Separations and Reactors
Design Project

Production of Allyl Chloride

Process Objective Function

We must now complete gathering information that will allow our firm to increase allyl chloride capacity by building a new plant in La Nueva Cantina, Mexico. To accomplish this goal, we request that your design team complete the estimate for the *minimum* allyl chloride market price such that the construction and operation of a new plant, which will produce 20,000 metric tons/y of allyl chloride, will be profitable. Compare your calculated minimum cost for allyl chloride with the current selling price. It can be found in the *Chemical Marketing Reporter* at the Evansdale Library along with the cost of the raw materials. The break-even price of allyl chloride is to be used as the objective function to optimize the process. The equation to be used to estimate this price is given below:

(Allyl Chloride Produced per Year) (C_B) =
Annuity Value of Total Installed Cost + Annual Cost of Raw Materials + Annual Utility Cost - Annual Revenue from By-products - Annual Credit from Fuel Gas and Steam

where C_B is the break-even price for cumene

The above equation for estimating the cost of allyl chloride is based on the minimum price that allyl chloride could be sold for to cover our operating expenses. A 10-year plant lifetime and an interest rate of 15% should be used.

Allyl Chloride Production Reactions

We have developed a new catalyst which we plan to implement in the new design. This catalyst can work at any pressure from atmospheric up to 40 bar. The active temperature range is between 400°C and 540°C. Below 400°C, the catalyst is essentially inactive. As long as the temperature in the reactor never exceeds 540°C, the carbon formation reaction is completely suppressed. With the suppression of this reaction, a shell-and-tube packed bed configuration can be used which is significantly less expensive than the fluidized bed used in our other plants. The kinetics for the reactions are given below.

For the primary reaction:

$$C_3H_6 \quad + \quad Cl_2 \xrightarrow{k_1} C_3H_5Cl \; + \; HCl$$

propylene allyl chloride

$$r_1 = k_1 p_p p_{Cl} \quad \text{kmole / kg cat s kPa}^2$$

$$k_1 = 0.322 \exp\left(\frac{-63{,}200}{RT}\right)$$

For the secondary reactions:

$$C_3H_6 \quad + \quad Cl_2 \xrightarrow{k_2} C_3H_5Cl \; + \; HCl$$

propylene 2 – chloropropene

$$r_2 = k_2 p_p p_{Cl} \quad \text{kmole / kg cat s kPa}^2$$

$$k_2 = 1.83 \times 10^{-5} \exp\left(\frac{-16{,}000}{RT}\right)$$

$$C_3H_6 \quad + \quad 2Cl_2 \xrightarrow{k_3} C_3H_4Cl_2 \; + \; 2HCl$$

propylene 2 - 3 dichloropropene

$$r_3 = k_3 p_p p_{Cl}^2 \quad \text{kmole / kg cat s kPa}^3$$

$$k_3 = 1.27 \times 10^{-3} \exp\left(\frac{-72{,}100}{RT}\right)$$

where the units of the activation energy are kJ/kmol, the units of pressure are kPa, and the temperature is in Kelvin.

For a shell and tube packed bed, the recommended configuration, the following data may be assumed:

catalyst particle diameter d_p = 3 mm
catalyst particle density ρ_{cat} = 2000 kg/m^3
void fraction ε = 0.50
heat transfer coefficient from packed bed to tube wall h = 60 W/m^2°C
use standard tube sheet layouts as for a heat exchanger
if tube diameter is larger than in tube sheet layouts, assume that tube area is 1/3 of shell area

Separation Section

The crude allyl chloride product leaving the feed/reactor section must be purified. Initially, the unreacted propylene, unreacted chlorine, and gaseous HCl are separated from the chlorides. The HCl is absorbed into deionized water to make the aqueous HCl product. The operating costs should include the required amount of water. The propylene and chlorine are not absorbed and can be recycled. It may be assumed that all unreacted propylene and chlorine is recycled (at 40°C and about the same pressure at which the reactor operates), and that all gaseous HCl goes to aqueous product. The design of this portion of the process is being contracted to AcidCorpÔ, and you are not required to design this part of the process. AcidCorpÔ informs us that the estimated capital cost (purchased) for their part of the process is $1.25 million, and that annual operating costs exclusive of deionized water are about $325,000. They require the crude allyl chloride feed stream to their unit be saturated liquid at any pressure between 2 bar and 40 bar.

The process described above may be simulated with one or more component separators. The chlorides stream is then separated into three purified streams in a series of distillation columns. Both by-product streams should be purified so they can be sold. It is part of the assignment to determine the optimal sequence for these distillation columns. Only the column which purifies the allyl chloride product needs to be designed in detail.

If refrigeration is needed anywhere in the separation section, the cost given for refrigeration should be used. A refrigeration cycle need not be designed.

Specific Assignments

General

Optimize the process using decision variables of your choosing. You should choose as decision variables the design variables most strongly affecting the objective function.

ChE 112 - Separations

Determine the number of distillation columns required, their location, and enough information for each distillation column to cost it. The distillation column that provides the allyl chloride product should be designed in detail.

ChE 172 - Reactors

The reactor is a packed bed with countercurrent cooling. Therefore, optimize the process for this reactor. You must choose and discuss your choice of decision variables. At no place along the length of the process side of the reactor should the temperature exceed 540°C. Also, the reactor process side inlet temperature must be at least 400°C so the reaction can commence. A filler material is available which has the same density, diameter, void fraction, heat capacity, price, etc., of the catalyst. It is inert and may be installed within the reactor without catalyzing the reaction. Since Chemcad has no allowance for the Ergun equation, hand estimate the pressure drop on the process side of the reactor and plug it into Chemcad for each simulation. Your design team must provide a copy of the design equations that include the Ergun equation, and plots of coolant and reactor temperature, pressure, and concentrations of the chemical species versus reactor length for the optimal reactor design. Solve these equations using Polymath or another ordinary differential equation solver. Repeat this design/analysis for the other reactor type. Discuss/compare both the analytical and Chemcad design.

Chemcad Hints

Use SRK for the entire process.

For heat exchangers with multiple zones, it is recommended that you simulate each zone with a separate heat exchanger. Actual equipment may include several zones, so costing should be based on the actual equipment specifications.

For the distillation columns, you should use the shortcut method (SHOR) to get estimates for the rigorous distillation simulation (TOWR or SCDS). The shortcut method may be used until an optimum case is near. It is then expected that everyone will obtain a final design using rigorous simulation of the columns.

When simulating a process using “fake” streams and equipment, it is absolutely necessary that the process flow sheet that you present not included any “fake” streams and equipment. It must represent the actual process.

Cost Data

Equipment Costs (Purchased)

Pumps	$\$630\ (\text{power, kW})^{0.4}$
Heat Exchangers	$\$1030\ (\text{area, m}^2)^{0.6}$
Compressors	$\$770\ (\text{power, kW})^{0.96} + 400\ (\text{power, kW})^{0.6}$
Turbine	$\$2.18 \times 10^5\ (\text{power output, MW})^{0.6}$ assume 65% efficiency
Fired Heater	$\$635\ (\text{duty, kW})^{0.8}$ assume 80% thermal efficiency assume can be designed to use any organic compound as a fuel
Vessels	$\$[1.67(0.959 + 0.041P - 8.3 \times 10^{-6}P^2)] \times 10^z$ $z = (3.17 + 0.2D + 0.5 \log_{10}L + 0.21 \log_{10}L^2)$ D = diameter, m $0.3\text{ m} < D < 4.0\text{ m}$ L = height, m $L/D < 20$ P = absolute pressure, bar
Catalyst	\$2.25/kg
Reactor	Cost as vessel with appropriate additional volume for cooling coil (fluidized bed) or tubes (shell and tube packed bed)
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
Storage Tank	$\$1000V^{0.6}$ V = volume, m^3

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.

Raw Materials

Chlorine (highest purity)	see *Chemical Marketing Reporter*
Propylene (polymer grade)	see *Chemical Marketing Reporter*

Products

Allyl Chloride (99.9 mole% required)	see *Chemical Marketing Reporter*
2-chloropropene (95 mole% required)	\$0.15/kg
2-3 dichloropropene (95 mole % required)	\$0.10/kg
20°Baumé HCl solution (31.5 wt%)	see *Chemical Marketing Reporter*

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
Cooling Water available at 516 kPa and 30°C return pressure ≥ 308 kPa return temperature is no higher than 45°C	\$0.16/GJ
Refrigerated Water available at 516 kPa and 10°C return pressure ≥ 308 kPa return temperature is no higher than 20°C	\$1.60/GJ
Refrigeration	\$60/GJ

Equipment Cost Factors

Pressure (absolute)	< 10 atm, 0.0 10 - 20 atm, 0.6 20 - 40 atm, 3.0 40 - 50 atm, 5.0 50 - 100 atm, 10	does not apply to turbines, compressors, vessels, packing, trays, or catalyst, since their cost equations include pressure effects
Carbon Steel	0.0	
Stainless Steel	4.0	

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

Heat Exchangers

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

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

Other Information

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

Unless specifically stated in class, the information in this document is that which is valid for this project only. Any information in the sophomore projects not specifically stated in this document is invalid for this project.

Deliverables

Each group must deliver a report (two identical copies, one for each professor) written using a word processor. The report should be clear and concise. The format is explained in the document *Written Design Reports*. Any report not containing a labeled PFD and a stream table, each in the appropriate format, will be considered unacceptable. PFDs from CHEMCAD are generally unsuitable unless you modify them significantly. When presenting results for different cases, graphs are superior to tables. For the optimal case, the report appendix should contain details of calculations that are easy to follow. There should be separate appendices for each class, ChE 112 and ChE 172, each containing calculations appropriate for the respective class. These may be handwritten if done so neatly. Calculations that cannot be easily followed will lose credit.

Each group will give an oral report in which the results of this project will be presented in a concise manner. The oral report should be between 15-20 minutes, and each group member must speak. A 5-10 minute question-and-answer session will follow. Instructions for presentation of oral reports are provided in a separate document entitled *Oral Reports*. The oral presentations will be Wednesday, April 22, 1997 starting at 11:00 a.m. and running until approximately 3:00 p.m. It is possible that some presentations will be on Thursday, April 23, 1997, beginning at 11:00 am. Attendance is required of all students during their classmates' presentations (this means in the room, not in the hall or the computer room). Failure to attend any of the above required sessions will result in a decrease of one-letter grade (per occurrence) from your project grade in ChE 112 and ChE 172.

The written project report is due by 11:00 a.m. Wednesday, April 22, 1997. Late projects will receive a minimum of a one letter grade deduction.

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.