ChE 182
Major #1
Acrylic Acid Process

Background

The plant at which you are employed currently manufactures acrylic acid in Unit 300 by the catalytic oxidation of propylene. Plant capacity is on the order of 50,000 metric tons per year of acrylic acid, with acetic acid produced as a salable by-product.

Acrylic Acid Production Reactions

The reactions for acrylic acid production from propylene as follows:

$$\underset{\textit{propylene}}{C_3H_6} + \frac{3}{2}O_2 \rightarrow \underset{\textit{acrylic acid}}{C_3H_4O_2} + H_2O \tag{1}$$

$$\underset{\textit{propylene}}{C_3H_6} + \frac{5}{2}O_2 \rightarrow \underset{\textit{acetic acid}}{C_2H_4O_2} + CO_2 + H_2O \tag{2}$$

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

The reaction kinetics are of the form:

$$-r_i = A_i \exp\left[-\frac{E_i}{RT}\right] p_{propylene} p_{oxygen}$$

where *i* is the reaction number above, and

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

Process Description

The propylene is fed from a storage tank. Air is compressed as a source of oxygen. Steam is used to provide thermal ballast for the exothermic heat of reaction. After being mixed, the feeds enter the reactor. Reactor effluent proceeds to a quench tower (T-301) where the reaction is rapidly quenched, to avoid further oxidation, with a cool acrylic acid recycle stream. Additional recovery of acrylic acid and acetic acid occurs in an absorber, T-302. The stream leaving the absorption section is a dilute, aqueous acid mixture. It then proceeds to an extraction unit, X-301, which contains and extractor and a solvent recovery tower. This unit was designed and is operated under contract by ExtractoCorp. Stream 15 contains virtually all of the acrylic acid and acetic acid fed to X-301. Final purification occurs in T-303, where 99.9 mole% acrylic acid is produced as the bottom product, and 95 mole% acetic acid is produced as the top product. The acrylic acid product is cooled prior to being sent to storage. The acrylic acid temperature should never exceed 90°C in order to avoid spontaneous polymerization.

Short-Term Problem

We have been having problems with T-303. In the past, we have had trouble meeting the acetic acid by-product purity specification, which has tightened over the years. T-303 has been pushed to its design limits in order to meet the tougher acetic acid specifications. In March 1997, prior to the annual shut down, a tray loading study of the tower showed that operation at that time was very close to flooding. This meant that the purity specification on acetic acid could not be increased further without lowering the acrylic acid purity, which is, of course, the more important product.

It was decided to change the design of the column by retrofitting T-303 with four new trays. The original design of the column had four additional trays below the feed, but these were removed many years ago, the reason for doing so now being unknown. When this was done, a new feed nozzle was installed four trays above the original feed nozzle, but the original feed nozzle was left intact. With the addition of the four new trays and the return to the original feed nozzle, the number of trays above the feed was increased to increase the acetic acid purity. Details of the column operation prior to the March 1997 shut down and the modifications to the column implemented during the shut down are detailed in Appendix 3.

When the column was brought on line in early April 1997, the acetic acid purity was, as expected, increased and now currently is slightly in excess of specification. Since the column retrofit, some additional changes in performance of Unit 300 have been observed. First, the acrylic acid pumps, P-304 A/B, have required significant maintenance, and both bearings and impellers had to be changed. Second, during a very hot spell (in excess of 100°F), the acrylic acid product has failed to meet its color specification, which is water white. Test samples from the storage tank show the product to be cloudy, and this has caused some concern from our customers who require strict adherence to this specification. Tests of the cooling water system showed the inlet cooling water temperature to be 35°C during this heat wave. Concurrent with this problem was an upset in the inhibitor monitoring pump, which meters inhibitor into the acrylic

acid storage tank in order to suppress polymerization. It is believed that loss of the inhibitor was the cause of the loss of color specification, but we require confirmation of this.

Your assignment is to analyze this situation, to suggest causes for the observed problems with the acrylic acid product, and to suggest possible remedies for these problems. Suggested remedies should be able to be implemented without another shut down.

Long-Term Problem

Additional concerns in the plant include the long-term increased demand for acrylic acid and the need to increase production levels further. A 20% increase in acrylic acid production is the target number. At present, the purification column is a bottleneck and would have to be improved before any capacity increase could be considered. A recent visit from a tower packing vendor has given some hope that the tower could be debottlenecked further by the use of a high-capacity, low pressure drop column packing, SupraFlow (SF).

An increase in production capacity is a long-term goal that will surely require additional capital expenditures. The quench and extraction sections are being investigated by other groups and ExtractoCorp, respectively. Your assignment is to investigate what is required to increase capacity of the reactor and cooling loop by 20%. Specifically, you should estimate the minimum additional cost in the reactor and cooling loop (R-301, E-301, and P-301 A/B) associated with scale up acrylic acid of production by 20%. If there are several low-cost alternatives, the profitability of these alternatives should be compared using an appropriate economic analysis.

Deliverables

A written report of your results, an analysis of your results, your conclusions, and your recommendations is required by 9:00 am, Monday, November 3, 1997. There will be an oral presentation of your results which will be scheduled between Monday, November 3, 1997 and Friday, November 7, 1997. More details about the written and oral reports are given below.

Report Format

This report should be brief. Most of the report should be an executive summary, not to exceed 10 double-spaced, typed pages, which summarizes your diagnosis, recommendations, and rationale. Figures and tables may be included (do not count against page limit) in the executive summary. An appendix should be attached which includes items such as the requested calculations. These calculations should be easy to follow. The confidentiality statement should be the very last page of the report.

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

Oral Presentation

You will be expected to present and defend your results to ST's management representatives some time between November 3 and November 7, 1997. Your presentation should be 15-20 minutes, followed by about a 30 minute question and answer period. Make certain that you prepare for this meeting since it is an important part of your assignment. You should also prepare a hard copy of your transparencies to be handed in at the beginning of your report.

Late Reports

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

- late report on due date before noon: one letter grade
- late report after noon on due date: two letter grades
- late report one day late: three letter grades
- more than one day late: failing grade

Appendix 1

Figure 1, on the next page, is a flowsheet of Unit 300 as it was designed. The stream table which follows identifies design operating conditions, which, as far as we know, reflect the actual operating conditions prior to the shut down.

C-301 A/B Inlet Air Blower
E-301 Molten Salt Cooler
P-301 A/B Molten Salt Circulation Pumps
R-301 Reactor
T-301 Quench Tower
T-302 Off-Gas Absorber
P-302 A/B Quench Pumps
E-302 Quench Cooler
X-301 Extraction Unit
T-303 Acid Tower
E-303 Acid Reboiler
P-303 A/B Acid Reflux Pumps
V-301 Acid Reflux Drum
E-304 Acid Condenser
P-304 A/B Product Pumps
E-305 Product Cooler

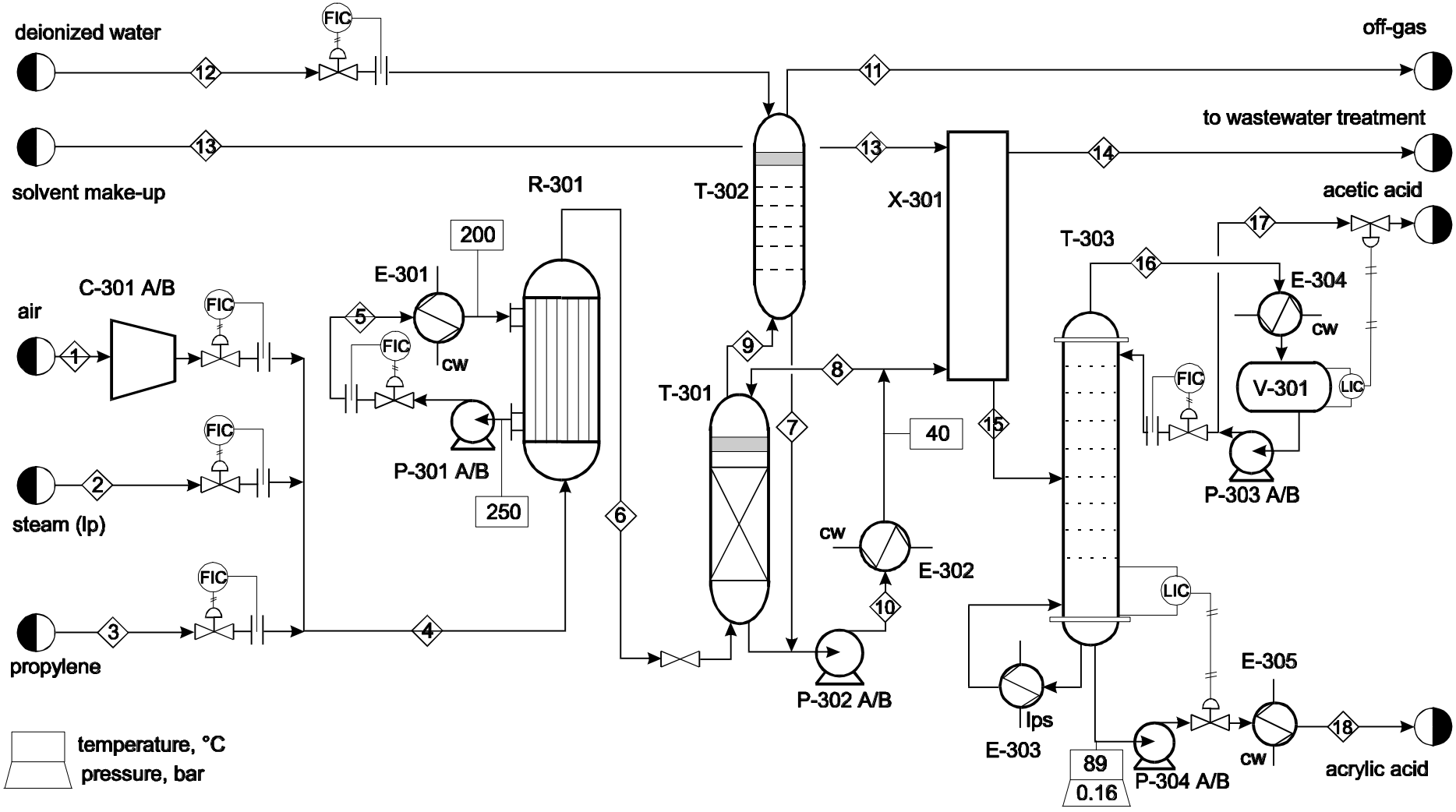


Figure 1: PFD for Unit 300 - Acrylic Acid from Proyplene

Table 1: Stream Flow Table

Stream No.	1	2	3	4	5	6	7	8	9
Temperature (°C)	25	159	25	191	250	310	63	40	40
Pressure (bar)	1.0	6.0	11.5	4.3	3.0	3.5	2.0	2.4	1
Vapor Fraction	1.0	1.0	1.0	1.0	0.0	1.0	0.0	0.0	0.0
Mass Flow (tonne/h)	39.05	17.88	5.34	62.27	1070.0	62.27	3.08	1895.	37.89
Mole Flow (kmol/h)	1362.9	992.3	127.0	2482.2	-	2444.0	148.5	85200.0	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	150.1
Acetic Acid	-	-	-	-	-	6.54	0.65	415	1.11
Acrylic Acid	-	-	-	-	-	87.79	6.99	5915	7.97

Table 1: Stream Flow Table (continued)

Stream No.	10	11	12	13	14	15	16	17	18
Temperature (°C)	50	48	25		102	90	47	47	40
Pressure (bar)	2.4	1.0	5.0		1.10	0.19	.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 2: Utility Summary

Stream Name	cw to E-301	cw to E-302	lps to E-303*	cw to E-304	cw to E-305
Temp °C	32	32	160	32	32
Pressure bar	4.00	4.00	10.00	4.00	4.00
Flowrate in 10^3kg/h	1,995	1,923	2.190	235.4	16.70

*throttled and desuperheated at exchanger

Appendix 2
Cost Information

Raw Materials

Propylene (polymer grade)	See *Chemical Marketing Reporter*

Products

Acrylic Acid	See *Chemical Marketing Reporter*
Acetic Acid	See *Chemical Marketing Reporter*

Utility Costs

See Table 3.4

Equipment Costs and Cost Factor

Use CAPCOST

Appendix 3
Operating Information for T-303

Data for Tower, T-303 prior to Shutdown

Extensive data gathering was done for T-303 prior to shut down. The conditions shown below reflect typical operating data prior to the shutdown.

Top temperature = 47ºC

Bottom temperature = 89ºC

Top pressure = 7 kPa

Bottom pressure = 16 kPa

Reflux rate = 193.3 kmol/h

Condenser duty = -4920 MJ/h

Cooling water supply temperature = 32ºC

Cooling water return temperature ≈ 37ºC (maximum allowable is 45°C)

Reboiler duty = 4872 MJ/h

Top product purity = 95 mol% acetic acid

Bottom product purity = 99.9 mol% acrylic acid

% flooding = 94%

Feed tray location = 22

Bottom product flow = 86.9 kmol/h

= 6260 kg/h (6460 l/h)

Top product flow = 6.31 kmol/h

= 366 kg/h (360 l/h)

Tower diameter = 2.0 m

Number of trays = 31

Trays are sieve trays with 18% open area and ¼ inch holes with a 1 inch weir

Other data along with changes made during shutdown are shown in Figure 2

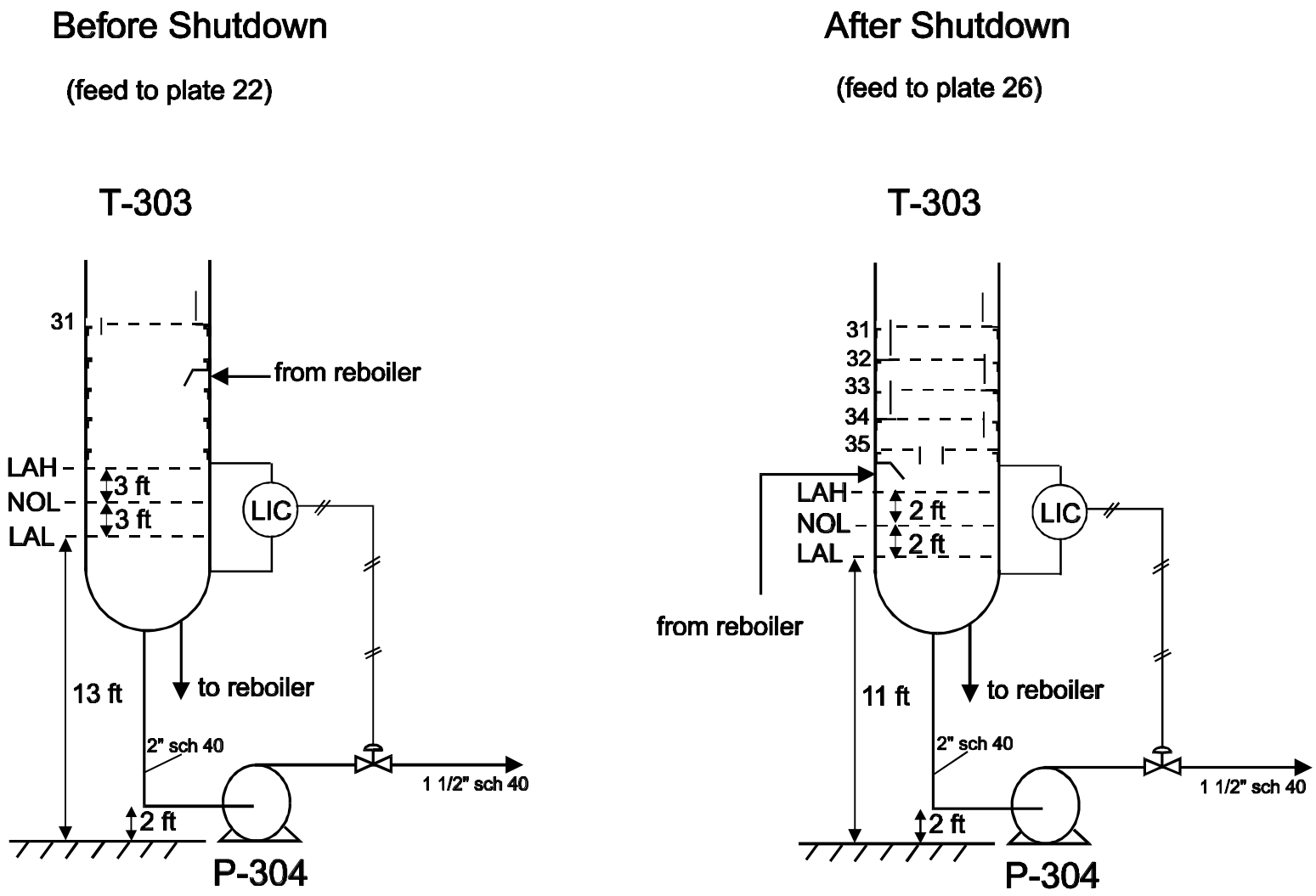


Figure 2: Modifications to T-303

Data for pump P-304 A/B prior to Shutdown

Destination pressure = 1.0 bar

Static head at storage tank = 15 ft

Heat exchanger pressure drop = 5 psi = 0.34 bar

Discharge piping - equivalent length = 800 ft

- pipe size = 1 ½ inch schedule 40

Suction piping - equivalent length = 45 ft

- pipe size = 2 inch schedule 40

Pressure in T-303 = 17 kPa = 0.17 bar

Details of pump circuit for bottom of column is given in Figure 3 and a pump curve for E-304 is given in Figure 4.

Design Data for Condenser (E-304)

Number of 3/4 in tubes (20 ft long and 17 BWG) = 374
Configuration = shell and tube, fixed tube sheet, 1 shell – 2 tube passes
Cooling water in tubes, process fluid in shell
Cooling water inlet temperature = 32ºC
Cooling water outlet temperature = 37ºC
Process fluid temperature = 47ºC (condensing – no subcooling)
Duty = 4920 MJ/h
Cooling water velocity in tubes = 1.225 m/s
h_{cw} = 4899 W/m^{2}ºC
$h_{process}$ = 2500 W/m^{2}ºC
$h_{fouling}$ (inside tubes) = 2000 W/m^{2}ºC
Resistance for cw = 20%
Resistance for process = 32%
Resistance for fouling = 48%
U = 811 W/m^{2}ºC
Heat exchanger area for E-304 = 136.6 m^2

For the small changes in process temperature that are like to occur during your analysis, you may assume that the condensing film heat transfer coefficient ($h_{process}$) is constant.

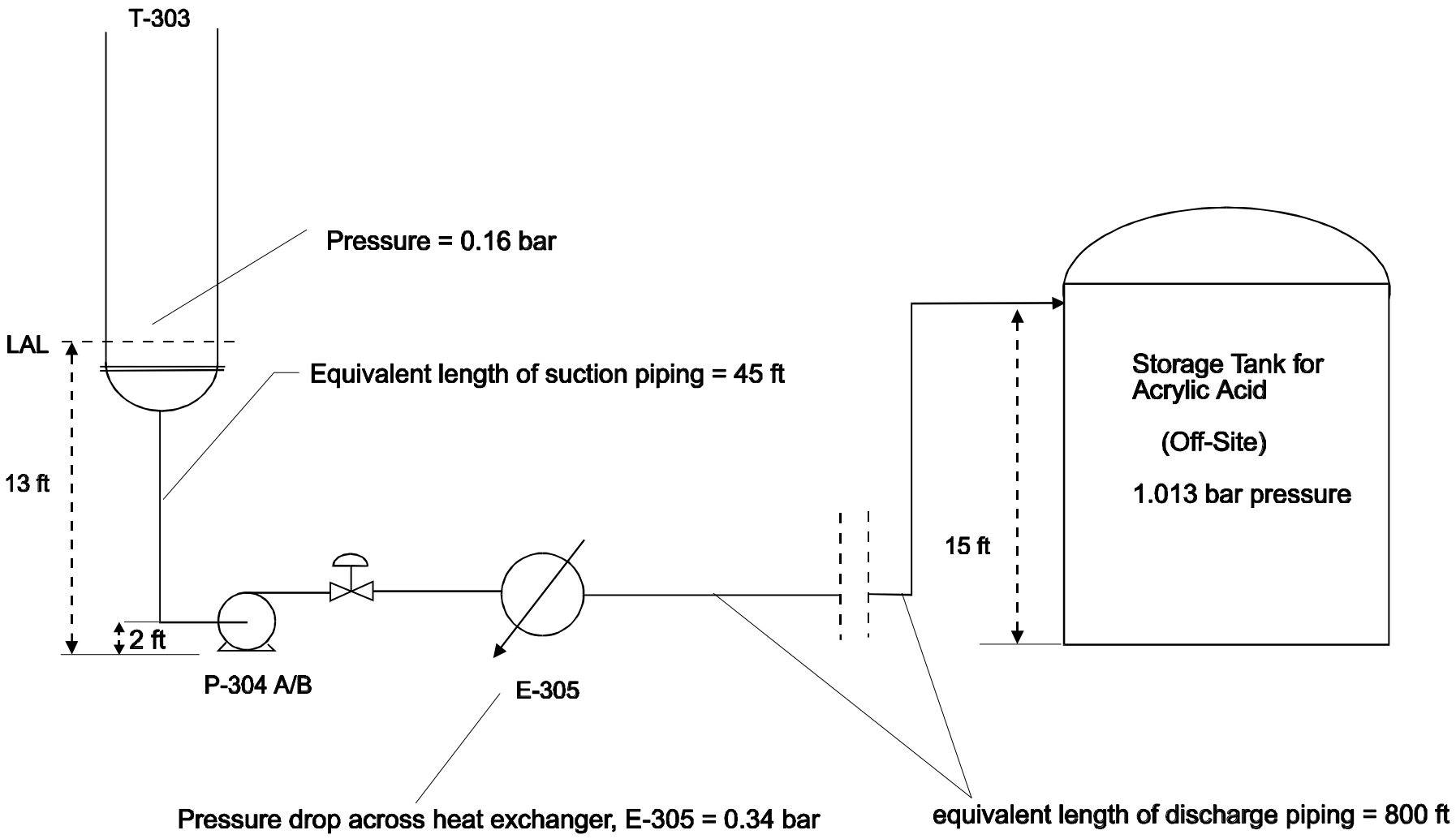
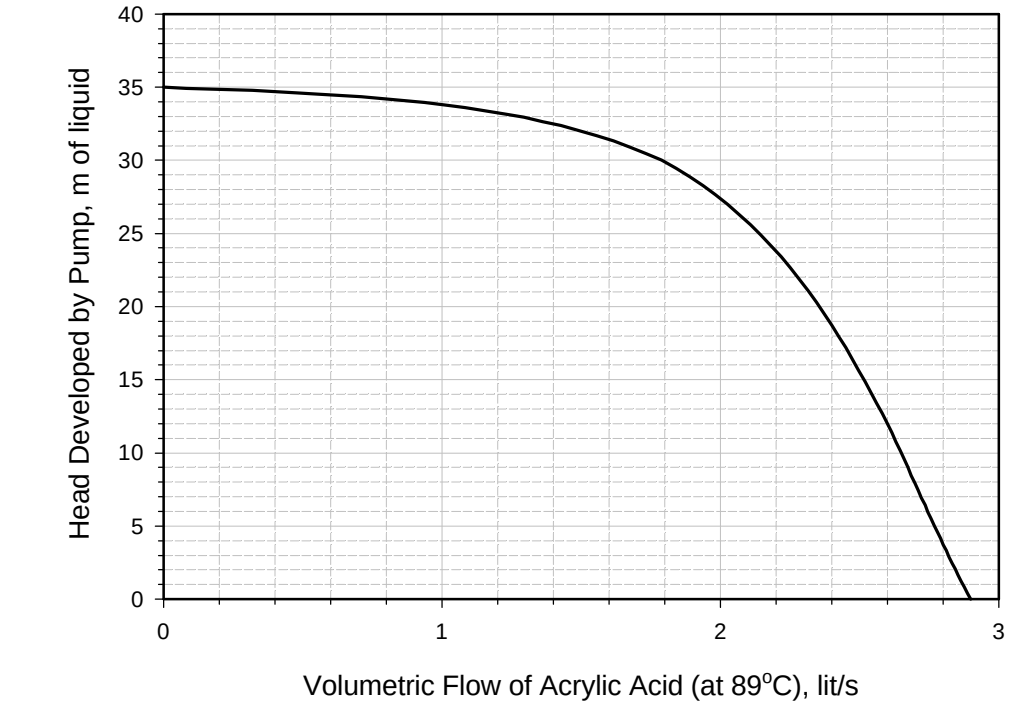


Figure 3: Operating Conditions for Bottoms Pump before Shutdown.



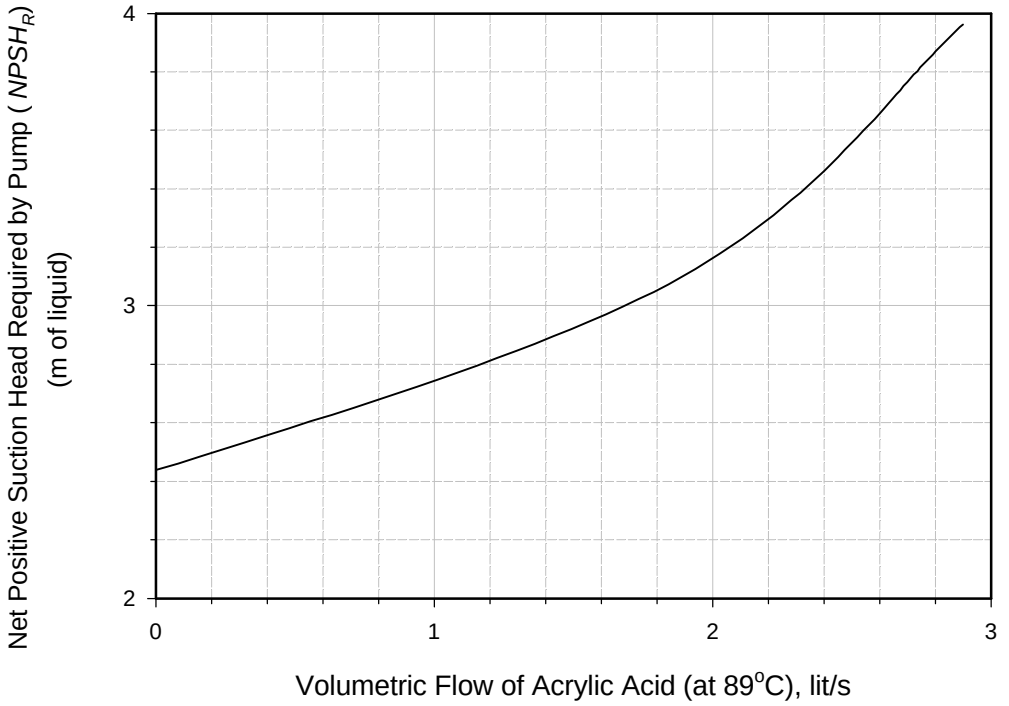


Figure 4: Pump Curve for P-304 A/B

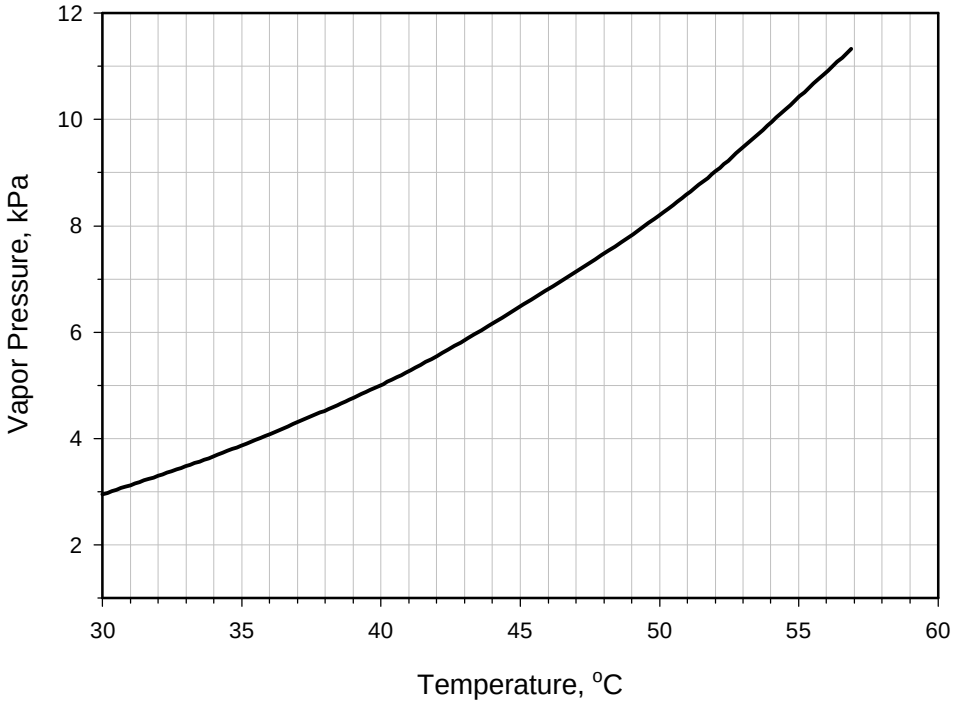
Design Data for Reboiler (E-303)

Heat Exchanger area for E-303 = 43 m^2
Condensing steam temperature = 116ºC (throttled and desuperheated using lps)
Process fluid temperature = 89ºC
Duty = 4870 MJ/h

For this analysis, you should assume that the overall heat transfer coefficient is a very weak function of temperature driving force and it is unaffected by flow of steam or process fluid. Therefore, as a first approximation, assume that the overall heat transfer coefficient, *U*, is constant.

Vapor pressure for the top and bottom products as functions of temperature is given in Figure 5.

Vapor Pressure of Overhead Acetic Acid Product as a Function of Temperature



Vapor Pressure of Bottoms Acrylic Acid Product as a Function of Temperature

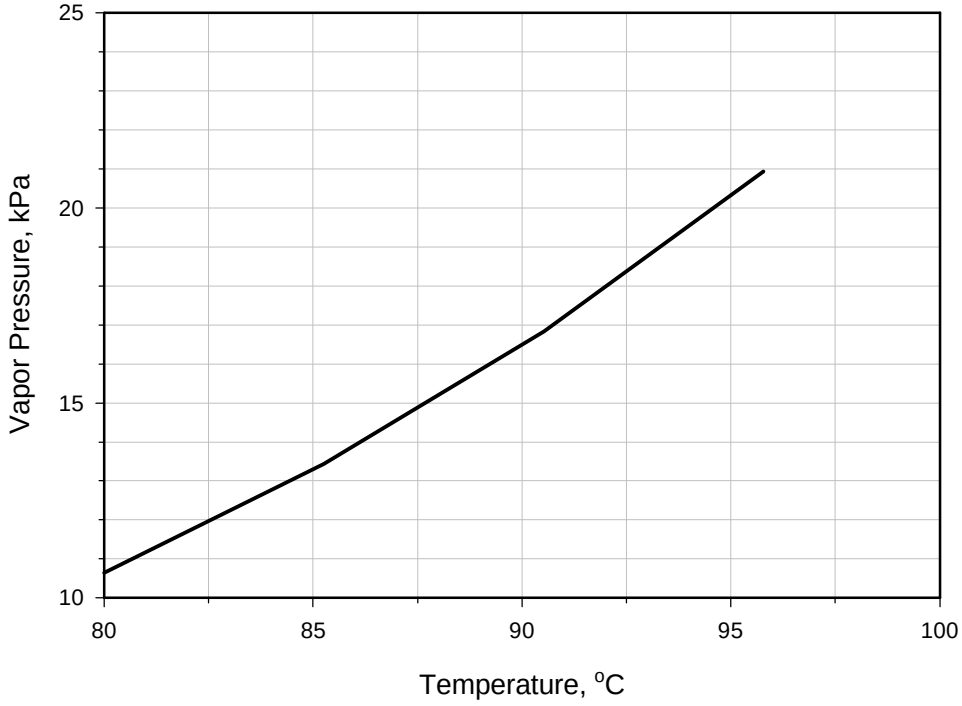


Figure 5: Vapor PressureVariation with Temperature for Top and Bottom Products

Appendix 4
Operating Information for Reactor Cooling Loop

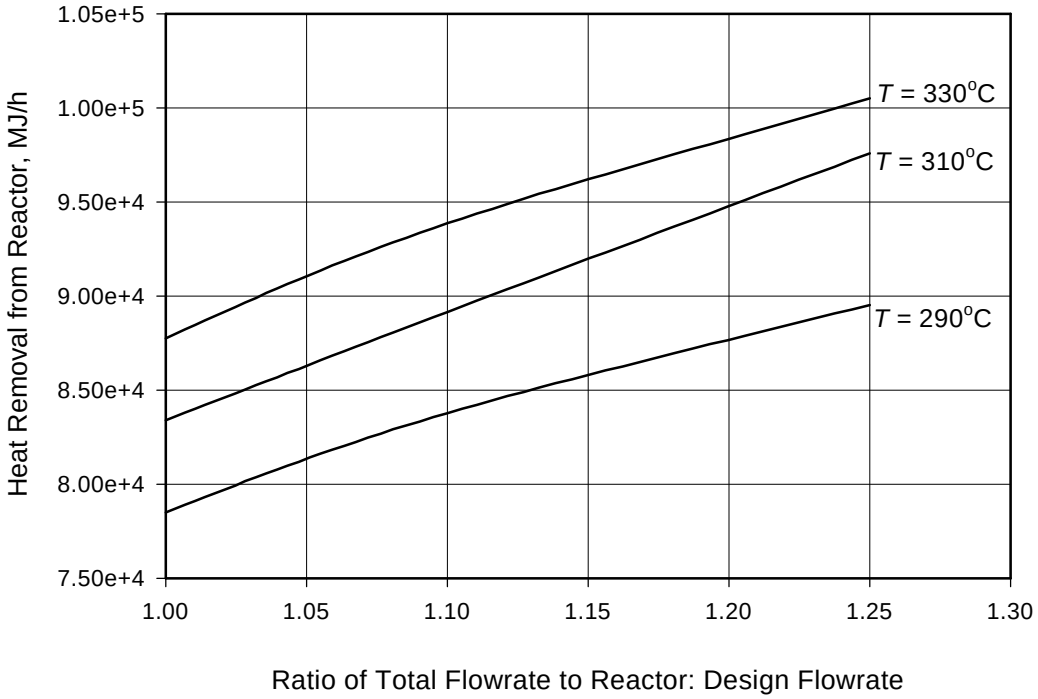
Characteristics of Fluidized Bed Reactor, R-301

The performance of the acrylic acid reactor is complex, due in part to the competing reactions and also because the hydrodynamics of the fluidized bed are complex and do not change linearly. In order to help you in evaluate the performance of this reactor, a series of case studies were carried out, and the results of these cases are summarized below.

The operation of the reactor [for the same reactor geometry, the same catalyst, and same active bed volume (catalyst volume)] can be varied over a narrow range of operating parameters. The maximum feed flowrate that can be handled by the existing internal cyclone system within the reactor is approximately 125% of the current flow. The operating temperature can be increased to 330ºC from the current condition of 310ºC. The reactor temperature can also be reduced to 290ºC. Operation outside these temperature limits is not recommended due to the possibility of quenching the reaction at lower temperatures than 290ºC and reactor integrity concerns at temperatures above 330ºC. The conversion of propylene in the reactor at different operating temperatures and different flowrates is presented in Figure 6 (lower graph). The horizontal axis is plotted as the new flow divided by the current (design) flow. Thus, a value of 1.25 represents an increase in inlet gas flow of 25% compared to the present conditions. The composition of the inlet gas is assumed to be the same as currently used, i.e., the air, propylene, and steam flows all increase by 25%. From preliminary work with the air feed compressor (C-301), it is believed that the maximum flow increase of air will be close to 25%. This fact, coupled with the amount of solids that the cyclones can handle, suggests that a 25% increase in the feed gas flow is a bottleneck for the system and that you should not exceed this flow when analyzing the reactor.

The selectivity of the reactions is a strong function of temperature but are not affected by flowrate over the range in which we are interested. The selectivity and yield are given below for three temperatures. You may interpolate linearly to obtain values at intermediate temperatures.

Temperature in Reactor	**Selectivity**	**Yield**
	$\frac{\text{Acrylic Acid}}{\text{Acetic Acid}}$	$\frac{\text{Acrylic Acid}}{\text{Total Propylene Reacted}}$
290ºC	15.65	0.8233
310ºC	13.40	0.7817
330ºC	11.60	0.7357



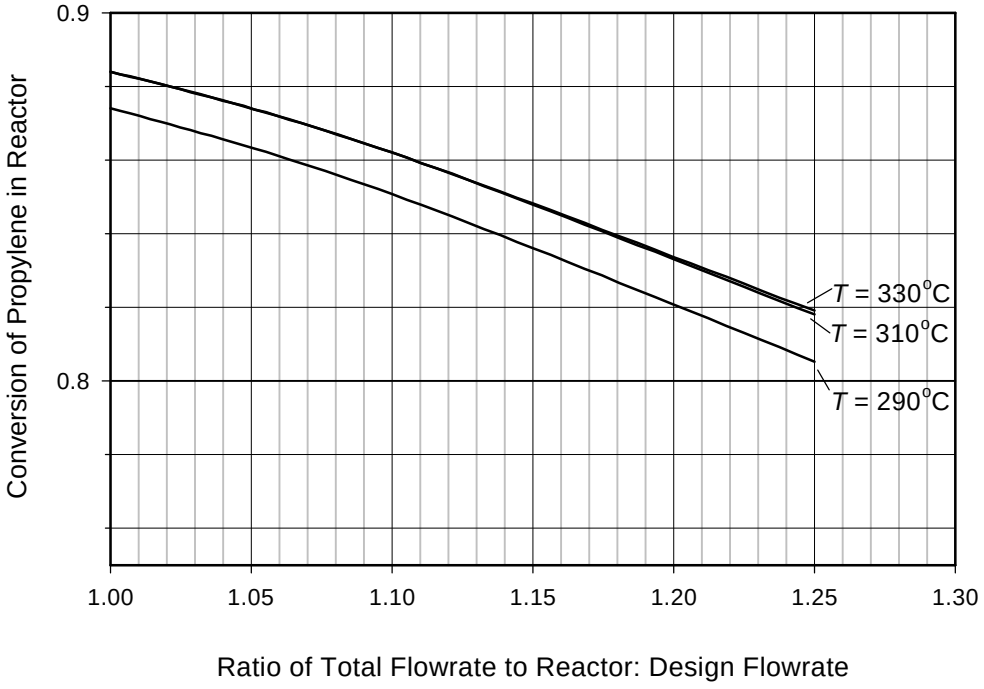


Figure 6: Conversion and Heat Removal Rate for Reactor, R-301, at Different Flows and Temperatures

Design Details of E-301 – Molten Salt Cooler

Temperature of cooling water in = 32°C
Temperature of cooling water out = 42ºC
Temperature of molten salt in = 250ºC
Temperature of molten salt out = 200ºC
Area = 160 m^2
Duty = 83400 MJ/h

Cooling water flow can be increased by approximately 30% without long term erosion problems. For this heat exchanger, it has been estimated that the heat transfer resistances are approximately equal, i.e., $h_{cw} \approx h_{ms}$.

The properties of the molten salt used for this service are as follows:

Density = 2000 kg/m^3
Melting point = 143ºC
Thermal conductivity = 0.606 W/m K
Viscosity = 0.0017 kg/m s (at 425ºC)
= 0.017 kg/s at (200ºC)
Specific heat = 1560 J/kgºC
Vapor Pressure at 250°C < 1 kPa

Design Details of Heat Exchanger in Fluidized Bed Reactor, R-301

Heat transfer area in fluidized bed = 1420 m^2
Temperature of molten salt in = 200ºC
Temperature of molten salt out = 250ºC

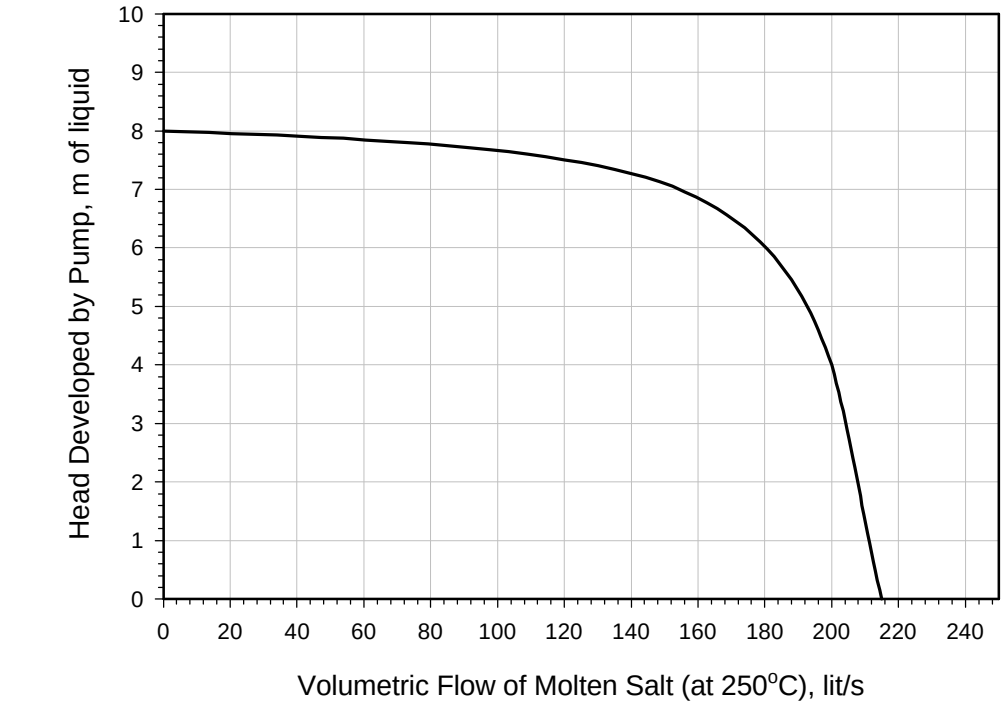
All resistance to heat transfer is on the fluidized bed side (outside tubes).

For the increase in flow being considered here, you should assume that the heat transfer coefficient on the fluidized bed side of the reactor does not change.

Pump Circuit for Molten Salt

The following data were obtained from a plant inspection a few weeks ago and represent the current operating conditions.

Pressure drop through E-301 = 29 kPa
Pressure drop through heat transfer tubes in R-301 = 37 kPa
Pressure drop through loop piping = 21 kPa
Pressure drop across control valve = 53 kPa
The pump curve for P-301 is shown in Figure 7.



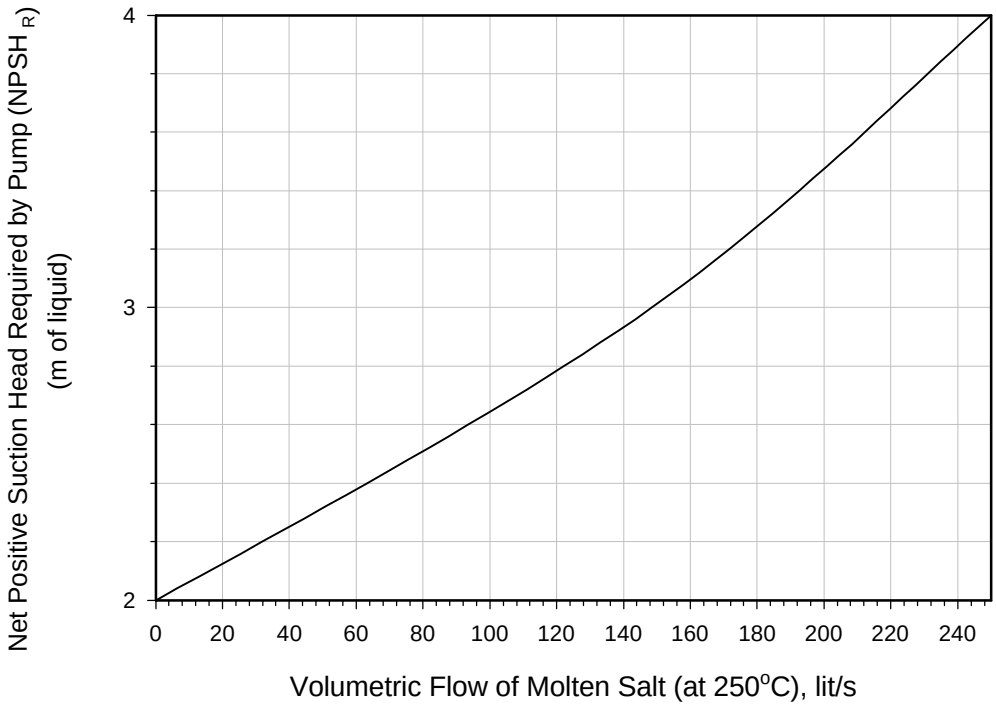


Figure 7: Pump Curve for P-301 A/B