1/23/98

ChE 183
Major #2

Design of a New Facility to Produce Polymer-Grade Acrylic Acid

1. ASSIGNMENT

The market for polymer grade acrylic acid continues to grow, and we are looking for ways to expand our production capacity. In your previous assignment, you were asked to look at ways of increasing capacity at our existing facility. Our company is also considering building a new, grass roots facility at a location in the U.S. which will better serve our growing customer base. The purpose of this assignment is to perform a preliminary process design on a new grass roots facility to produce 50,000 tonnes/yr of polymer grade acrylic acid (99.9 mol%).

2. BACKGROUND INFORMATION ON CURRENT ACRYLIC ACID PROCESS

From your previous assignment you will be familiar with some aspects of our current process for producing acrylic acid. A diagram of the current process is shown in Figure 1. A brief description of the process follows.

The process shown in Figure 1 is designed to produce 50,000 metric tons per year of 99.9% by mole acrylic acid product. The number of operating hours is taken to be 8000/yr. Air (Stream 1), low pressure steam (Stream 2), and propylene (Stream 3) are fed to the fluidized bed reactor where the following reactions take place.

$$C_3H_6 + \frac{3}{2}O_2 \rightarrow \underset{\text{Acrylic Acid}}{C_3H_4O_2} + H_2O \qquad \text{Reaction 1}$$

$$C_3H_6 + \frac{5}{2}O_2 \rightarrow \underset{\text{Acetic Acid}}{C_2H_4O_2} + CO_2 + H_2O \qquad \text{Reaction 2}$$

$$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O \qquad \text{Reaction 3}$$

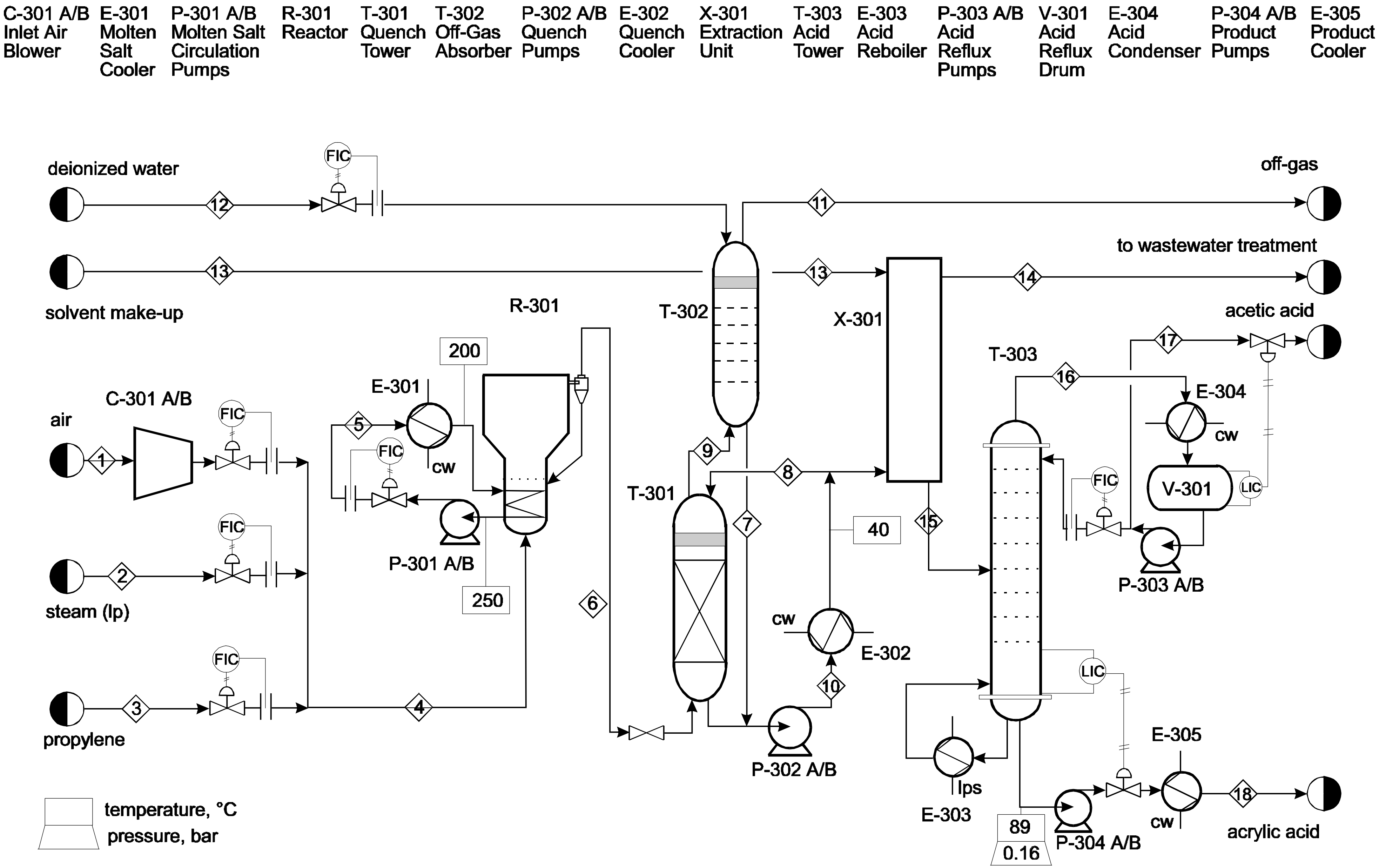

Figure 1: PFD for Unit 300 - Acrylic Acid from Propylene

These reactions are kinetically controlled at the conditions used in the process, i.e., equilibrium lies far to the right. The reactor configuration used for this process is a fluidized bed, and it is assumed that the bed of catalyst behaves as a well-mixed tank, i.e., it is isothermal at the temperature of the reaction. The operating temperature for this catalyst must lie in the range of 290 - 330°C in order to avoid damage to the catalyst and to maintain acceptable reaction rates. A molten salt loop is used to remove the exothermic heat of reaction from the reactor.

It is imperative to cool the reactor effluent, Stream 6, quickly in order to avoid further homogeneous oxidation reactions which may occur in the downstream equipment. These oxidation (combustion) reactions decrease product yield and are potentially very dangerous since the composition of the reactor effluent may still be within the explosive limits. This cooling is achieved by rapidly quenching the reactor effluent with a cool recycle, Stream 8, of dilute aqueous acrylic acid in T-301. Additional recovery of acrylic acid and acetic acid (a by-product) is achieved in the absorber, T-302. The stream leaving the absorption section is a dilute aqueous acid, Stream 8A. In order to reduce the high costs of distilling all this water, the organic acids are extracted from this aqueous solution using a solvent. Thus, Stream 8A is sent to a liquid-liquid extractor (included as part of X-301) to remove preferentially the acid fraction from the water prior to purification. There are many possible solvents that can be used as the organic phase in this separation; high solubility for acrylic acid and low solubility for water are desirable. Some examples include ethyl acrylate, ethyl acetate, xylene, diisobutyl ketone, methyl isobutyl ketone, and diisopropyl ether (DIPE). DIPE is currently used in this process. The organic phase from the liquid-liquid extractor is sent to a solvent recovery column, included in X-301, where the diisopropyl ether (and some water) is recovered overhead and returned to the extractor. The bottom stream from this column, Stream 15, contains virtually all the acrylic acid and acetic acid in Stream 8A. This is sent to the acid purification column, T-303, where 95% by mole acetic acid by-product is produced overhead, Stream 17, and 99.9 % by mole acrylic acid, Stream 18, is produced as a bottom product and cooled prior to being sent to storage.

The aqueous phase from the extractor is sent to a wastewater column (also included in X-301), where a small amount of DIPE is recovered overhead and returned to the extractor. The bottom product, Stream 14, containing water and trace quantities of solvent and acid, is sent to wastewater treatment.

2.1 REACTION KINETICS AND REACTOR CONFIGURATION

The kinetics for the reactions presented above are described by the following rate expression:

$$\text{where} \qquad -r_i = k_{o,i} \exp\left[\frac{-E_i}{RT}\right] p_{propylene}\, p_{oxygen}$$

Partial pressures are in kPa and the activation energies and pre-exponential terms for Reactions 1-3 are given below:

i	E_i kcal/kmol	$k_{o,i}$ kmol/m^{3}reactor h/(kPa)^2
1	15,000	1.59×10^5
2	20,000	8.83×10^5
3	25,000	1.81×10^8

The gas flow is assumed to be plug flow through the bed, with 10% of the gas bypassing the catalyst. This latter assumption is made in order to simulate the gas channeling that occurs in real fluid bed reactors.

2.2 SAFETY CONSIDERATIONS

As with any reaction involving the partial oxidation of a fuel-like feed material (propylene), considerable attention must be paid to the composition of hydrocarbons and oxygen in the feed stream. Operation outside the explosive limits is usually recommended for this reaction. The conditions used in this process actually lie between the lower and upper explosion limits. However, the use of an essentially isothermal fluidized bed significantly reduces the possibility of a temperature runaway leading to an explosion. The second safety concern is that associated with the highly exothermic polymerization of acrylic acid which occurs in two ways. First, if this material is stored without appropriate additives, free radical initiation of the polymerization can occur. Second, acrylic acid dimerizes when in high concentrations at temperatures greater than 90°C, thus much of the separation sequence must be operated under high vacuum in order to keep the bottom temperatures in the columns below this critical value.

2.3 VAPOR-LIQUID AND VAPOR-LIQUID-LIQUID EQUILIBRIUM

The results of the process simulation given in Figure 1 were obtained using a UNIQUAC/UNIFAC thermodynamics package on CHEMCAD™ and should give reasonable results for preliminary process design. When simulating a distillation column for the removal of acrylic acid from a relatively dilute aqueous solution, you should use the NRTL thermodynamics model for the distillation column only.

3. DESIGN OF NEW GRASS ROOTS FACILTY

Over the many years of operation, several improvements and process changes have been made and many others have been suggested but never implemented. The design of a new facility gives us the opportunity to investigate many of these possible improvements.

3.1 BACKGROUND MATERIAL ON THE NEW PROCESS

Solvent Extraction Unit, X-301

One of the recurring problems with the current process has been the excessive loss of solvent (DIPE). This has caused increases in operating costs that have significantly affected the profitability of our plant. The need for the DIPE is twofold. First, if a single column were used to separate the acrylic acid from the water it would be very large (approx. 30 ft in diameter and over a hundred feet tall.) Second, the water and acetic acid form an azeotrope (approx. 90% water – 10% acetic acid), which makes the subsequent purification of acetic acid impossible without the addition of a third component either as a extractive solvent or as an azeotrope breaker. It has been suggested that the solvent extraction system could be eliminated if the amount of steam fed into the reactor were reduced. The purpose of the steam is twofold. First, the steam acts to dilute the feed and adds thermal ballast, i.e., reduces the likelihood of a temperature excursion in the reactor, which coupled with the isothermal operation of the reactor virtually eliminates the chance of a runaway reaction. Second, coking reactions that can deactivate the catalyst are suppressed when steam is present. We have found that with new catalysts the amount of steam that needs to be added to suppress the coking reactions is significantly reduced. In fact, the new catalyst that we are considering for the new plant requires only 1 kg steam/kg of propylene in the feed to the reactor.

Catalytic Reactor

In general, the fluidized bed reactor has operated satisfactorily throughout the life of the existing process. The use of a packed bed reactor (shell and tube design with the catalyst in the tubes) may offer certain advantages over the fluidized bed. In the design of the packed bed reactor, the composition of the feed should lie outside the explosive (flammability) limits given below:

	Propylene	Acrylic Acid	Acetic Acid
LFL	11.1 %	2.8 %	4.0 %
UFL	2.0 %	31.0 %	19.9 %

For mixtures of gases, the following equations should be used to predict the mixture flammability limits:

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}} \qquad UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}}$$

where

LFL_i and UFL_i are the lower and upper flammability limits for component *i* in volume (mole) % of component *i* in fuel and air,
y_i is the mole fraction of component *i* on a combustible basis, and

n is the number of combustible species.

Indeed, nowhere in the packed bed reactor should the composition lie within the explosive limits. Operation outside these limits can be accomplished by diluting the feed with an inert gas such as nitrogen. The above calculations for LFL and UFL are based strictly on mixtures of fuel and air only. When an inert material is used the above relationships must be changed. The easiest way to do this is to compute the minimum oxygen concentration (*moc*) which can be calculated as follows:

$$moc = LFL\left(\frac{\text{moles of oxygen for complete combustion}}{\text{moles of fuel (hydrocarbons)}}\right)$$

If the inlet concentration of oxygen to the reactor is lower than the *moc*, then the mixture is not explosive. A sample calculation for a gas mixture is shown in the appendix.

In addition, the temperature of catalyst in the reactor should never exceed 330ºC to avoid catalyst damage by sintering. If a fluidized bed reactor is used, then the feed may lie within the above limits but the catalyst must still never exceed 330ºC.

Reactor Effluent Quench

Currently, the reactor effluent, Stream 6, is quenched by contacting with a large circulating stream of weak aqueous acrylic acid solution. The heat load for cooling the reactor effluent is provided by heat exchanger E-302, and this heat is dissipated using cooling water. There are significant gains to be made if this heat can be recovered. Since it is important to quench the reaction immediately after Stream 6 leaves the reactor, it has been suggested that the stream be cooled to below 200ºC (at which point combustion reactions will not occur) by the direct injection of an inert material such as steam or nitrogen. The hot gas can now be cooled using a conventional heat exchanger and thus this energy can be used for more useful purposes.

3.2 BASE-CASE DESIGN

You should first determine the economics for a base-case design. This base-case design should use the process flow diagram provided in Figure 1. You should estimate the size of all the equipment using the guidelines in Chapter 9 of Analysis, Synthesis, and Design of Chemical Processes by Turton, Bailie, Whiting, and Shaeiwitz to make preliminary cost estimates of the equipment. Then use CAPCOST to estimate the fixed capital investment, *FCI*. You should also estimate the cost of manufacturing, COM_d, (see Chapter 3) and finally estimate the *NPV* and *DCFROR* of the plant using the following economic information.

Taxation rate = 40%
After tax internal hurdle rate = 8% p.a.
Construction time = 2 years (Start up after the end of the second year)

FCI spread evenly over the two years of construction
Plant life = 10 years after start up
Depreciation schedule = 5 year MACRS

3.3 PROCESS IMPROVEMENTS

Using the information given in this assignment and any other ideas that you have, you should optimize the process with respect to the Net Present Value. Necessary information about different process units is contained in the Appendix at the end of this assignment.

4. WRITTEN REPORT

The written report is due on Monday, February 23rd at 9:00 a.m. This should be a full written report not to exceed 15 double-spaced, typed pages, which summarizes your recommendations and rationale. Figures and tables should be included (do not count against page limit). The written report should also include a brief executive summary not to exceed 3 double-spaced pages. An appendix should be attached that includes items such as sample calculations. These calculations should be indexed at the front of the appendix and be legible and easy to follow. A signed copy of the confidentiality statement (included at the end of this assignment) should be the very last page of the report. Please use a three-ring binder to hold the report. This binder will be returned with the corrected report.

The information listed below must be included in the main part of the written report.

a. A breakdown of the economics of the base case, including a fixed capital investment (*FCI*) summary, a summary of the cost of manufacturing (*COM*), the net present value (*NPV*) and, the discounted cash flow rate of return (*DCFROR*) for the project.

b. A breakdown of the economics of the optimum case, including a fixed capital investment (*FCI*) summary, a summary of the cost of manufacturing (*COM*), the net present value (*NPV*) and, the discounted cash flow rate of return (*DCFROR*) for the project.

c. For the optimum case you must provide a PFD of the process, a flow summary table including mass and molar flowrates, temperatures, pressures, vapor fractions, and component mole flows for all the major process streams.

d. For the optimum case you must provide a list of all the major equipment costs and specifications.

The written report is a very important part of the assignment. Poorly written and/or organized reports will require re-writing. Be sure to follow the format outlined in the guide for written reports and also refer to Chapter 22 of your textbook. Failure to follow the prescribed format will be grounds for a re-write.

5. ORAL REPORT

You will be expected to present and defend your results to ST's management representatives some time between February 23 and February 27, 1998. Your presentation should not exceed 20 minutes and will be followed by a 30 minute question and answer period. Make certain that you take time to prepare adequately for this meeting since it is a very important part of your assignment. Some guidelines on how to prepare visuals for an oral presentation are given in Chapter 22 of your textbook. You should also prepare a hard copy of your transparencies to be handed in at the beginning of your oral report.

6. LATE REPORTS

Late reports are unacceptable. The following severe penalties will apply:

- Late reports on the due date before noon: one letter grade.
- Late reports after noon on the due date: two letter grades.
- Late report one day late: three letter grades.
- More than one day late: failing grade.

Appendix

Table A.1: Flow Table for Acrylic Acid Process in Figure 1

Stream No.	1	2	3	4	5	6	7	8	8A	9
Temperature (°C)	25	159	25	191	250	310	63	40	40	40
Pressure (bar)	1.0	6.0	11.5	4.3	3.0	3.5	2.0	2.4	2.4	1.1
Vapor Fraction	1.0	1.0	1.0	1.0	0.0	1.0	0.0	0.0	0.0	1.0
Mass Flow (tonne/h)	39.05	17.88	5.34	62.27	1070.0	62.27	3.08	1895	27.47	37.89
Mole Flow (kmol/h)	1362.9	992.3	127.0	2482.2	-	2444.0	148.5	85200	1249.62	1342.9
Component Mole Flow (kmol/h)					Molten Salt					
Propylene	-	-	127.0	127.0	-	14.7	-	-		14.7
Nitrogen	1056.7	-	-	1056.7	-	1056.7	-	-		1056.7
Oxygen	280.9	-	-	280.9	-	51.9	-	-		51.9
Carbon Dioxide	-	-	-	-	-	60.5	-	-		60.5
Water	25.3	992.3	-	1017.6	-	1165.9	140.9	78870	1156.7	150.1
Acetic Acid	-	-	-	-	-	6.54	0.65	415	6.11	1.11
Acrylic Acid	-	-	-	-	-	87.79	6.99	5915	86.81	7.97

Table A.1: Flow Table for Acrylic Acid Process in Figure 1 (cont'd)

Stream No.	10	11	12	14	15	16	17	18
Temperature (°C)	50	48	25	102	90	47	47	40
Pressure (bar)	2.4	1.0	5.0	1.1	0.19	0.07	1.1	2.5
Vapor Fraction	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Flow (tonne/h)	1922.5	37.35	2.54	20.84	6.63	11.59	0.37	6.26
Mole Flow (kmol/h)	86449.6	1335.4	141.0	1156.43	93.19	199.66	6.34	86.85
Component Mole Flow (kmol/h)								
Propylene		14.7	-	-	-	-	-	-
Nitrogen	-	1056.7	-		-	-	-	-
Oxygen	-	51.9	-	-	-	-	-	-
Carbon Dioxide	-	60.5	-	-	-	-	-	-
Water	80026.7	150.2	141.0	1156.4	0.30	9.45	0.30	-
Acetic Acid	421.1	0.46	-	0.03	6.08	189.9	6.03	0.05
Acrylic Acid	6001.8	0.98	-	-	86.81	0.31	0.01	86.80

Table A.1: Flow Table for Acrylic Acid Process in Figure 1 (cont'd)

Utility	cw	cw	lps	cw	cw
Equipment	E-301	E-302	E-303	E-304	E-305
Temperature In (°C)	32	32	160	32	32
Flow (tonne/h)	1,995	1,923	2.19	235.4	16.70

Table A.2: Cost Information for Raw Materials, Products, and Utilities

Raw Materials

Propylene (polymer grade)	See *Chemical Marketing Reporter*

Products

Acrylic acid (99.9 mol%)	See *Chemical Marketing Reporter*
Acetic acid (95 mol%)	See *Chemical Marketing Reporter*

Utility Costs

See Table 3.4	Analysis, Synthesis, and Design of Chemical Processes by Turton, Bailie, Whiting, and Shaeiwitz
Nitrogen for inerting etc.	$0.20/ kg

Note that cooling water should be charged at a cost of $0.16 per GJ regardless of the return temperature. The maximum return temperature for cooling water is 45ºC. Note also that the credit for condensate return is approximately the same as boiler feed water.

Table A.3: Equipment Sizing and Costing

For the accuracy required in this project, the design heuristics given in Tables 9.4 through 9.18 should be used to make preliminary size estimates of process equipment. With these estimates of equipment size, the appropriate cost estimate in CAPCOST should be used. There are a few exceptions to this rule that are given below.

REACTOR COST

Fluidized Bed Reactor

For a fluidized bed reactor (including all cyclones and solids handling equipment) use an installed cost of $\$2\times10^5\ [\text{Area}(\text{m}^2)]^{1/2}$, where the area refers to the total heat transfer area in the reactor. For the heat transfer between the tubes (containing molten salt or Dowtherm™ A) and the fluidized bed, you may assume a heat transfer coefficient of 200 $\text{W/m}^{2\circ}\text{C}$. You should also assume that 10% of the gas fed to the reactor bypasses the catalyst. This accounts for the bypassing of gas that occurs in real fluidized bed reactors. Thus, the absolute maximum conversion that can occur in the fluidized bed is 90%.

Packed Bed Reactor

For a packed bed reactor, with the catalyst in the tubes, use an installed cost of 3 times the equivalent cost of a shell and tube heat exchanger (use floating head from CAPCOST) based on the outside area of the tubes. You should assume that the catalyst for the packed bed operation has the following properties:

Catalyst particle diameter, d_p = 3 mm
Catalyst particle density, ρ_{cat} = 1600 kg/m^3
Void fraction, ε = 0.50
Heat transfer coefficient from packed bed to tube wall, h = 60 $\text{W/m}^{2\circ}\text{C}$
Use standard tube sheet layouts as for heat exchangers. If the tube diameter is greater than 1.5" assume that the cross-sectional area of the tubes is 33% of the cross sectional area of the shell.
Shell diameter is a function of heat transfer characteristics and frictional losses
It is suggested that either a molten salt or Dowtherm™ A heat transfer medium be used to cool the reactor.

Since the reaction is very exothermic, you may wish to add inert packing to the catalyst in order to increase the effective heat transfer area. Assume that the added packing has the same physical characteristics as the catalyst.

SOLVENT EXTRACTION, SEPARATION AND PURIFICATION (EQUIPMENT X-301)

COST

The design of the solvent extraction and associated equipment in X-301 is very complicated and beyond the scope of the current design. If you choose to use this option then a separate contractor (ExtractoCorp) will carry out the design. This contractor has supplied us an estimate of the installed and operating cost of the extraction unit that can be used for preliminary design purposes. These costs are as follows:

Installed cost of X-301 = $\$16\times10^{6}$[actual water flowrate in Stream 8A {kmol/h}/1156.7 {kmol/h}]$^{0.3}$

Operating cost of X-301 = $\$5.05\times10^{6}$[actual water flowrate in Stream 8A {kmol/h}/1156.7 {kmol/h}]$^{0.7}$ per year

Clearly, there is a great incentive to reduce the amount of water sent to the extraction unit.

DISTILLATION COLUMN TO SEPARATE ACRYLIC ACID FROM WATER AND ACETIC ACID

You may also wish to compare the price of the extraction unit with that of a distillation column to separate the acrylic acid from the water and acetic acid. The following data should be used when the design of this distillation column is considered.

Use the NRTL (non-random two liquid) thermodynamic package for this distillation column. Note that the BIPs (binary interaction parameters) for water, acrylic acid and acetic acid are supplied by CHEMCAD. Do not use this package for the whole process (use UNIQUAC/UNIFAC), but just for this column. Note that acetic acid and water form an azeotrope. This means that you will be able to separate the acrylic acid from the water and acetic acid by distillation, but you will not be able to separate the resulting mixture of acetic acid and water by further distillation. For this scenario, it is recommended that the acetic acid be neutralized, at a cost of $0.10 per kg of acetic acid, and the resulting water and neutralized acid stream be sent to wastewater for tertiary treatment (see Table 3.4 in the textbook).

Table A.4: Example Calculation of Minimum Oxygen Concentration (*moc*)

Consider an equimolar mixture of propane and butane.

1. What is the *moc* for this mixture?
2. How much nitrogen would need to be added to a stoichiometric mixture of fuel and air to obtain a non-explosive mixture?

Answer

1. Using subscript 1 for propane and 2 for butane we have: LFL_1=2.1 and LFL_2=1.6
   For complete combustion, we have:

$$C_3H_8 + 5O_2 \rightarrow 4H_2O + 3CO_2$$

propane

$$C_4H_{10} + \frac{13}{2}O_2 \rightarrow 5H_2O + 4CO_2$$

butane

For an equimolar mixture, the ratio of oxygen to fuel for complete combustion is 5.75.

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}} = \frac{1}{\frac{0.5}{2.1} + \frac{0.5}{1.6}} = 1.8162$$

$$moc = 1.8162(5.75) = 10.44\%$$

Basis 1 mole of fuel.
Stoichiometric oxygen = 5.75
Nitrogen = (79)(5.75)/(21) = 21.63
Total moles = 1 + 5.75 + 21.63 = 28.38
% oxygen = (5.75)(100)/(28.38) = 20.26%

The mixture will not be explosive so long as the oxygen concentration is less then 10.44%.

Let *N* be the number of moles of nitrogen added per mole of fuel

$\therefore$(5.75)(100)/(28.38 + *N*) = 10.44% $\Rightarrow \boxed{\mathbf{N = }\text{ 26.70 moles}}$

Thus, by adding 26.7 moles of nitrogen per mole of fuel in a stoichiometric air fuel mixture, the resulting stream will lie just at the *moc* for the mixture (i.e., it is not an explosive mixture).