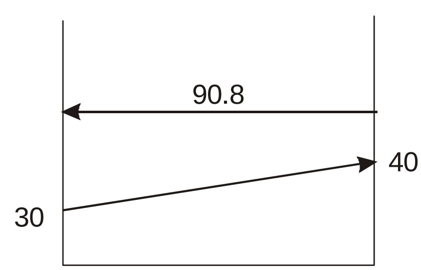
Q = 12,951.45 MJ/h
ΔT_{lm} = 34.65°C
condensing organic h = 1500 W/m^{2}K
cooling water h = 1000 W/m^{2}K
$U \approx$ 600 W/m^{2}K
A = 173.05 m^2
$m = Q/[4.184(10)]$ = 309,547.08 kg/h (denominator is in kJ/kg)

E-407



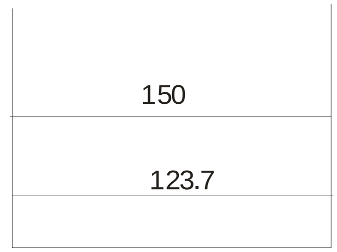
Q = 15,742.13 MJ/h
ΔT_{lm} = 24.98°C
condensing steam h = 6000 W/m^{2}K
boiling organic h = 5000 W/m^{2}K
steam desuperheated to 150°C
$U \approx$ 2727.27 W/m^{2}K
A = 64.19 m^2
$m = Q/2085$ = 7550.18 kg/h (denominator is λ of steam kJ/kg)

E-408



Q = 46,274.20 MJ/h
ΔT_{lm} = 55.68°C
condensing organic h = 1500 W/m^{2}K
cooling water h = 1000 W/m^{2}K
$U \approx$ 600 W/m^{2}K
A = 384.75 m^2
$m = Q/[4.184(10)]$ = 1,105,979.92 kg/h (denominator is in kJ/kg)

E-409



Q = 45,476.36 MJ/h
ΔT_{lm} = 26.33°C
steam desuperheated to 150°C
condensing steam h = 6000 W/m^{2}K
boiling organic h = 5000 W/m^{2}K
$U \approx$ 2727.27 W/m^{2}K
A = 175.92 m^2
$m = Q/2085$ = 21,811.20 kg/h (denominator is $C_p\Delta T$ of water in kJ/kg)

T-401

from Chemcad 33 ideal stages, feed at 17 (one subtracted for condenser)
sieve trays
flooding within reasonable range from Chemcad
D = 3.0 m
tray spacing = 0.305 m (= 12 in)
from O'Connell correlation in Chemicad, 0.54 average overall column efficiency
weir height = (0.051 m)(0.54) = 0.0275 m (= 1.08 in)
$\Rightarrow$ 61 stages (so column about 61 ft tall =18.6m)
feed at 17(61/33) = 31

T-402

from Chemcad 87 ideal stages, feed at 43 (one subtracted for condenser)
bubble cap trays
flooding within reasonable range from Chemcad
D = 6.9 m
tray spacing = 0.1525 m (6 in)
from O'Connell correlation in Chemicad, 0.55 average overall column efficiency
weir height = (0.051 m)(0.55) = 0.028 m (1.1 in)
$\Rightarrow$ 158 stages (so column about 79 ft tall = 24.1 m)
feed at 43(158/87) = 78

H-401

from Chemcad Q = 63544 MJ/h = 17.65 MW
but this heater must also heat steam used in E-402 (Stream 25)
total flow is Stream 4 on PFD
so Q = 17.65[(3000+1016)/3000] = 23.62 MW
designed for Q = 25.00 MW
split between Streams 6 and 25 is controlled by ratio controller, but the ratio can be changed

Information on other equipment is not available.