Fluid Mechanics, Heat Transfer, Thermodynamics
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 37 wt% 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 flow diagram (PFD) is shown in Figure 1. You should use this as a starting point. Your assignment is to complete the mini-designs described later in this document.

Chemical Reaction

Unit 800 produces formalin (37 wt% formaldehyde in water) from methanol using a silver catalyst process. Figure 1 illustrates the current process.

Air is compressed and preheated, fresh and recycled methanol are pumped and preheated, and these two streams are mixed to provide reactor feed. The feed mixture should be 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:

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O \qquad (1)$$

$$CH_3OH \rightarrow HCHO + H_2 \qquad (2)$$

The selectivity for the first reaction to the second reaction is 9/1. The reactor effluent enters a partial condenser in which most of the methanol, formaldehyde, and water are condensed with the oxygen, nitrogen, and hydrogen remaining in the gas phase. The vessel, V-801, allows the vapor and liquid phases to disengage, with the vapor leaving the process (to be burned to dispose of the hydrogen), and with the liquid being separated in T-801 to recycle the methanol.

Process Details

Feed Stream and Effluent Streams

Stream 1: air feed at 25°C and atmospheric pressure

Stream 2: methanol feed at 25°C and atmospheric pressure, assumed pure

Stream 14: formaldehyde-water mixture, less than 1 wt% methanol allowed

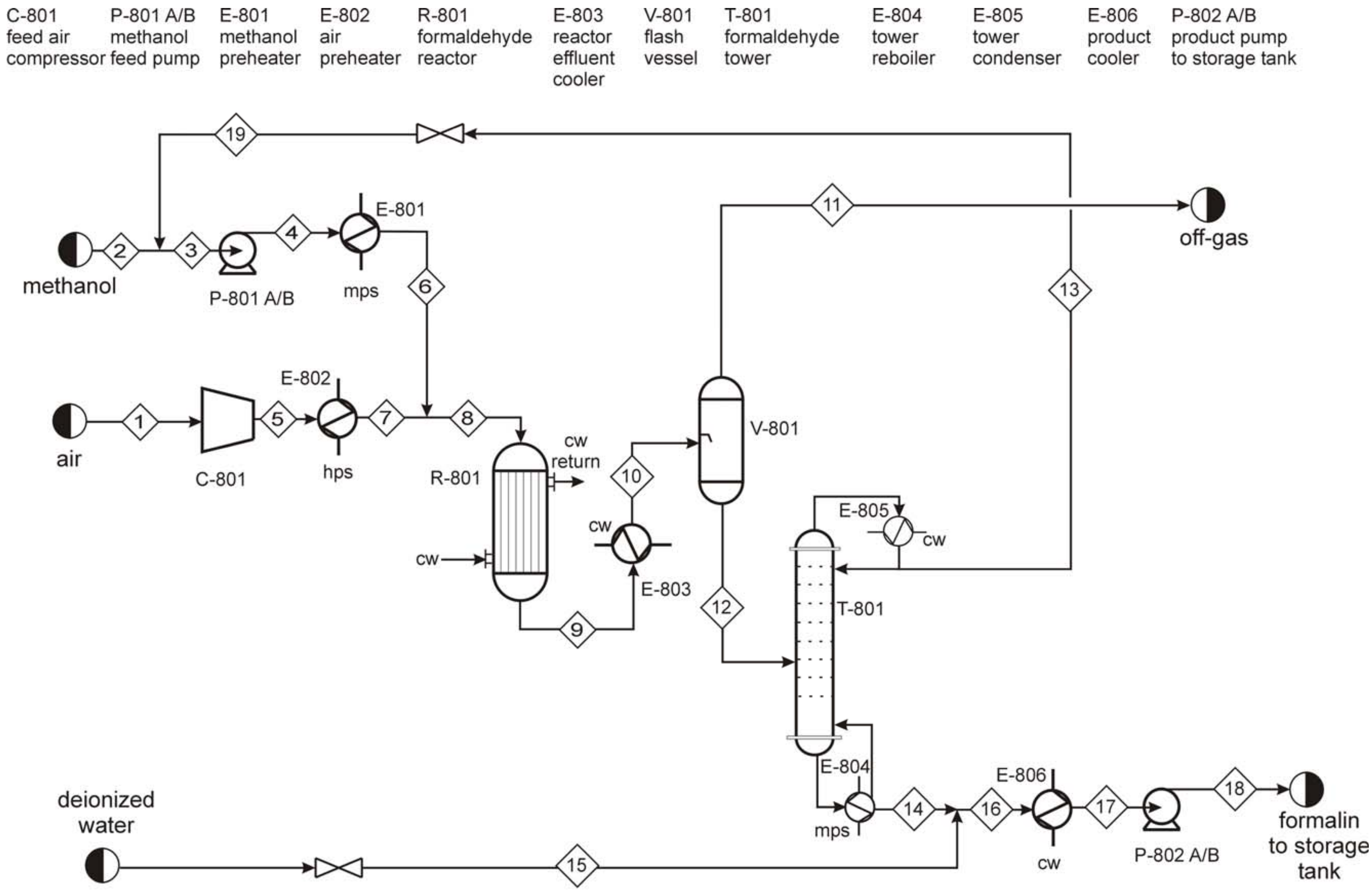

Figure 1: Unit 800 Formalin Production from Methanol

Stream 15: deionized water at any pressure below source pressure, at source temperature, mixed with Stream 14 so Streams 16-18 at 37 wt% formaldehyde Stream 15:

Stream 18: formalin – *i.e.*, 37 wt% formaldehyde in water – This is the stream that must be at a flowrate equivalent to 50,000 tonne/y.

Equipment

Air Compressor (C-301)

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 methanol feed to 150°C
E-802 heats (or cools – if so, change utility) air to 200°C, pressure drop of 25 kPa on the process side for each heat exchanger

Reactors (R-801)

outlet temperature is at 200°C, conversion in the reactor is 100% of the limiting reactant, selectivity for the reaction in Equation 1 relative to the reaction in Equation 2 is 9/1, 25 kPa pressure drop in heat exchanger portion, reactor is actually wire gauze with catalyst supported above a shell-and-tube heat exchanger, which must be sized, cost is for heat exchanger plus 25%

Heat Exchanger (E-803)

cools and partially condenses reactor effluent, pressure drop 25 kPa

Flash Vessel (V-801)

allows the vapor and liquid produced in E-803 to be separated, there is pressure drop at inlet that can be designed for any value

Distillation Column (T-801)

Of the methanol in Stream 12, a sufficient amount enters Stream 13 so that the 1 wt% methanol constraint on Stream 14 is not violated. 99.5% of the formaldehyde and water in Stream 12 enters Stream 14.

Heat Exchangers (E-804 and E-805)

reboiler and condenser, respectively, for T-801

Heat Exchanger (E-806)

cools product to between 35°C and 45°C, pressure drop specified in assignment section

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

Assignment

The assignment consists of the following "mini-designs."

1. Fluid Mechanics and Heat Transfer

<u>Design Problem</u>

You are to optimize the design of the product cooler (E-806) and the pump to the storage tank (P-802 A/B). The amount of heat to be removed from the process streams in E-806 must be determined from a ChemCAD simulation using base-case conditions given in this assignment. For exchanger E-806, a detailed design is required for the optimum case determined in this mini-design. For the optimization portion, you may estimate heat transfer areas (and subsequently costs) using the following overall heat transfer coefficients:

Liquid-liquid = 250 $W/m^2 {}^\circ C$
Boiling liquid-liquid = 600 $W/m^2 {}^\circ C$
Gas-liquid = 60 $W/m^2 {}^\circ C$
Condensing gas-liquid = 500 $W/m^2 {}^\circ C$

For the final design of the heat exchanger, you must calculate heat transfer coefficients in detail.

The objective function for the optimization should be the Equivalent Annual Operating Cost (EAOC, \$/y) for this section only, that is defined as:

$$EAOC = CAP\left(\frac{A}{P}, i, n\right) + AOC \tag{3}$$

where *CAP* (\$) is the capital investment for all the equipment (includes pumps, heat exchanger, piping, valves, etc.), *AOC* (\$/y) is the annual operating cost (includes utility costs for heat exchanger and pump), and

$$\left(\frac{A}{P}, i, n\right) = \frac{i(1+i)^n}{\left[(1+i)^n - 1\right]} \tag{4}$$

where i = 0.15 (15% rate of return) and n = 10 (ten-year plant life).

The cost for the pump, piping components, and heat exchangers are given in the Appendix. You are to determine the optimal pipe diameter, pipe schedule, pump power, heat exchanger area, heat exchanger tube size/pitch that minimizes the EAOC. The pressure drops for each exchanger may be estimated from:

15 kPa for the shell-side fluid if 1 inch 16 BWG tubes at 1.25 in square pitch
35 kPa for the tube-side fluid if 1 inch 16 BWG tubes

For other configurations, the pressure drops can be obtained by the scaling methods illustrated in CHE 310 class.

For E-806, which you will design in detail, you may use the above approximate pressure drops in the calculations to determine optimal pipe diameter. However, in the detailed heat exchanger design, you should evaluate the pressure drops using the appropriate relationships.

In order to evaluate the amount of piping required for the mini-design, you may assume that all the exchangers are located 3 m above grade (ground level), and that the pump is located at grade with the inlet 0.3 m above grade and the outlet 0.6 m above grade. The pump will be installed in parallel with a spare. Valves must be included to allow one pump to be in operation while the other pump is idle. The tank is 50 m from the pump outlet and has a height-to-diameter ratio of 3/1. The normal fill volume for a tank is 80% of the total volume. E-806 is located 5 m from the mixing point for Streams 14 and 15 (where this mini-design “starts”), with the mixing point 2 m above grade. Elbows should be added as needed. The pump must develop sufficient head to pump the product to 1 m above the fill level of the tank. Both the pumps and heat exchanger should have isolation valves (gate) that are normally wide open, but which can be closed to isolate each unit for maintenance. An elevation diagram (side view) and a plot plan (top view), drawn approximately to scale and with distances and elevations shown, should be included.

A discussion of the NPSH/cavitation issues associated with P-802 A/B should be included.

Design of Heat Exchanger, E-806

You should perform a detailed design of E-806. You should assume that utilities are available at the conditions specified in the Appendix of this problem statement. For this heat exchanger design, you should report the following information, as needed for the design:

- 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 and their arrangement (spacing, pitch, type)
- Diameter, 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 to the mini-design.

Performance Problem

The location of this plant is such that there are significant fluctuations in cooling water temperature over the course of the year. While the design is to be completed assuming an average inlet cooling water temperature of 30°C, it may fluctuate between 25°C and 35°C depending on the season. Stream 18 must be no higher than 45°C. An analysis of different operating conditions for E-806 for different cooling water temperatures should be included as part of this mini-design. Graphical presentation of this result is most desirable.

2. Thermodynamics – (ChE 320)

The overall economics of many processes depend strongly upon the ability to recycle valuable raw materials. This process is no different. We must be able to model accurately the thermodynamics of the water-methanol-formaldehyde mixture (plus remaining dissolved O_2, N_2, and H_2) that leaves the flash vessel. Inaccuracies in the thermodynamics of the vapor-liquid equilibrium of this mixture can lead to inaccurate calculations of the cost of the distillation tower and the overall cost of the plant. More drastically, poor choice of a thermodynamic package can cause poor design of the tower and result in being unable to purify the product and recycle the expensive raw materials.

You are to investigate the vapor-liquid equilibrium between water, methanol, and formaldehyde by examining the vapor-liquid equilibrium between different pairs of these components. Specifically, you are to investigate the vapor-liquid equilibrium between water and methanol, water and formaldehyde, and methanol and formaldehyde, in addition to the ternary mixture. First of all, check different thermodynamics packages in Chemcad to see if there are differences between the predictions of the packages. The term thermodynamics package means the choice of *K*-value and enthalpy calculation methods. At a minimum, you should investigate ideal, SRK, Peng-Robinson, UNIQAC, UNIFAC, UNIFAC/UNIQAC, plus the recommendation of the expert system if it differs from those listed above. Specifically, examine the *T-xy* diagrams of the pairs of components using the same thermodynamics packages at a variety of possible operating pressures (1-5 atm) for the separation section. The presence of azeotropes strongly affects the ability to do separations. What do you observe? Compare the predictions of the different packages. Explain and discuss reasons for any differences observed.

We have located one set of *K*-values for the ternary mixture from the *DECHEMA* data series [1], shown in Table 1; however, you are encouraged to find any additional data for the binary and ternary mixtures to assist you in determining the optimal thermodynamics package. The method for taking data such as in Table 1 and entering it into Chemcad will be demonstrated in class.

Table 1: *K*-values for the formaldehyde (FA), methanol (ME), and water (W) mixture at 101.325 kPa [1]

T (K)	K_{FA}	K_{ME}	K_W
340.25	0.265795	1.093852	0.490700
345.25	0.336040	1.435370	0.394286
347.95	0.373567	1.598036	0.452808
357.75	0.545828	2.559065	0.607135
370.75	0.693056	2.589226	1.105342
373.05	0.7302963	2.5946	1.1977758

3. Safety Analysis Report

When designing a chemical process, it is important to know the properties of the chemicals being consumed and produced in the process. The reactivity and toxicity of the reactants and products will not only affect the design but will also affect the procedures that might be implemented during an unscheduled event such as an emergency shutdown. The purpose of the safety analysis report is to make management aware of risks to personnel due to the flammability and toxicity of all chemicals consumed or produced in the process. As a minimum, the MSDS (material and safety data sheets) for all these chemicals should be provided in an appendix, and a brief discussion of the major concerns for each chemical should be given as a separate section of the report. This should include general concerns and concerns that are specific to the operating conditions in this process. In addition, a brief discussion of possible safety hazards for each piece of equipment in your process should be provided. Finally, a feature of your process design that addresses one of these concerns should be explained.

4. Chemcad/Process Improvements

A Chemcad simulation of one case of the process shown in Figure 1 should be provided. It is your choice whether this is a base case or a final case. You may suggest any process improvements that do not violate the laws of physics. An explanation of the rationale for such process improvements should be provided, including an economic analysis, if possible.

Other Information

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

Suggested Plan of Attack

The safety analysis can begin as soon as the project is distributed. A good place to find MSDS sheets is http://siri.org. The Chemcad simulation can be done next, as soon as we demonstrate Chemcad in class. The choice of thermodynamics package should be performed next, as this choice will affect flowrates through the process units. The fluid mechanics/heat transfer design is best done last; however, a spreadsheet template for the optimization and heat exchanger design can be developed earlier.

Deliverables

Written Reports

Each group must deliver a report written using a word processor. Three identical copies should be submitted, one for each instructor. The written project reports are due by 11:00 a.m. Thursday, November 29, 2007. Late projects will receive a minimum of a one letter grade deduction.

The report should be clear and concise. For the correct formatting information, refer to the document entitled *Written Design Reports*. The report must contain a labeled process flow diagram (PFD) and a stream table, each in the appropriate format. The PFDs from Chemcad are generally unsuitable unless you modify them significantly. Figure 1 should be used as a template for your PFD. When presenting results for different cases, graphs are superior to tables. For the optimal case, the report appendix should contain details of calculations that are easy to follow. There should be separate appendices for each “mini-project.” These may be hand written if done neatly. Alternatively, Excel spreadsheets may be included, but these must be well documented so that the reader can interpret the results. Calculations that cannot be easily followed and that are not explained will lose credit.

Since this project involves “mini-designs,” it is suggested that the report be organized as follows. There should be a general abstract and introduction. Then, there should be a results section followed by a discussion section for each “mini-design.” General conclusion and recommendation sections should follow. At a minimum, there should be one appendix for each of the “mini-designs” with detailed calculations that are easy to follow.

In order to evaluate each group member's writing skills, the results and discussion sections for each mini-design should be written by a different group member. The authorship of each of these mini-reports should be clearly specified in the report. Although the individual written portions of the reports must be authored by a single group member, it is the intent of the instructors that group members should help each other in writing different sections. To this end, we recommend that you seek input, such as proofreading and critiques, from other members of your group.

The reports will be evaluated as follows:

- course-specific technical content – 50%
- oral presentation – 20%
- written report – 20%
- technical quality of general sections (safety, simulation, etc.) – 10%

A historical account of what each 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. Each mini-report should be limited to 4-5 double space pages plus figures and tables.

Oral Reports

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. Each group member should speak only once. A 5-10 minute question-and-answer session will follow, and all members must participate. Refer to the document entitled *Oral Reports* for instructions. The oral presentations will be Thursday November 29, 2007, from 11:00 a.m. to 2:00 pm. 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 310, ChE 311, and ChE 320***.

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. You should be aware that these revisions/clarifications may be forthcoming.

References

1. Gmehling, J., U. Onken, and W. Arlt, *Vapor-Liquid Equilibrium Data Collection*, Chemistry Data Series (Aqueous-Organic Systems – Supplement 1), Vol. 1, Part 1a, DECHEMA, 1981, pp. 474-475.

Appendix
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, you should 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, no limit)
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)

Storage Tanks

$$\log_{10}(\text{purchased cost}) = 4.85 - 0.397\log_{10} V + 0.145[\log_{10} V]^2$$

V = volume of tank (m^3, 90, 30000)

Additional Cost Information

Piping straight pipe $/m = 5.0 (nominal pipe diameter, in)$(1+(\text{sch } \#)/20)^{0.25}$
sch = schedule number for pipe
use the same sch number for fittings and valves

fittings (except valves) $/fitting = 50.0 (nominal pipe diameter, in)$(1+(\text{sch } \#)/20)^{0.25}$

Valves for gate (isolation) valves \$100 $(\text{nominal pipe diameter, in})^{0.8} (1+(\text{sch } \#)/20)^{0.25}$
for control valve use \$1000 $(\text{nominal pipe diameter, in})^{0.8}(1+(\text{sch } \#)/20)^{0.25}$

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

Equipment Cost Factors

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

Pressure	< 10 atm, PF = 0.0	does not apply to turbines, compressors, vessels,
(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	

Carbon Steel MF = 0.0
Stainless Steel MF = 4.0