Energy Balances, Numerical Methods
Design Project

Production of Allyl Chloride

Process Description

Figure 1 is a preliminary process flow diagram (PFD) for the allyl chloride production process. The production rate is to be 20,000 tonne/y. The raw materials are propylene and chlorine. The propylene feed (Stream 1) and chlorine feed (Stream 2) are saturated liquids at 25°C. Both feeds are pure and are pumped up to the desired pressure by pumps P-101 and P-102. These streams are combined with the recycle propylene (Stream 10) and are then vaporized and superheated to the desired reactor temperature in a fired heater (H-101). The fired heater outlet (Stream 3) is sent to a packed bed reactor (R-101) in which allyl chloride and other side products are formed. The reactor effluent (Stream 4) is sent to a separator unit (T-101) in which several separations occur. In reality, this separations unit consists of many different pieces of equipment. For the purpose of this project you should perform an overall energy and material balance on T-101. Deionized water is added to T-101 in order to dissolve the hydrogen chloride gas and chlorine. You may also assume that all the chlorine dissolves in the water and is converted to hydrochloric acid in an additional processing step not shown in Figure 1. The cost of this conversion is $0.05/kg of chlorine. Stream 7 contains all the deionized water, hydrogen chloride and chlorine which enters T-101. Stream 7 leaves T-101 as a liquid at 50°C The vapor stream leaving the separations unit (Stream 6) is nearly pure propylene with small amounts of allyl chloride. This stream is compressed in the recycle gas compressor (C-101) and returned to the front end of the process as Stream 10. Stream 8, contains pure allyl chloride and leaves the process as a liquid at 50°C. Stream 9 contains all the other chlorinated hydrocarbons plus a small amount of allyl chloride. Stream 9 leaves the process as a liquid at 50°C. The energy to cool Stream 4 and partially condense it is provided by cooling water, as shown in Figure 1.

Process Details

Feed Streams

Stream 1: pure propylene, 25°C and a saturated liquid.

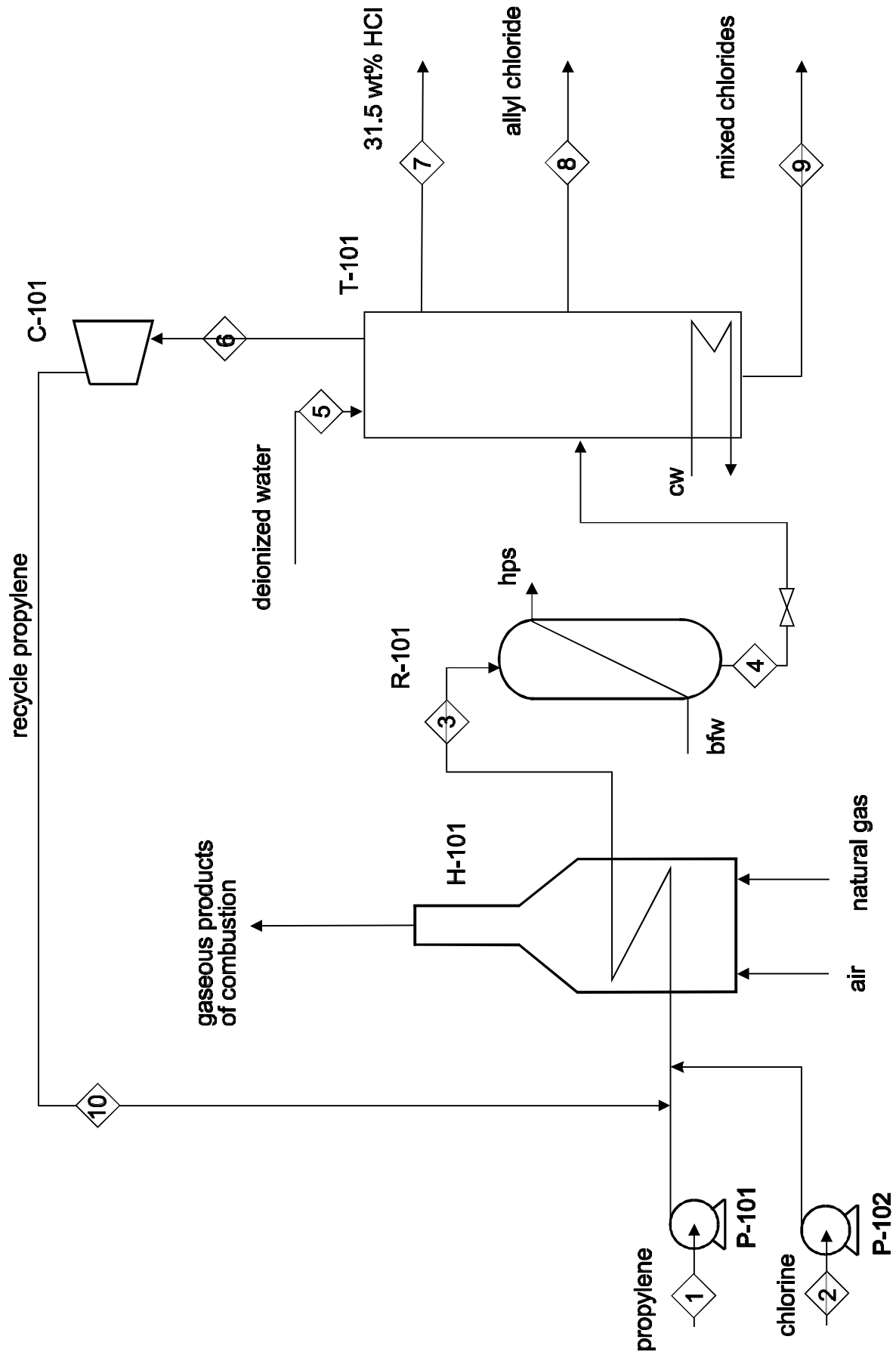Stream 2: pure chlorine, saturated liquid at 25°C

Figure 1: Preliminary Process Flow Diagram for the Allyl Chloride Process

Product Streams

Stream 7:   31.5wt% (20° Baumé) hydrochloric acid.

Stream 8:   Allyl chloride product - assume that 99% of the allyl chloride leaving T-101 as a liquid leaves in Stream 8. Also assume that the purity of this stream is 100 mol% allyl chloride.

Stream 9:   Mixed chlorides product - assume that this contains all the by-product chlorinated hydrocarbons formed in the reactor plus a small amount of allyl chloride.

Equipment

Pump (P-101):
  This pump increases pressure of the propylene feed to between 1000 and 1400 kPa. Pump operation may be assumed isothermal, and the cost of energy may be neglected. (Both of these assumptions are valid for this semester's design only.)

Pump (P-102):
  The pump increases the pressure of the chlorine feed to between 1000 and 1400 kPa.. Pump operation may be assumed isothermal, and the cost of energy may be neglected. (Both of these assumptions are valid for this semester's design only.)

Compressor (C-101)
  The compression costs (electricity) are given by the following equation

$$\$/h = 0.02\dot{m}\left[\left(\frac{P_{out}}{P_{in}}\right)^{0.3} - 1\right]$$

  where $\dot{m}$ is the mass flowrate of vapor (kg/h) through the compressor. This is the cost of the electricity to operate the compressor.

Fired Heater (H-101):
  The fired heater heats, vaporizes, and superheats the mixed feed up to the desired reactor operating temperature. Air and natural gas must be fed to the fired heater. Natural gas is priced at its LHV. The fired heater is 75% efficient based on the energy required to heat the process stream.
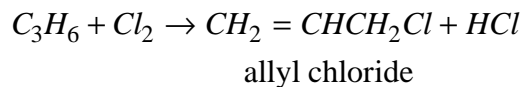
Reactor (R-101):

The reactor feed must be between 440°C and 520°C and between 1000 kPa and 1400 kPa. The reactor should operate at a pressure of at least 50 kPa above that of the separator. The propylene in the reactor feed must be present in at least 100% excess based on the chlorine feed to the reactor. Conversion of the limiting reactant and the selectivity for each reaction are given in Table 1. The selectivity and conversion can be assumed not to vary with pressure for the range of pressures considered here. The reactor may be assumed isothermal, and the exothermic heat of reaction is removed by vaporizing boiler feed water to make high-pressure steam. Credit may be taken for the high-pressure steam.

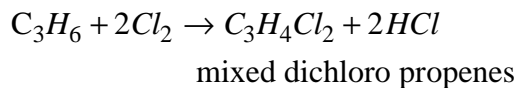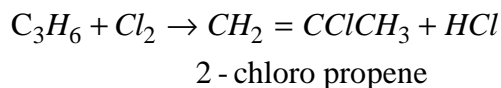Table 1: Selectivity and Conversion as a Function of Reactor Temperature

Temperature (°C)	Selectivity allyl chloride all products	Selectivity 2-chloro propene dichloro propene	Single Pass Conversion
440	13.22	0.489	55%
460	10.49	0.389	70%
480	8.43	0.312	82%
500	6.85	0.253	92%
520	5.62	0.208	99%

The following reactions occur:

Main reaction

$$C_3H_6 + Cl_2 \rightarrow CH_2 = CHCH_2Cl + HCl$$
allyl chloride

Side reactions

$$C_3H_6 + Cl_2 \rightarrow CH_2 = CClCH_3 + HCl$$
2 - chloro propene

$$C_3H_6 + 2Cl_2 \rightarrow C_3H_4Cl_2 + 2HCl$$
mixed dichloro propenes

Separation Unit (T-101)

This is actually a combination of many heat exchangers, distillation columns, pumps, and other vessels. The temperature of the Separator is maintained at 50°C which is the lowest practical temperature when using cooling water. The pressure is lowered in order to

separate the propylene from the chlorinated organics, hydrogen chloride and chlorine. You should assume that all the propylene leaves in the vapor. All the other components (except allyl chloride) leave in the liquid streams. The allyl chloride distributes itself between the vapor and liquid streams leaving T-101. The distribution depends on the pressure at which the separation unit operates. A table of information for this unit is given below.

Table 2: Distribution of Allyl Chloride in T-101

Pressure of T-101 kPa	% of allyl chloride entering T-101 which leaves as liquid	% of allyl chloride entering T-101 which leaves as vapor
800	90.0	10.0
900	92.0	8.0
1000	93.5	6.5
1200	96.0	4.0

Of the allyl chloride which leaves T-101 in Streams 8 and 9, 99% of the allyl chloride leaves in Stream 8 and the remainder leaves in Stream 9. Stream 8 may be assumed to be 100% pure allyl chloride. All the 2-chloropropene and mixed dichloro propenes leave in Stream 9. Both Streams 8 and 9 leave as liquids at 50°C.

All the hydrogen chloride entering T-101 leaves in Stream 7 as a liquid at 50°C. This stream also contains all the water and chlorine fed to T-101. Stream 7 should contain enough water so that when all the chlorine is converted to HCl the resulting stream is 31.5 wt% HCl. This stream can be sold for profit. Note that there is a charge for converting the chlorine to HCl.

Equipment Cost

You may assume the total installed equipment cost to be $15.4 million.

Utility Costs

Low-Pressure Steam (446 kPa, saturated) $3.00/1000 kg

Medium-Pressure Steam (1135 kPa, saturated) $6.50/1000 kg

High-Pressure Steam (4237 kPa, saturated) $8.00/1000 kg

Natural Gas (446 kPa, 25°C) $3.00/10⁶ kJ

Electricity $0.05/kW hr

Boiler Feed Water (at 549 kPa, 90°C) $300.00/1000 m³

Deionized Water $0.30/1000 kg
    available at 516 kPa and 30°C

Cooling Water $20.00/1000 m³
    available at 516 kPa and 30°C
    return pressure ≥ 308 kPa
    return temperature should be 40°C.

Physical Property Data

Use data from References [1] or from any handbook (such as Reference [2]). The following data are not readily available in these references.

Liquid Heat Capacity (at 25°C)
    Assume that the liquid heat capacity for all organic liquids is given by

$$C_p(kJ/kmol/°C) = 174.3 + 0.325T, \quad T \text{ in } °C$$

Vapor Heat Capacities (all figures in the table below are in kJ/kmol/°C)
    Vapor heat capacities may be interpolated or extrapolated from the following table.

Table 3: Heat Capacity Data for Vapors

Temperature (K)→ Component ↓	300	500	700	800
chlorine	34.0	36.2	36.9	37.1
propylene	65.0	93.5	117.5	127.7
hydrogen chloride	29.2	29.3	30.1	30.6
chlorinated organics	75.3	106.8	128.9	137.5

Latent Heat of Vaporization at 25°C

Propylene   331 kJ/kg
Chlorine   248 kJ/kg
Hydrogen Chloride   246 kJ/kg
Chlorinated Organics   394 kJ/kg
2-chloro propene   334 kJ/kg
dichloro propene   309 kJ/kg

Standard Heats of Reaction at 25°C

Table 4: Heat of Reaction Data for Main and Side Reactions

Main Product Formed by Reaction	Heat of Reaction at 25°C (kJ/mol propylene)
allyl chloride	-112
2-chloro propene	-121
dichloro propene	-222

Economic Analysis

When evaluating alternative cases, 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 allyl chloride (the product), hydrochloric acid (use 20° Baumé), propylene, and chlorine should be obtained from the *Chemical Marketing Reporter*, which is in the Evansdale Library. A credit of 0.1 $/kg may be taken for the mixed chlorides stream.

Other operating costs are those for utilities, such as steam, cooling water, natural gas, and electricity. You are expected to perform appropriate energy balances or use the information given in this assignment to estimate the utilities for H-101, R-101, T-101, and C-101 plus any other equipment requiring utilities that you decide to add to the process.

The capital cost annuity is an ***annual*** cost (like a car payment) associated with the ***one-time***, fixed cost of plant construction. The calculation of the annuity value has been covered in ChE 38.

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.

Deliverables

Each group must deliver a report written using a word processor. The report should be clear and concise. The format is explained in a separate document. Any report not containing a labeled PFD and a stream table will be considered unacceptable. When presenting results for different cases, graphs are generally superior to tables. The report appendix should contain details of calculations for the optimal case. These calculations may be (neatly) hand-written. Calculations which can not be followed easily will lose credit.

Each group will give an oral report in which the results of this project are presented in a concise manner. The oral report should be no more than 15 minutes, and each group member must speak. A five-minute question-and-answer session will follow. Instructions for presentation of oral reports will be provided in a separate document. However, the best way to learn how to present an oral report, other than actually presenting one, is to make time to see some of the oral reports presented by the juniors the week before you are to present your report.

As mentioned in the cover memo, the written project report is due upon presentation of the oral report. The oral reports will be Monday, April 21, 1997 (ChE 38 class) and Wednesday, April 23, 1997 (ChE 41 class). There will be a project review on Friday, April 25, 1997 (ChE 41 class). In addition, everyone must attend at least one (and preferably both) of the senior design presentations, either on Tuesday, April 23, 1995, or on Thursday, April 25, 1995 (substitutes for Thursday ChE 38 class). Furthermore, attendance is required of all students during their classmates' presentations (this means in the room, not in the hall or the lounge). Failure to attend any of the above required sessions will result in a decrease in one letter grade (per occurrence) from your project grade in both ChE 38 and ChE 41.

Anyone not participating in this project will automatically receive an F for ChE 38, regardless of other grades earned in this classes.

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 of the problem statement. You should be aware that these revisions/clarifications may be forthcoming.

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, p. 9-74