DESIGN OF AN ACRYLIC ACID PRODUCTION PROCESS

(Courtesy of the Department of Chemical Engineering at West Virginia University)

Introduction

Acrylic acid (AA) is used as a precursor for a wide variety of chemicals in the polymers and textile industries. There are several chemical pathways to produce AA, but the most common one is via the partial oxidation of propylene. The usual mechanism for producing AA utilizes a two-step process in which propylene is first oxidized to acrolein and then further oxidized to AA. Each reaction step usually takes place over a separate catalyst and at different operating conditions.

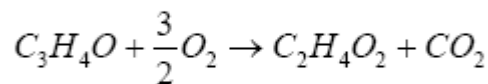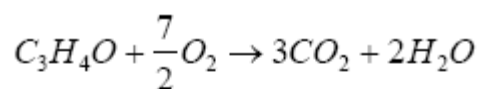The reaction stoichiometry is given below:

$$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O$$
$$\text{Acrolein}$$
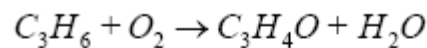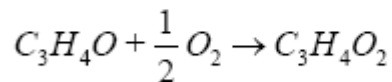
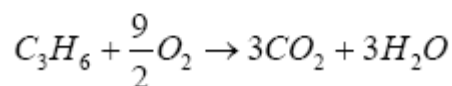$$C_3H_4O + \frac{1}{2}O_2 \rightarrow C_3H_4O_2$$
$$\text{Acrylic Acid}$$

Several side reactions may occur, most resulting in the oxidation of reactants and products. Some typical side reactions are given below:

$$C_3H_4O + \frac{7}{2}O_2 \rightarrow 3CO_2 + 2H_2O$$

$$C_3H_4O + \frac{3}{2}O_2 \rightarrow C_2H_4O_2 + CO_2$$
$$\text{Acetic Acid}$$

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

Therefore, a typical process set-up consists of a two-reactor system with each reactor containing a separate catalyst and operating at conditions so as to maximize the production of AA. The first reactor typically operates at a higher temperature than the second unit.

Acrylic acid is produced by the catalytic partial oxidation of propylene in the presence of steam at elevated temperature and ambient pressure. We wish to begin the design of a process to produce 75,000 metric tons of acrylic acid per year. Your job is to analyze the simplified acrylic acid production process, to suggest profitable operating conditions, and to write a final report summarizing your findings. Note that optimization is NOT required in this design project.

Process Description

Figure 1 is a preliminary process flow diagram (PFD) for the acrylic acid production process. The raw materials are propylene and oxygen. Steam in added to provide thermal ballast. The propylene feed may be assumed pure vapor at 446 kPa. The air feed, which may be considered to contain only oxygen, nitrogen, and water is also at 446 kPa. The steam is saturated at 446 kPa. The feeds are mixed and sent to the reactor (R-301) in which acrylic acid is formed. The reactions which occur are shown below. The reactor effluent is sent to a separation unit (S-301), in which all light gases (oxygen, nitrogen, carbon dioxide, and propylene) are separated as vapor in Stream 7. Stream 7 is split into Streams 8 and 9. Stream 8 is a recycle stream containing propylene, oxygen, nitrogen, and carbon dioxide. A pump is required in this stream which is not shown. Stream 9 is incinerated. Stream 10, containing water and acrylic acid is sent to a distillation column (T-301) to produce purified acrylic acid. The desired acrylic acid production rate is 75,000 metric tons/yr.

Process Details

Feed Streams

Stream 1: propylene, pure vapor, 25°C and 446 kPa

Stream 2: air at 218°C and 446 kPa
(it has been compressed from atmospheric pressure causing the temperature increase - the annual cost for this compression is $1.22M per compressor)
water present in amount to saturate air at 25°C and 1 atm

Stream 3: low-pressure steam

Stream 4: feed mixture should have the following components:
air (containing oxygen, nitrogen, and water vapor) 55 mole %
steam (added as steam) 40 mole%
propylene 5 mole %
you must determine the stream temperature

Effluent Streams

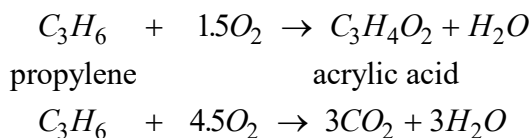Stream 9: waste gas stream to incinerator, credit may be taken for LHV of fuel

Stream 11: waste water stream, treatment cost $50.00/$10^6$ kg
must contain less than 0.03 wt % acrylic acid

Stream 12: acrylic acid product, 99.9 wt% purity.

Equipment

Reactor (R-301):

The following reactions occur:

$$C_3H_6 \ + \ 1.5O_2 \ \rightarrow \ C_3H_4O_2 + H_2O$$
$$\text{propylene} \qquad\qquad \text{acrylic acid}$$
$$C_3H_6 \ + \ 4.5O_2 \ \rightarrow \ 3CO_2 + 3H_2O$$

Selectivities and conversions at various temperatures are given in Table 1. These values are for the reactor operating pressure of 446 kPa and are independent of the amount of oxygen present, as long as propylene is the limiting reactant. Part of your assignment is to determine the best exit reactor temperature.

Table 1		
Selectivity and Conversion at Different Temperatures		
Temperature (°C)	**Selectivity (moles acrylic/ moles CO_2)**	**Conversion of Propylene**
200	10.0	0.04
250	10.0	0.05
300	9.77	0.11
350	8.91	0.22
400	7.24	0.36
450	4.90	0.50
500	2.45	0.63
550	0.891	0.76
600	0.655	0.83
650	0.610	0.86

Separator (S-301):

In this separator, all components other than acrylic acid and water exit in Stream 7. The acrylic acid and water vapor are partitioned between Streams 7 and 10 according to the property model you chose. Part of your task is to determine the optimum temperature and pressure for this separator. The separator pressure must be below 446 kPa.

Distillation Column (T-301):

In this distillation column, the water and acrylic acid in Stream 10 are separated. The column operates at vacuum conditions. Specifications are as follows. The column pressure is determined by the boiling point of acrylic acid at its maximum allowable temperature, 90°C. This is also the temperature of Stream 12. The temperature of

Stream 11 is the boiling point of water at the pressure of the column. Energy requirements are described with the heat exchange equipment below.

Heat Exchanger (E-301):

In this heat exchanger, you may assume that one-half of the flow of Stream 12, containing pure acrylic acid, is vaporized from saturated liquid to saturated vapor at 90°C. The cost is for the amount of low-pressure steam needed to supply the necessary heat.

Heat Exchanger (E-302):

In this heat exchanger, water is condensed from saturated vapor to saturated liquid at a rate three times the flow of Stream 11. The cost is for the amount of refrigerated water needed to remove the necessary energy.

Design of Heat Exchangers, E-301 and E-302

A detailed design of E-301 and E-302 is required for base-case conditions. It should be assumed that cooling water is available at the conditions specified in the Appendix of this problem statement. For this heat exchanger design, the following information should be provided:

- 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, if any, and their arrangement (spacing, pitch, type)
- Diameter, tube-wall thickness, shell-wall 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 two exchangers should be included along with a set of comprehensive calculations in an appendix for the design of the heat exchangers. You should use ASPEN Exchanger Design & Rating (EDR) in the ASPEN Plus simulator to carry out the detailed design.

Economic Analysis

When evaluating alternative cases, you should carry out an economic evaluation and profitability analysis, in which a number of economic criteria such as payback period, internal rate of return, and the following objective function should be used. It is the equivalent annual operating cost (EAOC), and is defined as

EAOC = -(product value - feed cost - other operating costs - 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 costs for acrylic acid (the product) and propylene (the feed) should be obtained from the *Chemical Marketing Reporter* or from the Internet

Other operating costs are utilities, such as steam, cooling water, natural gas, and electricity.

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:

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

where *FCI* is the installed cost of all equipment; *i* is the interest rate, *i* = 0.15; and *n* is the plant life for accounting purposes, *n* = 10.

For detailed sizing, costing, and economic evaluation including profitability analysis, you may use the Aspen Process Economic Analyzer (formerly Aspen Icarus Process Evaluator) in Aspen Plus Version 7. However, it is also a good idea to independently verify the final numbers based on other sources.

Other Information

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

You should assume that two streams that mix must be at identical pressures. Pressure reduction may be accomplished by adding a valve. These valves are not shown on the attached flowsheet, and it may be assumed that additional valves can be added as needed. In general, flow occurs from higher pressure to lower pressure. Pumps increase the pressure of liquid streams, and compressors increase the pressure of gas streams. The two locations where pumps are needed are Streams 11 and 12, to remove material from the tower operating at vacuum conditions. A small compressor or blower is also needed in Stream 8. For purposes of this design only, you may assume that Stream 8 is at whatever pressure is needed to allow it to mix with Stream 4, and that there is no cost associated with this pressure increase.

For preliminary calculations only, assume the following relationship for a compression or expansion operation:

$$\left(\frac{T_{out}}{T_{in}}\right) = \left(\frac{P_{out}}{P_{in}}\right)^{0.286}$$
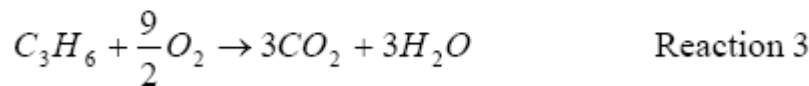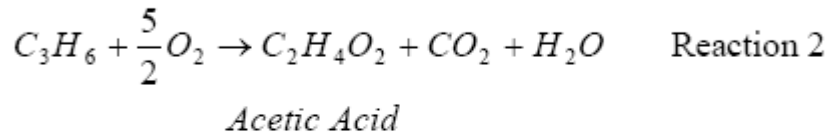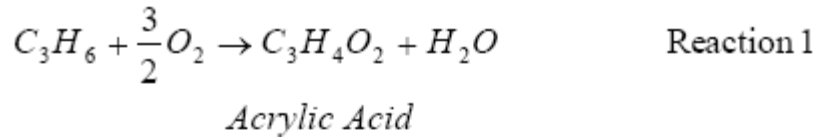
Additional Information

A base case process is shown in Figure 2. You are to reconcile Figure 2 with Figure 1 and decide what pieces are to be included in your final design. This process produces 75,000 metric tons per year of 99.9 mole % of acrylic acid (AA) product. The number of operating hours should be taken as 8000/yr. The reactor in the process shown in Figure 2 uses a proprietary catalyst that eliminates the production of the intermediate, acrolein. Therefore, this process requires only a single reactor. After reaction, it is essential to cool the products (reactor effluent) quickly to avoid further homogeneous oxidation reactions. This is achieved by rapidly quenching the reactor effluent, Stream 6, by injecting deionized water into it. The homogeneous combustion reactions will not take place so long as the reactor effluent is cooled to below 100ºC immediately after the reactor. Additional recovery of AA and acetic acid (a by-product) from the gas, Stream 7, leaving the phase separator (V-301) is achieved in the absorber, T-301.

The liquid stream, Stream 9, leaving the absorption section is a dilute aqueous acid. It is combined with the liquid from the phase separator, V-301, to form the feed to the extractor section, Stream 13. This stream is sent to the liquid-liquid extraction section, X-301, to remove preferentially the acid fraction from the water prior to purification. There are several columns, exchangers, pumps, vessels, and other miscellaneous equipment in X-301. **Do not to attempt** to design this section of the plant. This part of the design will be contracted out to another company. The organic phase leaving X-301, Stream 15, contains 99.5 % of the AA and acetic acid in Stream 13 and essentially no water or other components. This is sent to the acid purification column, T-302, where 95% by mole acetic acid byproduct is produced overhead and 99.9 % by mole AA is produced as a bottom product and cooled prior to being sent to storage.

The aqueous phase from the extractor, Stream 14, is sent to a wastewater treatment plant, where it is decontaminated prior to being returned to the environment.

Reaction Kinetics and Reactor Configuration

The reactions taking place are all irreversible. The reaction kinetics for the catalyst used in this process are given below:

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

Acrylic Acid

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

Acetic Acid

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

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

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 kinetics presented above are valid in the temperature range, 250 – 330ºC. Above 330ºC the catalyst starts to coke-up (carbon deposits on the surface of the catalysts causing it to deactivate), and below 250ºC the rate of reaction drops off rapidly. Due to these effects, the catalysts should never be operated outside of these temperature limits. The reactor configuration used for this process should be a packed bed reactor.

Safety Considerations

It is recommended that the steam-to-propylene ratio at the reactor inlet never be set less than 4:1 on a mole basis. This steam is used to inhibit the formation of coke on the catalyst below temperatures of 330ºC. 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. This stream is a potential explosion hazard. Operation outside

of the explosion limits (LEL and UEL) is strongly recommended for a packed bed reactor. The explosion limits for propylene in air at 25°C are LEL = 2.0 mol% propylene and UEL = 11.1 mol% propylene. At elevated temperatures and using a 4:1 steam-to-propylene ratio (see above) in the feed, the lower explosion limit (LEL) is changed significantly. In this case it is easier to define a minimum oxygen concentration (MOC) for the stream. Below the MOC, flame propagation and hence explosions are not possible. For the packed bed reactor you can assume an average value of MOC = 5.6 mol % oxygen. The UEL at typical temperatures used for this reaction is 15.3 mol % propylene. The second safety concern is that associated with the highly exothermic polymerization of AA which occurs in two ways. First, if this material is stored without appropriate additives, then free radical initiation of the polymerization can occur. This potentially disastrous situation is discussed by Kurland and Bryant [3]. Secondly, AA dimerizes when in high concentrations at temperatures greater than 90°C. Therefore, process conditions in the separation section (X-301 and T-302) should never exceed this temperature.

Final Comments

As with any open-ended problem; i.e., a problem with no single correct answer, the problem statement above is deliberately vague. You may need to fill in some missing data by doing a literature search, Internets search, or making assumptions. 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 may be forthcoming.
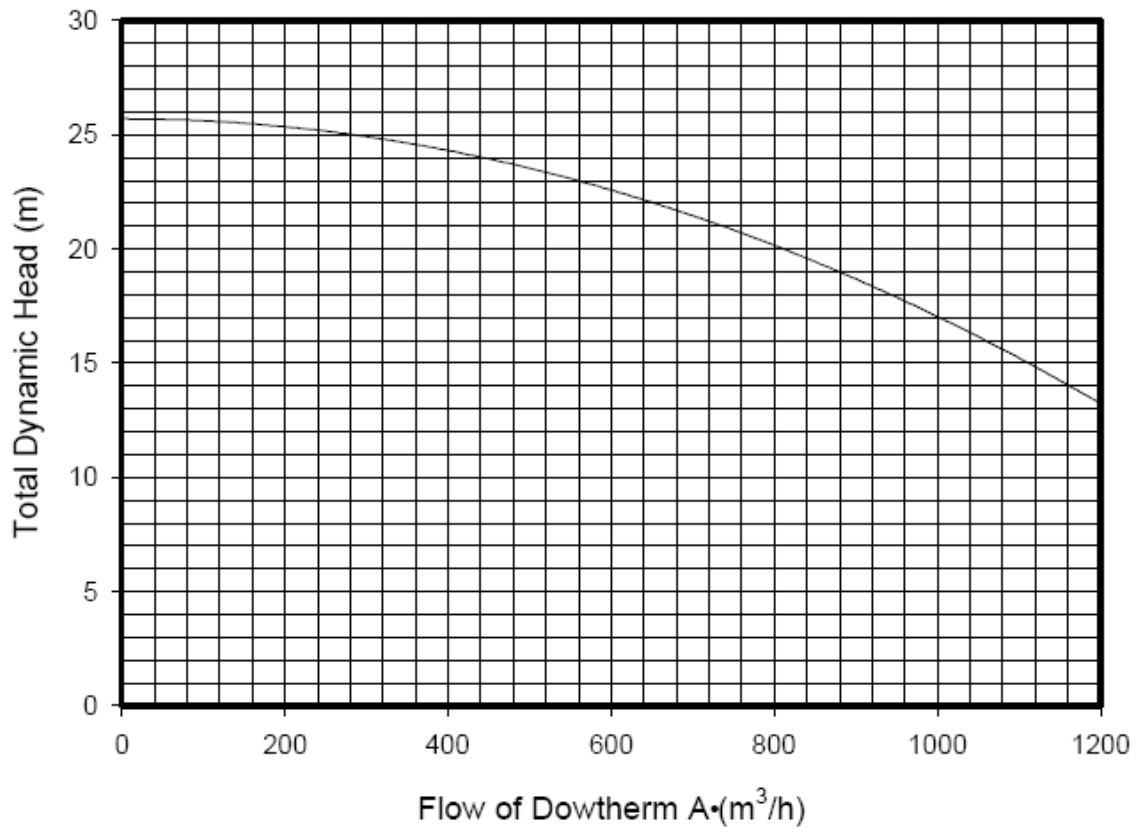
Moreover, in some areas (e.g. sizing/costing) you are given more data and information than what is needed. You must exercise engineering judgment and decide what data to use. Also you should also seek additional data from the literature or Internet to verify some of the data, e.g. the prices of products and raw materials.

Additional Data
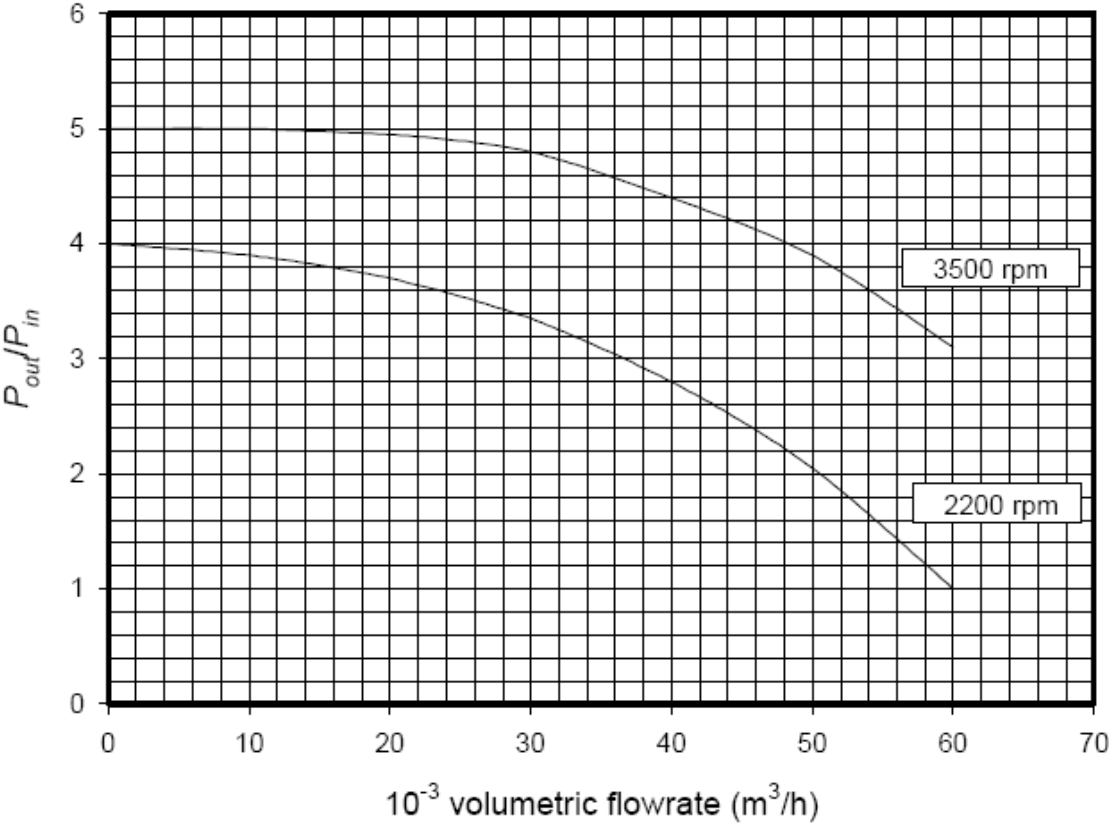
Compressor Curve for C-301

Pump Curve for the Dowtherm A Pump

Heat Exchangers

For heat exchangers that do not have to be designed in detail, use the following approximations for heat transfer coefficients to allow you to determine the heat transfer area and heat exchanger cost:

situation	h (W/m^2°C)
condensing steam	6000
condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60

Cost Data

Equipment Costs (Purchased)

Pumps	$630 (power, kW)$^{0.4}$
Heat Exchangers	$1030 (area, m^2)$^{0.6}$
Compressors	$770 (power, kW)$^{0.96}$ + 400 (power, kW)$^{0.6}$
Turbine	$2.18 \cdot 10^5$ (power output, MW)$^{0.6}$ assume 65% efficiency
Fired Heater	$635 (duty, kW)$^{0.8}$ assume 80% thermal efficiency assume can be designed to use any organic compound as a fuel
Vessels	$[1.67(0.959 + 0.041P - 8.3 \cdot 10^{-6}P^2)] \cdot 10^z$ $z = (3.17 + 0.2D + 0.5 \log_{10}L + 0.21 \log_{10}L^2)$ D = diameter, m 0.3 m < D < 4.0 m L = height, m L/D < 20 P = absolute pressure, bar
Catalyst	$2.25/kg
Packed Tower	Cost as vessel plus cost of packing
Packing	$(-110 + 675D + 338D^2)H^{0.97}$ D = vessel diameter, m; H = vessel height, m
Tray Tower	Cost as vessel plus cost of trays
Trays	$(187 + 20D + 61.5D^2)$ D = vessel diameter, m

Equipment Cost Factors

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

Carbon Steel   0.0
Stainless Steel 4.0

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

Raw Materials Costs

Propylene (polymer grade)   see *Chemical Marketing Reporter*
(available as a sat'd vapor at 25°C)

Product Prices

Acrylic Acid (99.9 mol%)   see *Chemical Marketing Reporter*
(1.0 bar, 40°C)

Acetic Acid (95 mole% required)   see *Chemical Marketing Reporter*
(1.0 bar, 40°C)

Utility Costs

Low Pressure Steam (600 kPa saturated)	$6.62/1000 kg
Medium Pressure Steam (1135 kPa saturated)	$7.31/1000 kg
High Pressure Steam (4237 kPa saturated)	$8.65/1000 kg
Natural Gas (446 kPa, 25°C)	$3.00/GJ
Fuel Gas (446 kPa, 25°C)	$2.75/GJ
Electricity	$0.06/kW h
Boiler Feed Water (at 549 kPa, 90°C)	$2.54/1000 kg
Distilled Deionized Water	$1.00/1000 kg

It may be assumed that pipes and valves are included in the equipment cost factors. Location of key valves should be specified on the PFD.

Cooling Water $0.16/GJ
available at 516 kPa and 30°C
return pressure ≥ 308 kPa
return temperature is no higher than 45°C

Refrigerated Water $1.60/GJ
available at 516 kPa and 10°C
return pressure ≥ 308 kPa
return temperature is no higher than 20°C

Refrigeration $60/GJ

References

1. Felder, R. M. and R. W. Rousseau, *Elementary Principles of Chemical Processes (2nd ed.)*, Wiley, New York, 1986.

2. Perry, R. H. and D. Green, eds., *Perry's Chemical Engineering Handbook (6th ed.)*, McGraw-Hill, New York, 1984.

3. Kurland, J.J. and D.B. Bryant, "Shipboard Polymerization of Acrylic Acid," Plant Operations Progress, **6**, 4, 203-207 (1987).

Solvent Extraction Unit, X-301

The design of the solvent extraction unit is very complicated and beyond the scope of the present project. However, the following economic information is available for estimating the profitability of the process:

Installed Cost of X-301 = 1.0×10^6 [flowrate of water in Stream 13 (kmol/h)]$^{0.3}$

Operating cost of X-301 = 0.7×10^6 [flowrate of water in Stream 13 (kmol/h)]$^{0.7}$

The above operating cost includes the cost of all utilities used by the unit, plus the cost of treating the wastewater, Stream 14, and the cost of make-up solvent, Stream 12.

Heat Exchangers

For heat exchangers, use the following approximations for heat transfer coefficients to allow you to determine the heat transfer area:

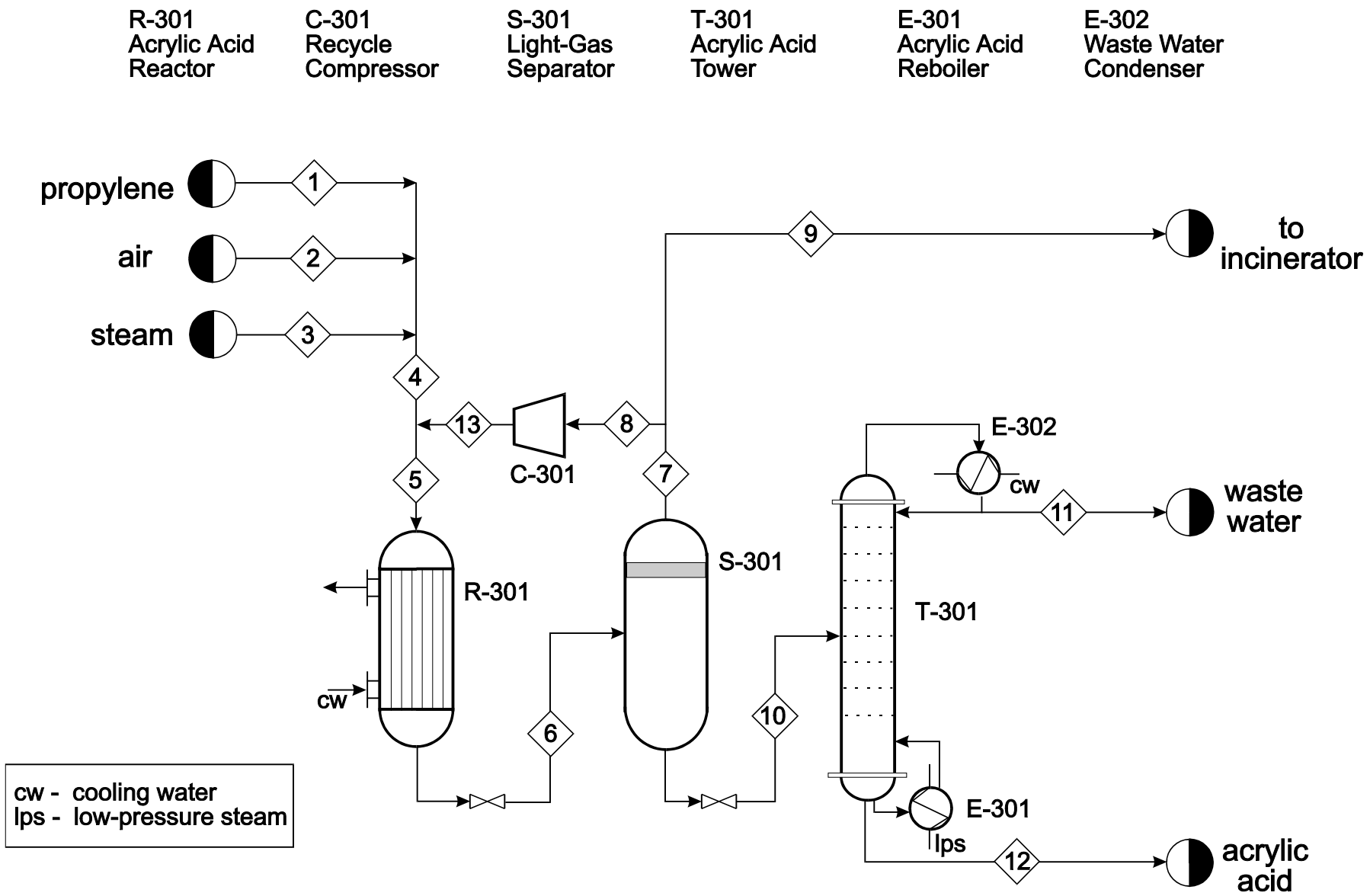|					
R-301	C-301	S-301	T-301	E-301	E-302
Acrylic Acid	Recycle	Light-Gas	Acrylic Acid	Acrylic Acid	Waste Water
Reactor	Compressor	Separator	Tower	Reboiler	Condenser

cw - cooling water
lps - low-pressure steam

Figure 1: Process Flow Diagram for Acrylic Acid Production

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Figure 2: PFD for Unit 300 – Acrylic Acid from Propylene