

Increasing the Production of 3-Chloro-1-Propene (Allyl Chloride) in Unit 600

Background

You are currently employed by the TBWS Corp. at their Beaumont, Texas plant, and you have been assigned to the allyl chloride facility. A serious situation has developed at the plant, and you have been assigned to assist with troubleshooting the problems which have arisen.

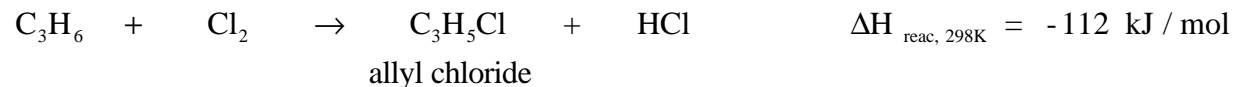
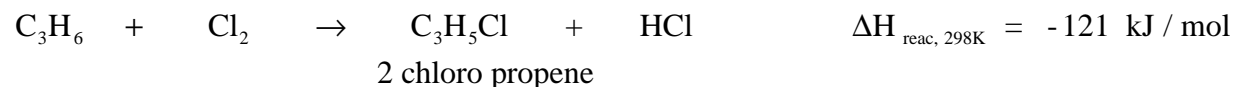
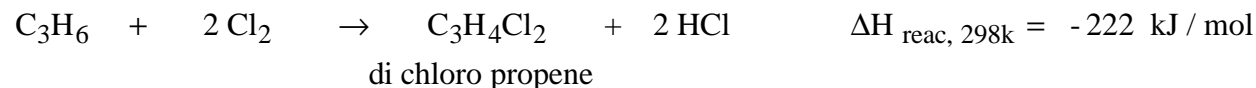
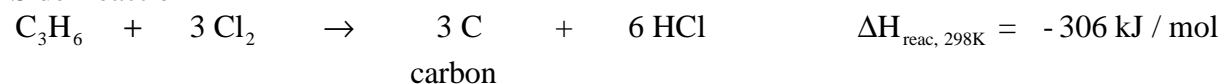
Recently your sister plant in Alabama was shut down by the EPA (Environmental Protection Agency) for violations concerning sulfur dioxide emissions from a furnace in their allyl chloride facility. Fortunately, the Beaumont facility had switched to natural gas as a fuel for their process in the early 1990s and, hence, is currently in compliance with the EPA and Texas regulations. However, the loss of the Alabama plant, albeit for a short time only, has put considerable pressure on the Beaumont plant to fulfill contractual obligations to our customers in Alabama for allyl chloride. Thus, part of your assignment is to advise management concerning the increase in production of allyl chloride that can be made at the Beaumont facility.

Another related issue which has been discussed by management is the long term profitability of both allyl chloride facilities. Allyl chloride is used as a precursor in the production of allyl alcohol, glycerin, and a variety of other products used in the pharmaceutical industry. More efficient plants have been built recently by our competitors and we are being slowly squeezed out of the market by these rival companies. We still maintain a loyal customer base due to our excellent technical and customer service departments and our aggressive sales staff. However, we have been losing an ever increasing share of the market since the late 1980s. At present, the future looks bleak, and if the profitability (and efficiency) of our facilities do not increase in the near future, we may be shut down in the next year or two, when some of our long term contracts come up for renewal. A second part of your assignment is to look into the overall profitability of the Beaumont allyl chloride facility and determine whether any significant improvements in the overall economics can be made.

Process Description of the Beaumont Allyl Chloride Facility

A process flow diagram (PFD) of the allyl chloride facility is provided in Figure 1. This process (Unit 600) is the one to which you have been assigned.

Allyl chloride is produced by the thermal chlorination of propylene at elevated temperatures and relatively low pressures. Along with the main reaction, several side reactions also take place and these are shown below:

Main Reaction**Side Reaction****Side Reaction****Side Reaction**

The propylene feed is heated in a furnace, fired by natural gas, and brought up to reaction temperature (design conditions are given in Tables 1 and 2). The chlorine is mixed with the hot propylene in a mixing nozzle and then fed to the reactor.

During the thermal chlorination process a significant amount of carbon can be produced, and it has a tendency to deposit on equipment which operates at temperatures above 400°C. For this reason the reactor chosen for this process is a fluidized bed with an inert solid, sand, on the reaction side. The sand provides a large surface area on which the carbon can deposit. It also acts as a scouring agent on the immersed heat transfer tubes in the reactor and prevents the build-up of carbon on the heat transfer surfaces. The carbon, which deposits preferentially on the sand, is removed by combustion in the solids regeneration unit shown in Figure 1. The regenerated sand is sent back to the reactor, thus maintaining a constant inventory of solids in the reactor. The heat produced in the reactor, by the exothermic chlorination reactions, is removed via the heat transfer tubes through which is circulated a heat transfer medium. The heat transfer fluid is a commercially available coolant called Dowtherm A™. Physical properties of this fluid are included in Table 3 of this assignment.

The gases leaving the reactor contain unreacted propylene along with the reaction products, as given in the flow table in Table 1. These hot gases are cooled in a waste heat boiler and a trim cooler prior to being sent for further processing, including the refining of the allyl chloride and the separation and recycle of unused propylene.

Specific Objectives of Assignment

Your immediate supervisor, Ms. Jane Curtis, has taken you around the allyl chloride facility and told you some of the details of the plant operation, and these are summarized below in the section on Additional Background Information. She has also provided you with a set of battery limit conditions, Table 4, for the utilities, feeds, and products which she has informed you are both current and accurate.

Your assignment is to provide a written report to Ms. Curtis by 9/23/96. This report, as a minimum, should contain the following items:

- (i) A cover letter to your supervisor.
- (ii) An executive summary style report covering the following major points:
 1. Findings on how much the throughput of Unit 600 can be increased in the short term (without the purchase of new equipment)
 2. Findings of any potential improvements which will increase the profitability of Unit 600. You should provide an estimate of the impact of these changes by calculating the equivalent annual operating cost, EAO, from the following equation (assume and internal discount rate for such improvements to be 15% p.a. before tax and all improvements should be calculated using a 5 year project life):

$$EAO = (Equip. Cost) \frac{i(1+i)^n}{(1+i)^n - 1} + YOC$$

where *Equip. Cost* is the installed equipment cost, *YOC* is the yearly operating cost of the equipment, $n=5$ and $i=0.15$. It should be noted that the potential improvements should be considered separately from the immediate increase in production required for 1 above.
 3. The effect that recommended changes will have on the health and safety of the plant personnel.
 4. Recommendations for immediate changes in plant operations and an estimated time schedule in which these changes might be implemented.
- (iii) A list of assumptions made in carrying out your study.
- (iv) An appendix giving details of all important calculations made in your study.

The written report should follow the guidelines outlined in Chapter 22 and the class handouts.

Additional Background Information

A process flow diagram is provided in Figure 1, and flow summary and equipment summary tables are given in Table 1 and 2. This information is for the reaction section of Unit 600 only. The separation section is being studied by another group and you should not consider any changes for this section at this time. The data given in the tables and on the PFD reflect the current operating conditions and have been checked recently by your operations department. Some additional information regarding the allyl chloride facility has been provided by Ms. Curtis and is summarized below:

1. The temperature in the reactor should not exceed 525°C, since above this temperature, there is excessive coke production leading to operating problems in the down stream units. It is further recommended that the reactor temperature be maintained at close to 510°C during any changes in process operations.
2. All process exchangers using cooling water are designed to have a 5 psi (0.34 bar) pressure drop on the cooling water side for the design flow rate of cooling water. The velocity of cooling water at design conditions was set at 2 m/s and long term operation at velocities above 3.5 m/s is not recommended due to increased erosion.
3. For the fluidized bed reactor you may assume that the pressure drop across the bed of sand remains essentially constant regardless of the flowrate.
4. The cyclone and regenerator were designed by the vendor of the equipment to be considerably oversized and are capable of handling any additional loads that might be required during this temporary change in operations.
5. The heat transfer coefficient between the fluidized bed and the immersed heat transfer coils (the outside coefficient) is known not to vary much with fluidizing gas flowrate and may be assumed constant regardless of process gas throughput.
6. The heat transfer tubes inside the fluidized bed are currently arranged as three parallel rows piped in series. Valving exists so that they be arranged as three rows of 9 tubes in parallel.
7. Flow of all process and utility streams may be considered to be fully developed turbulent flow. Thus the pressure drop through the equipment will be proportional to the square of the velocity.
8. The conversion of propylene and chlorine in the fluidized bed will be virtually unaffected by changes in gas throughput. This is due to the long gas residence time in the reactor. In fact, the reactor's main purpose is to provide a large surface area for coke deposition and to provide good heat transfer.
9. The crude allyl chloride (Stream 5 in Figure 1) must be delivered to the separations section at a minimum pressure of 2.10 bar.
10. A manufacturer's pump curve for the circulating Dowtherm A™ pumps is provided for your use and is given in Figure 2 of this assignment.
11. A set of original design calculations outlining the design of the units are provided for your information.

You have also taken a tour of the plant recently and in addition to confirming some of the points above with the operators you make the following observations:

1. The Dowtherm A™ recirculation pump (P-601 A) is making a high pitched whining noise.
2. Steam is leaking from the safety relief valve placed on top of E-602 (not shown on PFD).
3. Some of the insulation on the pipe leading from the reactor R-601 to E-602 has come loose and is hanging from the pipe.

Table 1: Flow Summary Table for Unit 600 - Crude Allyl Chloride Production Facility

Stream No.	1	2	3	4	5
Temperature (°C)	25	25	511	400	50
Pressure (bar)	11.7	6.44	2.77	11.34	2.09
Vapor Fraction	1.0	1.0	1.0	0.0	1.0
Molar Flowrate (kmol/h)					
propylene	75.89	-	58.08	-	58.08
chlorine	-	19.70	-	-	-
allyl chloride	-	-	15.56	-	15.56
2-chloro propene	-	-	0.46	-	0.46
di chloro propene	-	-	1.81	-	1.81
hydrogen chloride	-	-	19.70	-	19.70
Carbon	-	-	-*	-	-
Dowtherm™ A	-	-	-	4.62 kg/s	-
Total Mole Flow (kmol/h)	75.89	19.70	95.61	4.62 kg/s	95.61

* carbon formed but at a rate which does not affect the material balance.

Table 2: Equipment Design Parameters (Unit 600)

<p>J-601 Jet Mixer</p> <p>Pressure Drop = 0.20 bar at design conditions Operating Pressure = 3.24 bar (normal) = 5.00 bar (maximum)</p>	<p>E-601 Dowtherm™ Cooler</p> <p>Operating Pressure = 11.0 bar (normal) = 15.3 bar (maximum) Operating Temperature = 400°C (maximum) Duty = 2188 MJ/h Heat Transfer Area = 2.6 m²</p>
<p>H-601 Reactor Feed Preheater</p> <p><u>Process Side Conditions</u> Duty = 4000 MJ/h (normal) 5400 MJ/h (maximum) Operating Pressure = 3.58 bar (normal) = 5.00 bar (maximum) Operating Temperature = 545°C (maximum)</p>	<p>E-602 Waste Heat Boiler</p> <p><u>Tube Side</u> Operating Pressure = 2.77 bar (normal) = 3.50 bar (maximum)</p> <p><u>Shell Side</u> Operating Pressure = 6.0 bar (normal) = 8.0 bar (maximum)</p> <p>Duty = 2850 MJ/h Heat Transfer Area = 57.0 m²</p>
<p>R-601 Fluidized Bed Reactor</p> <p>Operating Temperature = 510°C (normal) = 525°C (maximum) Operating Pressure = 3.04 bar (normal) = 4.50 bar (maximum)</p> <p><u>Dimensions</u> Square cross section 3.1m by 3.1 m Fluidized bed height = 1.5 m Vessel height = 5 m Heat transfer area = 23.0m² Normal duty = 2188 MJ/h</p>	<p>E-603 Crude Allyl Chloride Cooler</p> <p><u>Tube Side</u> Operating Pressure = 2.43 bar (normal) = 3.50 bar (maximum)</p> <p><u>Shell Side</u> Operating Pressure = 4.0 bar (normal) = 5.0 bar (maximum)</p> <p>Duty = 1025 MJ/h Heat Transfer Area = 52.0 m²</p>
<p>P-601 A/B Dowtherm™ A Circulation Pumps</p> <p>Operating Pressure = 11.0 bar (normal) = 15.0 bar (maximum) Operating Temperature = 350°C (normal) = 400°C (maximum) ΔP (normal) = 1.53 bar (22.3 psi) ΔP (maximum) = 2.06 bar (30 psi) Power (motor) = 2.5 kW Flow Rate = 0.00068 m³/s (normal)</p>	

Table 3: Properties of Dowtherm A™ - Heat Transfer Fluid

Properties of Dowtherm A™ are listed below:

Temperature Use Range	Liquid 16°C - 400°C
	Gas 257°C - 400°C

Above 400°C Dowtherm A™ starts to decompose thermally.

Liquid Properties for 350-400°C

Thermal Conductivity	0.0943	W/m.K
Specific Heat Capacity	2630	J/kg K
Viscosity	1.4×10^{-4}	kg/m s
Density	680	kg/m ³
Vapor Pressure (400°C)	10.5	bar
Prandtl No. ($C_p \mu / k$)	3.9	

Table 4: Battery Limit Conditions for Feeds, Products and Utilities (Unit 600)

Conditions at which feed and utility streams are available and at which products and utility streams must be returned to the boundary of the process are known as the battery limit conditions. For Unit 600 the battery limit conditions which exist are listed below. The limiting conditions are given at the equipment and take into account the pressure loss in the associated supply and return piping.

Utility	Condition at Equipment	
Cooling Water	5 bar,	30°C
Cooling Water Return	4 bar,	<50°C
Boiler Feed Water	6 bar,	90°C
High Pressure Steam ¹	41 bar,	saturated
Medium Pressure Steam ¹	11 bar,	saturated
Low Pressure Steam ¹	6 bar,	saturated
Natural Gas	4 bar,	25°C

¹ steam pressure at sources, such as waste heat boilers, may exceed these values in order to overcome pressure losses in header piping.

Feeds and Products	Condition at Process Boundary
Propylene	25°C, saturated vapor
Chlorine	25°C, saturated vapor
Crude Allyl Chloride	50°C, >2.10 bar (Stream 5)

Process Design Calculations

Fluidized Bed Reactor, R-601

Heat generated in reactor = $Q_R = 2188$ MJ/h

Bed solids are $150\mu\text{m}$ sand particles with density (ρ_s) of 2650 kg/m³

At conditions in the reactor the process gas has the following properties

$\rho_g = 2.15$ kg/m³ and $\mu_g = 2.25 \times 10^{-5}$ kg/m s

Using the Correlation of Wen and Yu [1] we get:

$$Re_{p,mf} = [1135.7 + 0.0408 Ar]^{0.5} - 33.7$$

$$\text{where } Ar = \frac{d_p^3 g (r_s - r_g) r_g}{m_g^2} = \frac{(150 \times 10^{-6})^3 (9.81) (2650 - 2.15) (2.15)}{(2.25 \times 10^{-5})^2} = 372$$

$$\text{Therefore } Re_{p,mf} = [1135.7 + 0.0408 \sqrt{372}]^{0.5} - 33.7 = 0.2246$$

$$Re_{p,mf} = \frac{u_{mf} d_p r_g}{m_g} \therefore u_{mf} = \frac{(0.2246) (2.25 \times 10^{-5})}{(2.15) (150 \times 10^{-6})} = 0.0157 \text{ m/s}$$

Total volumetric flow of gas at inlet conditions to the bed = $V_{gas} = 0.5674$ m³/s

we need to get good heat transfer so we will operate the bed at 5 times u_{mf} which puts us into the bubbling bed regime.

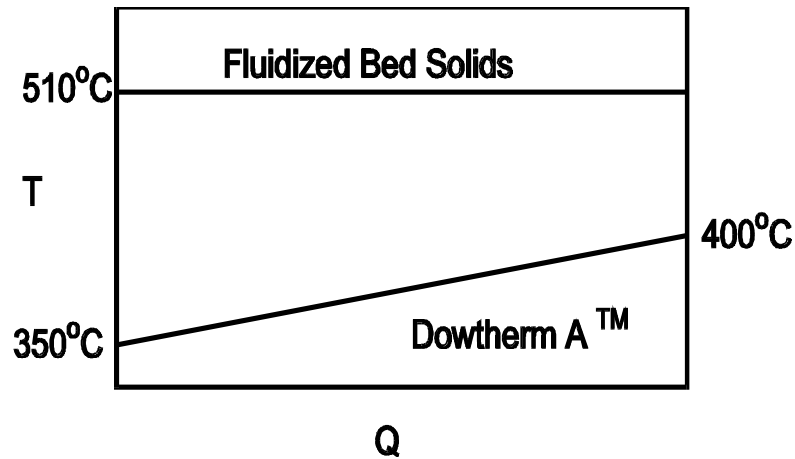
$$\text{Free bed area (without h.t. tubes)} = V_{gas} / 5u_{mf} = .5674 / (5 \times 0.0157) = 7.2 \text{ m}^2$$

Look at heat transfer area for fluidized bed

Heat transfer area required in bed = A_f

Overall heat transfer coefficient = U

Assume that the fluidized solids are well mixed and isothermal and assume that the cooling medium enters the bed at 350°C and leaves at 400°C which is the maximum operating temperature for DowthermTM A.



$$\Delta T_{lm} = \frac{(160 - 110)}{\ln(160/110)} = 133.4^\circ \text{C}$$

inside film heat transfer coefficient, h_i , is calculated from the Seider -Tate equation :

$$Nu = 0.023 Re^{0.8} Pr^{0.33} (\mu/\mu_w)^{0.14}$$

if we assume a velocity of 1.5 m/s inside a 3 inch sch 40 pipe (ID = 0.0779m, OD = 0.0889m) then

$$Re = (0.0779) (1.5) (680) / (1.4 \times 10^{-4}) = 567 \times 10^3$$

$$Nu = h_i d/k = 0.023 (567 \times 10^3)^{0.8} (3.9)^{0.33} = 1445$$

$$h_i = (1445) (0.0943) / (0.0779) = 1750 \text{ W/m}^2\text{K}$$

outside film heat transfer coefficient, $h_o = 250 \text{ W/m}^2\text{K}$ (from previous plant operating data)

fouling coefficient on inside = $2500 \text{ W/m}^2\text{K}$

$$d_i / d_o = 0.0779/0.0889 = 0.88$$

Ignoring the wall resistance we get the overall transfer coefficient U_o from

$$U_o = \frac{1}{\frac{1}{250} + \frac{0.88}{2500} + \frac{0.88}{1750}} = 206 \text{ W / m}^2\text{K}$$

$$A_f = \frac{Q_r}{U_o \Delta T_{lm}} = \frac{2188 \times 10^6}{(3600) (206) (133)} = 22.2 \text{ m}^2$$

now assuming tubes are 10 ft long and 3 inches in diameter (sch 40) the heat transfer area per tube is

$$\pi d_o L = (3.142) (0.0889) (10) (0.3048) = 0.8513 \text{ m}^2$$

\therefore number of tubes required , $N_T = 22.2 / 0.8513 = 27$ tubes.

Use 3 layers of 9 tubes piped in series and placed in horizontal rows in the bed each row occupies the following cross sectional area of bed

$$(9) (d_o) (L) = (9) (0.0889) (3.048) = 2.4 \text{ m}^2$$

\therefore total csa for bed = $2.4 + 7.2 = 9.6 \text{ m}^2$

use a square bed with side dimensions = $(9.6)^{0.5} = 3.1 \text{ m}$ (10.2 ft)

check velocity in tubes

csa for flow of Dowtherm ATM in tubes = $\pi d_i^2 / 4 = (3.142) (0.0779)^2 / 4 = 4.766 \times 10^{-3} \text{ m}^2$

flow of Dowtherm ATM = $6.797 \times 10^{-3} \text{ m}^3 / \text{s}$

\therefore velocity of DowthermTM A in tubes = $6.797 \times 10^{-3} / 4.766 \times 10^{-3} = 1.43 \text{ m/s} \Rightarrow$ assumption is **OK**

pressure drop in tubes

$Re = 5.41 \times 10^5$ \therefore friction factor, $f = 0.0045$ (with $e/d = 0.0006$)

$\Delta P = 2fL_{eq}\rho v^2 / d = (2) (0.0045) (680) (1.43)^2 L_{eq} / (0.0779) = 161 L_{eq}$

now L_{eq} = equivalent length of pipe in three rows of heat transfer pipes in fluidized bed

= $(27) (3.048) (1.5) = 123 \text{ m}$ (take 1.5 times length of pipe to account for fittings)

$\therefore \Delta P = (161) (123) = 0.198 \text{ bar}$

Set bed height (ht of sand above distributor plate) = 1.5 m

this gives a gas residence time in the bed of $(7.2) (1.5) (0.45) / 0.5674 = 8.6 \text{ s}$ this should be plenty of time since complete reaction should only take about 2-3 s

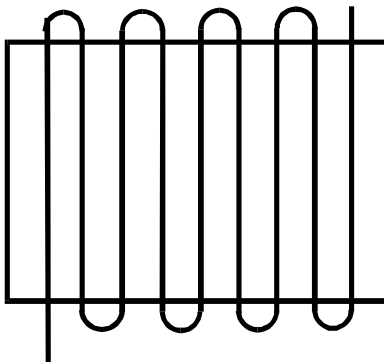
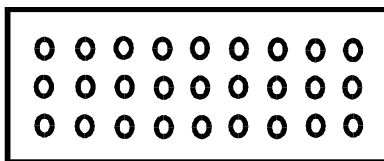
$\Delta P_{bed} = h_{bed} \rho_{sand} (1 - \epsilon) g = (1.5) (2650) (1 - 0.45) (9.81) = 0.214 \text{ bar}$

assume 0.04 bar for distributor loss and 0.064 bar for cyclones to give the overall equipment pressure drop

$$\Delta p_{reactor} = 0.214 + 0.04 + 0.016 = 0.27 \text{ bar}$$

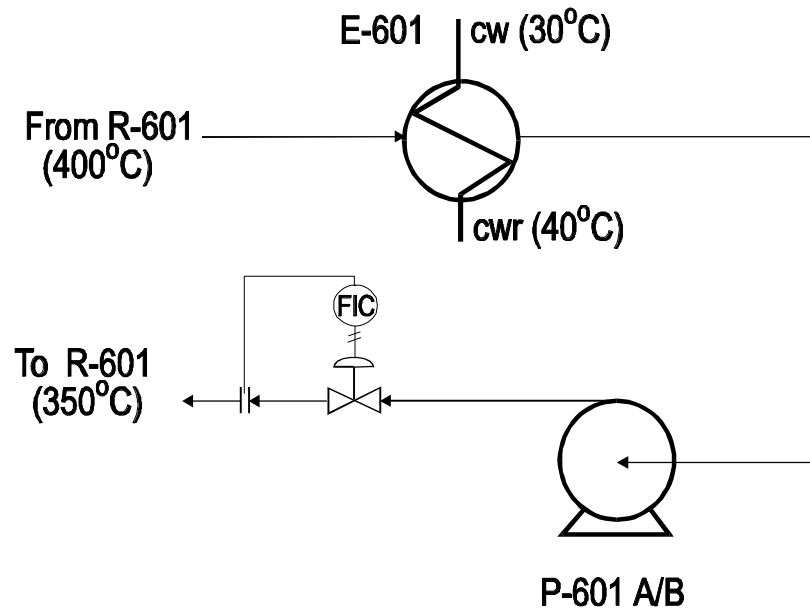
Design of Fluidized Bed is given in sketch below:

side view of bed showing 3 rows of 9 tubes



Overhead view of bed showing piping arrangement for one row,
each row is piped in series with the row below

Dowtherm A™ Cooling Loop



For exchanger **E-601** we have $\Delta T_{lm} = (360 - 320) / \ln(360/320) = 340^\circ\text{C}$ and $U = 850 \text{ W/m}^2 \text{ K}$ (approximately equal resistances on both sides and small fouling resistances) heat transfer area A is given by

$$A = 2188 \times 10^6 / (3600) (340) (850) = 2.1 \text{ m}^2$$

Use a double pipe heat exchanger since area is small

$$\text{cooling water flowrate} = 2188 \times 10^6 / (3600) (4180) (10) = 14.5 \text{ kg/s}$$

$$\text{Dowtherm flowrate} = 2188 \times 10^6 / (3600) (2630) (50) = 4.62 \text{ kg/s}$$

Pressure drop across the exchanger = 0.34 bar for Dowtherm and cooling water

Velocity of cooling water through exchanger set at 2 m/s

For pumps **P-601 A/B** assume

0.34 bar (5 psi) pressure drop across exchanger on Dowtherm side

0.14 bar (2 psi) pressure drop for piping

0.85 bar (12.4 psi) pressure drop across the control valve

0.20 bar (2.9 psi) pressure drop across the reactor exchanger

total loop pressure drop = 1.53 bar = 22.3 psi

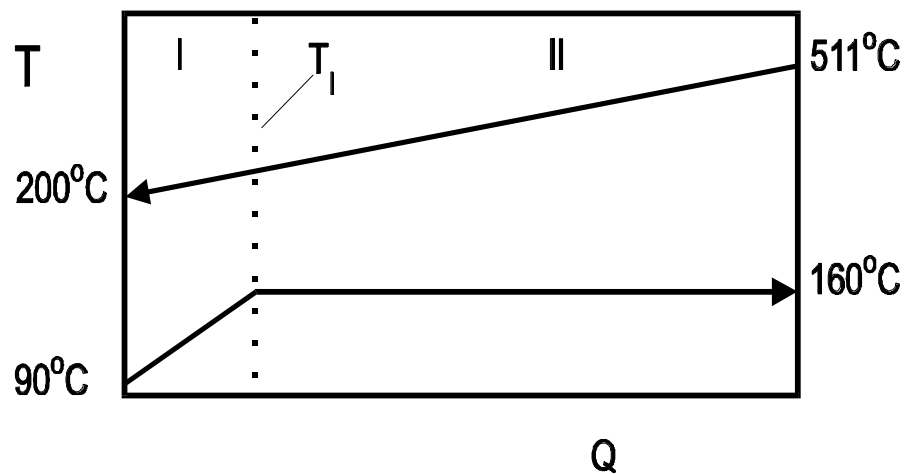
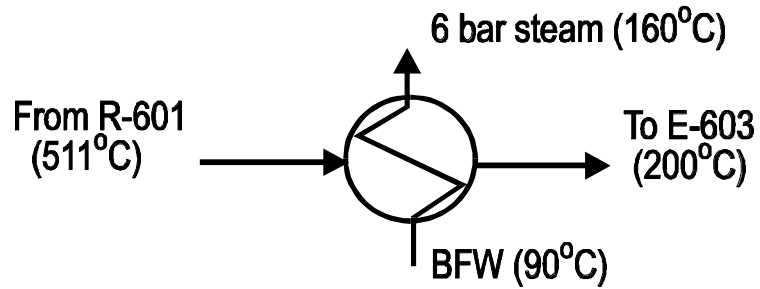
flow of Dowtherm = $4.62 / 680 = 6.797 \times 10^{-3} \text{ m}^3/\text{s} = 108 \text{ gpm}$

Power required for pumping liquid = $v\Delta P = (6.797 \times 10^{-3}) (1.55 \times 10^5) = 1.05 \text{ kW}$

assuming an efficiency of 45%, we get that the shaft power = $1.05 / 0.45 = 2.34 \text{ kW}$

use a 2.5 kW pump plus a spare

Waste Heat Boiler E-602



Zone I $U = 90 \text{ W/m}^2 \text{ K}$ (all resistance on gas side)

Zone II $U = 90 \text{ W/m}^2 \text{ K}$ (all resistance on gas side)

heat released as gas cools from 511 to 200°C is 2850 MJ/h = 792 kW

$$\Delta H_{\text{BFW-steam}} = 2380 \text{ kJ/kg}$$

$$\text{steam flowrate} = 792/2380 = 0.333 \text{ kg/s} \quad (h_{L, \text{sat}}=376.9, h_{L, \text{sat}}=675.5, h_{V, \text{sat}}=2756.9 \text{ kJ/kg})$$

$$Q_{90-160^\circ\text{C}, \text{Liq}} = (0.333) (675.5 - 376.9) = 99 \text{ kW}$$

$$Q_{160^\circ\text{C}, \text{Liq-Vap}} = (0.333) (2756.9 - 675.5) = 693 \text{ kW}$$

For Zone I

$$(T_1 - 200)/(511 - 200) = 99/792 \Rightarrow T_1 = 238.8^\circ\text{C}$$

$$\Delta T_{lm} = \frac{(239 - 160) - (200 - 90)}{\ln \frac{(239 - 160)}{(200 - 90)}} = 93.6^\circ \text{C}$$

$$A_I = Q_I / U_I \Delta T_{lm} F = 99 \times 10^3 / (90)(93.6) (1.0) = 11.8 \text{ m}^2$$

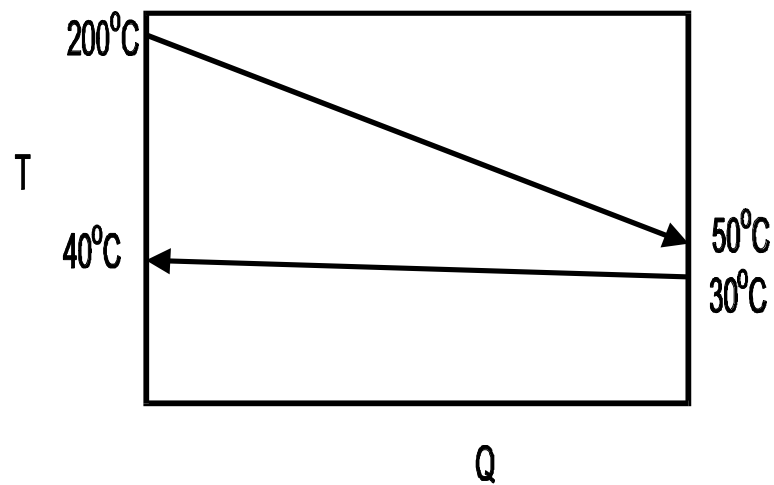
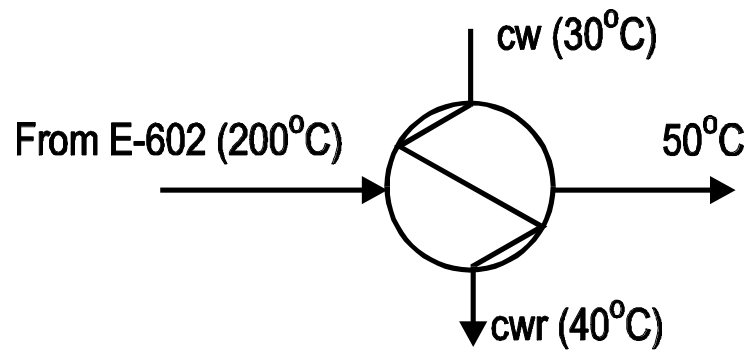
For Zone II

$$\Delta T_{lm} = \frac{(239 - 160) - (511 - 160)}{\ln \frac{(239 - 160)}{(511 - 160)}} = 182.4^\circ \text{C}$$

$$A_{II} = Q_{II} / U_{II} \Delta T_{lm} = 693 \times 10^3 / (90) (182.4) = 42.2 \text{ m}^2$$

$$\text{Total Area } A = A_I + A_{II} = 11.8 + 42.2 = 54 \text{ m}^2$$

Crude Allyl Chloride Cooler ,E-603



$$C_{p, \text{gas}} = 1490 \text{ J/kg.K}$$

$$Q = m C_{p, \text{gas}} \Delta T = (4590) (1490) (200 - 50) / 3600 = 0.285 \text{ MW}$$

$$m_{\text{cw}} = (0.285 \times 10^6) / (4180) (10) = 6.82 \text{ kg/s}$$

$$\Delta T_{\text{lm}} = (160 - 20) / \ln (160/20) = 67.3^\circ\text{C}$$

$$U = 90 \text{ W/m}^2 \text{ K}$$

$$A = Q/U\Delta T_{\text{lm}}F = (0.285 \times 10^6)/(90) (67.3) (0.95) = 49.5 \text{ m}^2$$

References

1. Wen, C.Y. and Y.H.Yu, AIChE J., **12**, 610 (1966)

H-601
Reactor
Feed Heater

R-601
Fluidized Bed
Reactor, Cyclone,
Regenerator

J-601
Jet Mixer

P-601 A/B
Dowtherm
Pump

E-601
Dowtherm
Cooler

E-602
Waste Heat
Boiler

E-603
Crude Allyl
Chloride Cooler

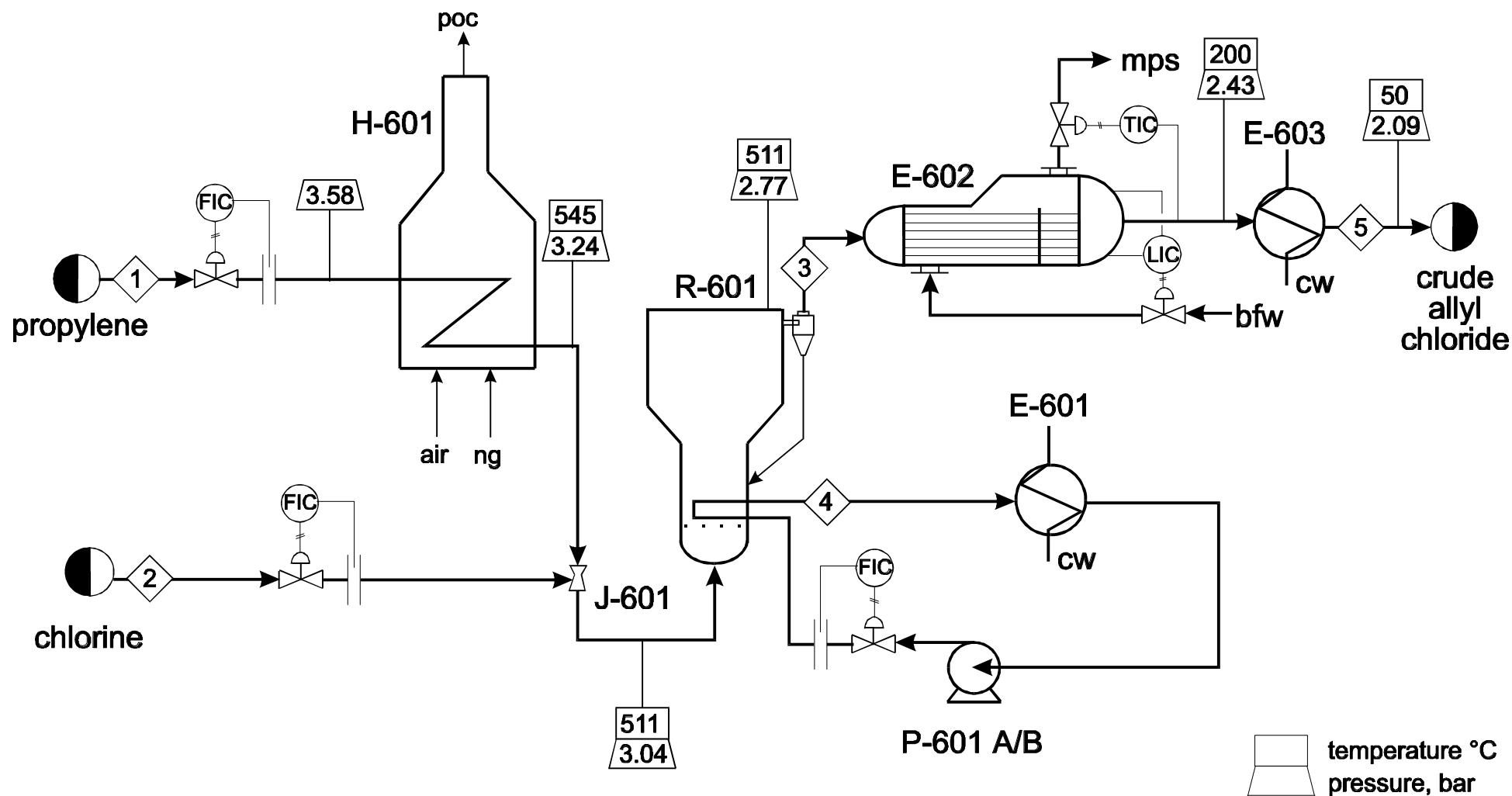


Figure 1: Reaction Section of Allyl Chloride Process

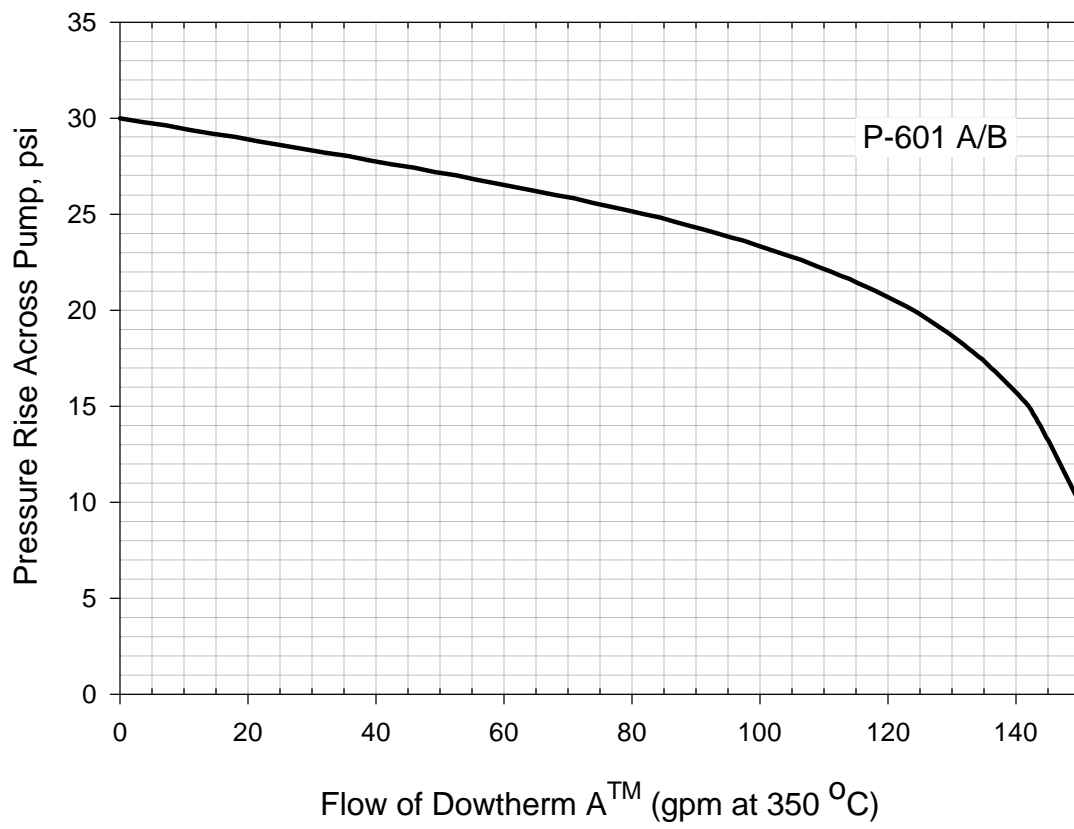


Figure 2: Pump Curve for P-601 A/B, Dowtherm ATM Circulation Pumps