Separations and Reaction Engineering
Design Project

Styrene Production

Your assignment is to continue evaluating the details of a process to produce 100,000 tonne/y of styrene from ethylbenzene in an 8200-hour year. This is the amount of styrene in the product stream, not the total mass of the product stream. The ethylbenzene feed is available from another part of the plant at 210 kPa and 136°C. The composition is 95 mol% ethylbenzene, 3 mol% toluene, and 2 mol% benzene. The styrene purity is to be 99.8 wt% liquid at 250 kPa. The liquid styrene temperature may not exceed 125°C to avoid spontaneous polymerization.

Chemical Reactions

The reactions for styrene production are as follows:

$$C_6H_5C_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_6H_5C_2H_3 + H_2 \tag{1}$$

ethylbenzene styrene hydrogen

$$C_6H_5C_2H_5 \xrightarrow{k_2} C_6H_6 + C_2H_4 \tag{2}$$

ethylbenzene benzene ethylene

$$C_6H_5C_2H_5 + H_2 \xrightarrow{k_3} C_6H_5CH_3 + CH_4 \tag{3}$$

ethylbenzene hydrogen toluene methane

Kinetics (subscripts on r refer to reactions in Equation (1) – (3) were obtained from the literature.[1] The positive activation energy can arise from non-elementary kinetics and/or from reversible reactions:

$$r_1 = 1.177 \times 10^8 \exp\left(-\frac{21{,}708}{RT}\right) p_{eb} \tag{4}$$

$$r_{-1} = 20.965 \exp\left(\frac{7804}{RT}\right) p_{sty}\, p_{hyd} \tag{5}$$

$$r_2 = 7.206 \times 10^{11} \exp\left(-\frac{49{,}675}{RT}\right) p_{eb} \tag{6}$$

$$r_3 = 1.724 \times 10^6 \exp\left(-\frac{21{,}857}{RT}\right) p_{eb}\, p_{hyd} \tag{7}$$

where p is in bar, T is in K, R = 1.987 cal/mol K, and r_i is in mol/m^3 reactor s. When simulating this, or any reactor in Chemcad, the units for the reactor may be set separately from the units for the rest of the simulation in the "more specifications" tab. The reaction units in Chemcad must be moles/reactor volume/time.

The styrene reaction may be equilibrium limited, and the equilibrium constant is

$$K = \left(\frac{y_{sty}\, y_{hyd}\, P}{y_{eb}}\right) \tag{8}$$

and

$$\ln K = 15.5408 - \frac{14{,}852.6}{T} \tag{9}$$

where T is in K and P is in bar.

The bulk catalyst density is 1282 kg/m^3, and the catalyst void fraction is 0.4.

Other Information

The cost for the initial charge of catalyst may be considered negligible. The catalyst maximum temperature is 600°C.

Superheated steam is added to the reactor feed to force the equilibrium to the right. Superheated steam may also be used as a source of high-temperature energy. Superheated steam may be returned to the steam plant, and its value is $8/GJ above saturation temperature, with the pressure at the level of the source of the superheated steam.

For an adiabatic, packed-bed reactor, the cost should be determined assuming the reactor is a vessel. The *L/D* ratio should be no less than five. For a shell-and-tube reactor, the reactor cost is twice the cost of a heat exchanger with the appropriate heat-transfer area.

Toluene and benzene can be returned elsewhere in the plant in the same stream; they need not be separated from each other. There is no credit available.

Specific Assignments

1. Separations Design – (ChE 312)

You are to determine the number of distillation columns required, their locations, their sequence, their type (tray of packed), and enough information for each column to determine their costs. The distillation column that purifies styrene should be designed in detail. A detailed design of a tray tower includes number of trays, tray spacing, diameter, reflux ratio, weir height, top and bottom pressure specifications, and design of auxiliary equipment (heat exchangers, pump, reflux drum, if present). A detailed design of a packed tower includes height, packing size and type, and the same other specifications as in a tray tower. For all columns in this project, you may assume that *HETP* = 0.6 m. For the distillation column, the better economical choice between a packed and tray tower should be determined. For either a packed or a tray distillation column, the optimum reflux ratio should be determined. Since the separation section of this process is likely to operate at a vacuum, issues associated with vacuum columns might impact the choice between a tray tower and a packed tower.

Note that a tower consists of a vessel with internals (trays or packing). The constraints on a vessel are typically a height-to-diameter ratio less than 20. However, it is possible to extend this ratio to 30 as long as the tower is less than about 3 ft (1 m) in diameter. For larger diameter towers, stresses caused by wind limit the actual height. Extra supports are needed for a height-to-diameter ratio above 20, even for smaller diameter columns. Therefore, there is a capital cost "penalty" of an additional 25% (only on the vessel) up to a ratio of 25, and a "penalty" of an additional 100% up to a ratio of 30.

You must choose the operating pressures for each column subject to constraints of operating temperature and available utilities. If vacuum columns are needed, pressure drop becomes a significant concern. As an alternative to tray towers, packed towers with a low-pressure-drop structured packing may be used. The packing factors for some packings are provided in Wankat[2] beginning on p. 394. Assume the HETP for the structured packing to be 0.6 m (see the definition of HETP in Wankat[2], p. 391, and the relationship between HETP and H_{OG} in Equation (16.36) in Wankat[2].), and that the pressure drop is 0.2 kPa/m (0.245 inch water/ft).

2. Reactor Design – (ChE 325)

Several reactor types may be considered for use in this design and should be optimized separately. The one resulting in the lowest EAOC should be identified. Options include an adiabatic, packed bed reactor (a series of these with interstage cooling, if needed), an "isothermal," packed bed reactor, and a packed bed reactor with heat exchange. An "isothermal" reactor is defined here as one with a specified outlet temperature, not necessarily the inlet temperature, and some form of heat exchange is needed to add or remove the heat of reaction to maintain constant temperature. Chemcad will model the entire reactor as "isothermal" at that temperature. It must be understood that this situation is not physically realistic. In a reactor with heat exchange, the temperature along the length of the packed-bed reactor is not constant. The temperature can be controlled by varying the temperature and flowrate of the heat-transfer fluid, heat-transfer area, and the catalyst/inert ratio.

If a heat-transfer fluid is used, it is circulated in a closed loop through the reactor, where its temperature is increased (if the reaction is endothermic) or decreased (if the reaction is exothermic). Then, heat is added (removed) from the fluid in a heat exchanger (or fired heater, if needed). The heat-transfer fluid is then pumped back to the reactor. The suggested heat-transfer fluid is molten salt, which is a mixture of 40 wt % sodium nitrite and 60 wt % sodium nitrate.

Properties of the molten salt mixture can be obtained from Chemcad from a stream with the appropriate composition.

The cost of a packed bed reactor can be estimated by adding the cost of a shell-and-tube heat exchanger to the cost of the process vessel required to house the catalyst tubes. The cost of the fluidized bed reactor should be taken to be twice the cost of the sum of a shell-and-tube heat exchanger and the process vessel required to house the heat-transfer tubes.

Remember that the required units in Chemcad for the reaction rate are kmol/m^3reactor hr. The reactor EAOC should include anything that will vary depending on your decision variables, *i.e.*, the cost to heat the feed and cool the reactor and product streams. For your best case, you should include a discussion of the temperature, pressure, and concentration profiles obtained from Chemcad.

3. Overall Design

The entire process should be optimized based on your choice of process topology and parametric optimization of decision variables appropriately chosen based on their importance to the decision variable.

The objective function for the optimization should be the Equivalent Annual Operating Cost (*EAOC*, \$/y) for this section only, that is defined as:

$$EAOC = CAP\left(\frac{A}{P}, i, n\right) + AOC \tag{12}$$

where *CAP* (\$) is the capital investment for the compressors, the heat exchangers, the reactor, and the distillation columns, *AOC* (\$/y) is the annual operating cost, which includes utility costs for the heat exchangers (including those associated with the distillation columns and compressors, and

$$\left(\frac{A}{P}, i, n\right) = \frac{i(1+i)^n}{\left[(1+i)^n - 1\right]} \tag{13}$$

where i = 0.15 (15% rate of return) and n = 10 (ten-year plant life).

Other Information

It should be assumed that a year equals 8200 hours. This is about 342 days, which allows for periodic shutdown and maintenance.

Deliverables

Written Reports

Each team must deliver a report written using a word processor. Two identical copies should be submitted, one for each instructor. The written project reports are due by 11:00 a.m. Tuesday, April 17, 2012. Late projects will receive a minimum of a one letter grade deduction.

The report should be clear and concise. For the correct formatting information, refer to the document entitled *Written Design Reports*. The report must contain a labeled process flow diagram (PFD) and a stream table, each in the appropriate format. The preferred software for preparing PFDs is Corel Draw. A PFD from Chemcad is unacceptable; however, it should be included in the appendix along with a Chemcad report for the optimized case. 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. These may be hand written if done neatly. Alternatively, Excel spreadsheets may be included, but these must be well documented so that the reader can interpret the results. Calculations that cannot be easily followed and that are not explained will lose credit.

Since this project involves three “mini-designs,” it is suggested that the report be organized with the following sections. There should be a general abstract and introduction. Then, there should be a results section for the optimized process, including the reactor and separators, that includes a PFD, stream table, and the overall economics.. The discussion section should have a sub-section dedicated to the overall optimization, a sub-section dedicated to the reactor design, and a sub-section dedicated to the separation design. A general conclusion and recommendation section should follow. At a minimum, there should be separate appendices for each mini-design containing detailed calculations that are clearly written, easy to follow, and appropriate for the respective class.

In order to evaluate each team member’s writing skills, the results and discussion sections for each mini-design should be written by a different team member. The authorship of each of these mini-reports should be clearly specified in the report. If there is a fourth team member, this person should author the introduction, conclusions, and recommendations. Although the individual written portions of the reports must be authored by a single team member, it is the intent of the instructors that team members should help each other in writing different sections. To this end, we recommend that you seek input, such as proofreading and critiques, from other members of your team.

The reports will be evaluated as follows:

- course-specific technical content – 40%
- oral presentation – 20%
- written report – 25%
- overall optimization – 15%

For a more detailed set of evaluation criteria that will be used, see the following web site (design project assessment, oral report assessment, written report assessment):
http://www.che.cemr.wvu.edu/ugrad/outcomes/rubrics/index.php

Each report will be assessed separately by both instructors. A historical account of what each team did is neither required nor wanted. Results and explanations should be those needed to justify your choices, not a litany of everything that was tried. Each mini-report should be limited to 4-5 double space pages plus figures and tables.

This report should conform to the Department guidelines. It should be bound in a folder that is not oversized relative to the number of pages in the report. Figures and tables should be included as appropriate.

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

The following information, at a minimum, must appear in the main body of the final report:

1. a computer-generated PFD (not a Chemcad PFD) for the recommended, optimum case,

2. a stream table containing the usual items,

3. a list of new equipment for the process, costs, plus equipment specifications (presented with a reasonable number of significant figures),

4. a summary table of all utilities used,

5. a clear summary of alternatives considered and a discussion, supported with figures, of why the chosen alternative is superior,

6. a clear economic analysis which justifies the recommended case

7. a discussion section pertinent to each class plus a general discussion section for optimization of the entire process

8. a Chemcad Consolidated report only for your optimized case (in the Appendix). This must contain the equipment connectivity, thermodynamics, and overall material balance cover pages; stream flows; equipment summaries; tower profiles; and tray (packing) design specifications (if you use Chemcad to design the trays (packing)). It should not contain stream properties. Missing Chemcad output will not be requested; credit will be deducted as if the information is missing.

Oral Reports

Each team 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 team member must speak. Each team member should speak only once. A 5-10 minute question-and-answer session will follow, and all members must participate. Refer to the document entitled *Oral Reports* for instructions. The oral presentations will be Tuesday, April 17, 2012, from 11:00 am to 2:00 p.m.; Wednesday April 18, 2012, from 1:00 p.m. to 3:00 pm; and Thursday, April 19, 2012, from 11:00 a.m. to 2:00 p.m. 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 312 and ChE 325***.

Teams

This project will be completed in teams of 3 or 4. More details of team formation and peer evaluation will be discussed in class.

References

1. Snyder, J. D. and B. Subramaniam, "A Novel Reverse Flow Strategy for Ethylbenzene Dehydrogenation in a Packed-Bed Reactor," *Chem. Engr. Sci.*, **49**, 5585-5601 (1994).

2. Wankat, P., *Separation Process Engineering, (3rd ed.)*, Prentice Hall PTR, Upper Saddle River, NJ, 2012.

Appendix 1
Economic Data

Equipment Costs (Purchased)

Note: The numbers following the attribute are the minimum and maximum values for that attribute. For a piece of equipment with a lower attribute value than the minimum, the minimum attribute value should be used to compute the cost. For a piece of equipment with a larger attribute value, extrapolation is possible, but inaccurate. To err on the side of caution, the price for multiple, identical, smaller pieces of equipment should be used.

Pumps

$$\log_{10}(\text{purchased cost}) = 3.4 + 0.05\log_{10} W + 0.15[\log_{10} W]^2$$

W = power (kW, 1, 300)
assume 80% efficiency

Heat Exchangers

$$\log_{10}(\text{purchased cost}) = 4.6 - 0.8\log_{10} A + 0.3[\log_{10} A]^2$$

A = heat exchange area (m^2, 20, 1000)

Compressors

$$\log_{10}(\text{purchased cost}) = 2.3 + 1.4\log_{10} W - 0.1[\log_{10} W]^2$$

W = power (kW, 450, no limit)
assume 70% efficiency

Compressor Drive

$$\log_{10}(\text{purchased cost}) = 2.5 + 1.4\log_{10} W - 0.18[\log_{10} W]^2$$

W = power (kW, 75, 2600)

Turbine

$$\log_{10}(\text{purchased cost}) = 2.5 + 1.45\log_{10} W - 0.17[\log_{10} W]^2$$

W = power (kW, 100, 4000)
assume 65% efficiency

Fired Heater

$$\log_{10}(\text{purchased cost}) = 3.0 + 0.66\log_{10} Q + 0.02[\log_{10} Q]^2$$

Q = duty (kW, 3000, 100,000)
assume 80% thermal efficiency
assume it can be designed to use any organic compound as a fuel

Vertical Vessel

$$\log_{10}(\text{purchased cost}) = 3.5 + 0.45\log_{10} V + 0.11[\log_{10} V]^2$$

V = volume of vessel (m^3, 0.3, 520)

Horizontal Vessel

$$\log_{10}(\text{purchased cost}) = 3.5 + 0.38\log_{10} V + 0.09[\log_{10} V]^2$$

V = volume of vessel (m^3, 0.1, 628)

Packed Tower — Cost as vessel plus cost of packing

Packing	$\log_{10}(\text{purchased cost}) = 3 + 0.97\log_{10} V + 0.0055[\log_{10} V]^2$ V = packing volume (m^3, 0.03, 628)
Tray Tower	Cost as vessel plus cost of trays
Trays	$\log_{10}(\text{purchased cost}) = 3.3 + 0.46\log_{10} A + 0.37[\log_{10} A]^2$ A = tray area (m^2, 0.07, 12.3)
Reactors	For this project, the reactor is considered to be a vessel or a heat exchanger.
Storage Tanks	$\log_{10}(\text{purchased cost}) = 4.85 - 0.397\log_{10} V + 0.145[\log_{10} V]^2$ V = volume of tank (m^3, 90, 30000)

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.

Chemical Prices

See http://www.icis.com/StaticPages/a-e.htm.

Utility Costs

Low-Pressure Steam (618 kPa saturated)	\$13.28/GJ
Medium-Pressure Steam (1135 kPa saturated)	\$14.19/GJ
High-Pressure Steam (4237 kPa saturated)	\$17.70/GJ
Natural Gas (446 kPa, 25°C)	\$11.00/GJ
Fuel Gas Credit	\$9.00/GJ
Electricity	\$0.06/kWh
Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg
Deionized Water available at 5 bar and 30°C	\$1.00/1000 kg
Cooling Water available at 516 kPa and 30°C return pressure ≥ 308 kPa return temperature is no more than 15°C above the inlet temperature	\$0.354/GJ

Refrigerated Water available at 516 kPa and 10°C return pressure ≥ 308 kPa return temperature is no higher than 20°C	\$4.43/GJ
Waste Treatment of Off-Gas	incinerated - take fuel credit
Low Temperature Refrigeration Coolant stream at -20°C	\$7.89/GJ
Very Low Temperature Refrigeration Coolant stream at -50°C	\$13.11/GJ
Wastewater Treatment	\$56/1000 m^3

Equipment Cost Factors

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

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

Carbon Steel MF = 0.0
Stainless Steel MF = 4.0