Energy Balances and Numerical Methods
Design Project

Styrene Production

Process Description

Figure 1 is a preliminary process flow diagram (PFD) for the styrene production process evaluated in the Fall semester 1999 in ChE 40. In this process, styrene is manufactured by the dehydrogenation of ethylbenzene in Unit 500. The reaction is endothermic, reversible, and limited by equilibrium. Reaction occurs at high temperature (800 - 950 K) and low pressure (0.4 - 1.4 bar) in order to shift the equilibrium to the right to favor styrene production. The raw material is ethylbenzene, which is preheated in E-501 to a saturated vapor. This is then mixed with steam (produced from the fired heater H-501) to provide the heat of reaction and to serve as an inert diluent to help shift the reaction to the right. The steam to ethylbenzene ratio entering R-501 in Stream 6 ranges between 6 and 12. Steam also tends to limit side reactions and helps to extend catalyst life by reducing coke formation on the catalyst. In reactor R-501 the process uses a proprietary iron catalyst that minimizes (but does not eliminate) side reactions at higher temperatures. For simplicity, assume that the only side reaction that occurs in R-501 is the hydrogenation of ethylbenzene to form toluene and methane.

The primary reaction is equilibrium limited and is assumed to approach 80% of equilibrium. The selectivity of the toluene side reaction is a function of reactor temperature. The reactor effluent, Stream 7, is cooled in E-502 to produce steam and then enters a three-phase separator (V-501). The bottom phase of V-501 is waste water stream (Stream 11), which must be decanted and sent for further processing before discharge. Stream 9 leaves the top of the separator and contains all the light gases (methane and hydrogen) and can be used as a fuel gas. Stream 10 contains most of the toluene, ethylbenzene, and styrene. Stream 10 flows through a pressure reducing valve and then enters a distillation train (T-501 and T-502) where most of the toluene is removed at the top of first column (T-501) in Stream 17. The remaining toluene and all the ethylbenzene and styrene leaving the bottom of this column in Stream 15 enter the second column (T-502). From T-502, Stream 20 is recycled and mixed with fresh ethylbenzene before the reactor. The bottom product of T-502 leaving in Stream 18 contains the styrene leaving Unit 500.
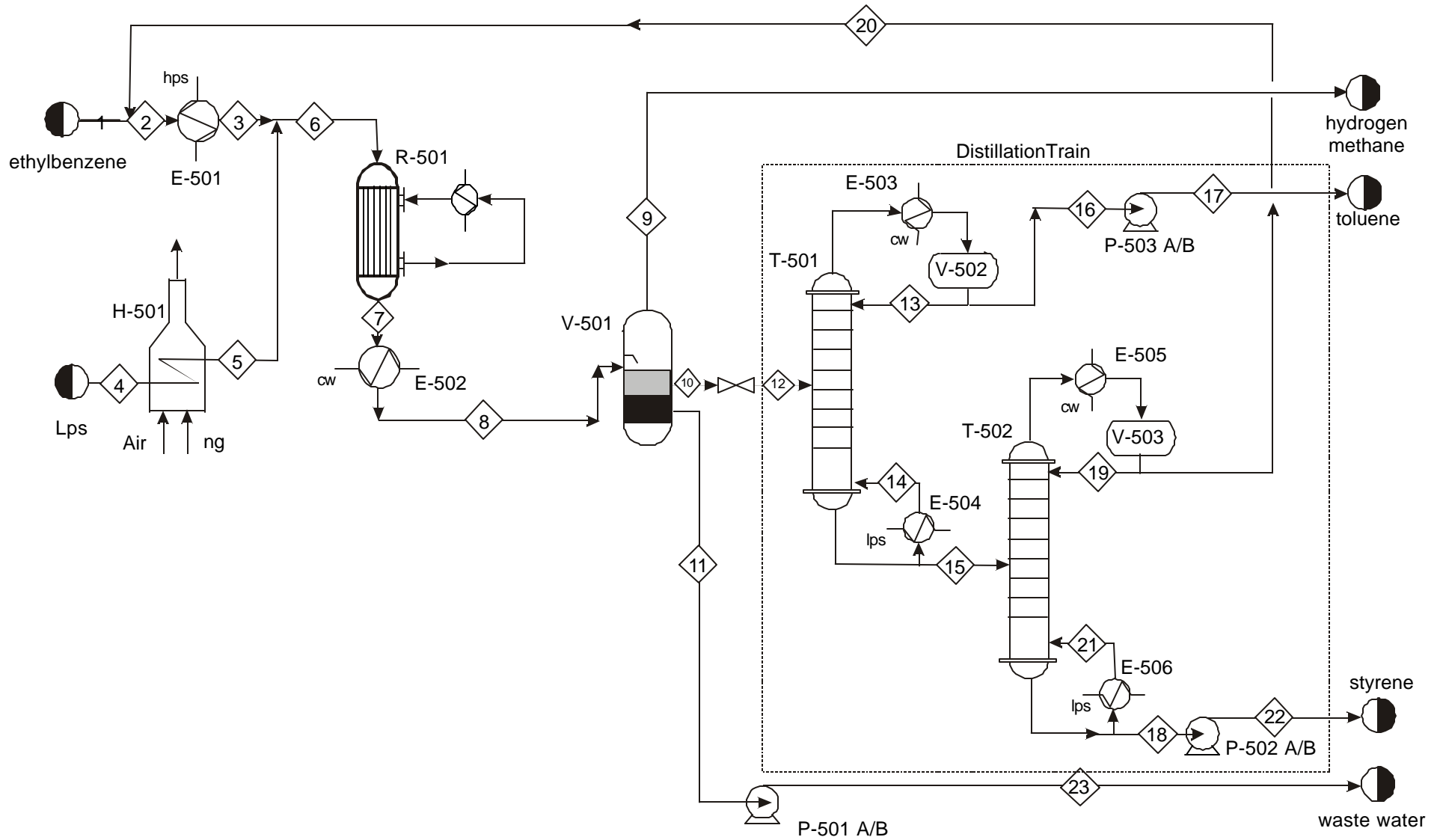
Process Details

Feed Streams

Stream 1:   fresh ethylbenzene, assume available as a liquid at 30EC.

Stream 4:   low-pressure process steam available from elsewhere in the plant, to be superheated and used as diluent and heat source for mixture entering reactor in Stream 6.

H-501	E-501	R-501	E-502	P-501A/B	V-501	T-501	E-503	E-504	V-502	T-502	E-505	E-506	V-503	P-502 A/B	P-503 A/B
steam heater	feed preheater	styrene reactor	product cooler	waste water pump	three-phase separator	toluene column	condenser	reboiler	reflux drum	styrene column	condenser	reboiler	reflux drum	styrene pump	toluene pump

Unit 500: Production of Styrene from Ethylbenzene

Effluent Streams

Stream 9:   light-gas stream of hydrogen and methane with traces of water vapor and small amounts of ethylbenzene and toluene. Take credit as a fuel gas for hydrogen and methane in this stream only.

Stream 17:   99% pure toluene with small amounts of ethylbenzene and styrene. The toluene in Stream 17 is at least 95% of the toluene produced. This stream can be sold as byproduct, but it should not exceed 2% of styrene production.

Stream 22:   styrene crude product of at least 99.0 wt% purity, 100,000 metric tons/yr, with small amounts of ethylbenzene. The styrene in Stream 22 is at least 98% of the styrene entering the distillation train.

Stream 23:   waste water stream from V-501; assume to be pure water for this design project, but Stream 11 must be processed at the associated waste-water treatment cost.
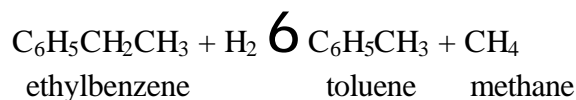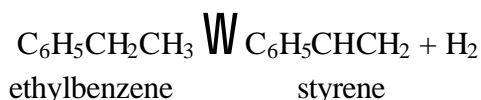
Recycle Stream.

Stream 20:   primarily ethylbenzene with some toluene and styrene; assume this stream leaves the top of T-501 as a saturated liquid at 60 kPa.

Equipment

Isothermal Fixed-Bed Catalytic Reactor (R-501)

The following reactions occur:

$$C_6H_5CH_2CH_3 \; W \; C_6H_5CHCH_2 + H_2$$
$$\text{ethylbenzene} \qquad\qquad \text{styrene}$$

$$C_6H_5CH_2CH_3 + H_2 \; 6 \; C_6H_5CH_3 + CH_4$$
$$\text{ethylbenzene} \qquad\qquad \text{toluene} \quad \text{methane}$$

The primary reaction for styrene production is equilibrium limited, and is assumed to run at 80% of equilibrium. The styrene equilibrium conversion is calculated according to the following gas-phase reaction equation:

$$K_{eq} = \frac{y_S \, y_{H_2} P}{y_{EB}}$$

where y_S, y_{H2}, and y_{EB} are mole fractions of styrene, hydrogen, and ethylbenzene, respectively, and P is the reactor total pressure in bar (1 bar = 100 kPa). The reaction equilibrium constant is a nonlinear function of temperature (in K) only, and is given as:

$$\ln K_{eq} = 15.5408 - \frac{14852.6}{T}$$

The side reaction is not equilibrium limited, but the fractional selectivity (*S*) for toluene formation in R-501 is temperature dependent and is given by the following:

$$S = S_0 T^n$$

where S_0 and *n* must be obtained by regression of data provided below by the company lab. These data should not be extrapolated outside the range 800 - 950 K. The catalyst cost is significant. Based on the anticipated reactor size for this unit, assume catalyst use is at 40 metric ton/yr for a 100,000 metric ton/yr styrene facility, with catalyst replacement required every 21 months.

Three-Phase Separator (V-501)

For purposes of this design project, assume the methane and hydrogen are insoluble in Streams 10 and 11, and the water is immiscible in the organic phase in Stream 10. Trace amounts of water vapor may be present in the methane/hydrogen gas in Stream 9. However, after decanting pure liquid water from V-501 in Stream 11, the styrene, ethylbenzene, and toluene are partitioned between Streams 9 and 10 according to Raoult's Law. You should optimize V-501 (using vapor-liquid equilibrium equations developed in class) for the best temperature and pressure to operate this unit in order to maximize the recovery of crude styrene in Stream 10. Although Stream 11 contains trace amounts of waste components, assume it has the properties of pure water but with the treatment costs associated with waste water. To minimize polymerization of the styrene product, this flash unit should be designed to operate between 0.5 and 1.5 bar and between 50 and 100EC.

Distillation Columns (T-501 and T-502)

From the separator, the organic liquid product stream (Stream 12) enters the distillation section of Unit 500. The columns operate at (or below) the normal boiling point of styrene at the desired column outlet pressure. To eliminate significant polymerization of styrene, the distillation units are operated at a moderate vacuum to keep the temperature low. The top product from T-501 (Stream 16) must contain at least 95% of the toluene entering the distillation train at a purity of 99%, with the rest of Stream 16 being ethylbenzene. This stream is pumped to another unit that makes toluene available for external sale at market prices. This unit is not considered in this design project.

The bottoms product from the toluene column (T-501) is further distilled in the ethylbenzene recycle column (T-502). The overhead ethylbenzene product, Stream 20, contains small amounts of toluene and styrene and is recycled to mix with Stream 1 before the reactor. The bottoms product of T-502 must be 99% pure styrene with at least 98% recovery of the styrene entering the distillation train, and the remainder is ethylbenzene.

For information only, inhibitors must be added (about 10-50 ppm) to reduce polymerization, but this will not be considered in this design. Also, further preparation of styrene for sale is done in another unit. These processes are not considered in this design project.

Other Equipment Considerations

Two streams that are to be mixed are required to be at identical pressures. Pressure reduction is accomplished by adding a reducing valve. For this design, it is assumed that valves are available as needed at no cost. Flow must occur from a higher pressure to a lower pressure. Pumps increase the pressure of liquid streams, and compressors are used to increase the pressure of gaseous streams. For example, locations where pumps are needed are in the liquid streams exiting V-501, T-501, and T-502, and to remove material from any towers operating under vacuum conditions. For this project, assume that pumps and compressors are available as needed at no cost and that there is no cost associated with any pressure increases. However, based on your design, the report should indicate placement of pumps, compressors and valves on the PFD.

Data

Some data needed to do this project are provided below. Additional property data are available in references [1] and [2].

Fractional Selectivity Data for Toluene

Temperature (K)	800	850	900	950
Fractional Selectivity (S)	0.01	0.03	0.06	0.13

Typical Costs and Selling Prices

Steam/Fuel (cost or credit)

Low-pressure steam (446 kPa, saturated)	$5.00/1000 kg
Medium-pressure steam (1135 kPa, saturated)	$7.31/1000 kg
High-pressure steam (4237 kPa, saturated)	$8.65/1000 kg
Natural gas or fuel gas (446 kPa, 25EC)	$3.00/GJ
Electricity	$0.05/kWh
Boiler feed water (at 549 kPa, 90EC)	$2.54/1000 kg

Cooling Water $0.16/GJ
available at 516 kPa and 30EC

return pressure 308 kPa

return temperature should be no more than 15EC above the inlet temperature

Refrigerated Water $1.60/GJ
available at 516 kPa and 10EC

return pressure 308 kPa

return temperature can be no more than 20EC

Process Water $0.04/1000kg
available at 300 kPa and 25EC

Waste Water Treatment $5/1000 kg

Recent Chemical Prices (Check current prices in the *Chemical Market Reporter* available in the WVU Evansdale Library)

Component	Price, $/kg
Ethylbenzene	0.55
Styrene	0.682
Toluene	0.484

Other Data

Annual operating hours	8000 (330 days)
Catalyst Cost	$1/kg
Catalyst Load	40 metric ton
Catalyst Replacement	21 months

Economic Analysis

When evaluating alternative cases, the objective function to be used is the equivalent annual operating cost (EAOC), 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. Updated costs for styrene (the product), toluene (the byproduct) and ethylbenzene (the feed) should be obtained from the *Chemical Market Reporter*, available in the Evansdale Library. The other operating costs are utilities, such as steam, cooling water, natural gas, and electricity. The capital cost annuity is an **annual** cost (like a car payment) associated with the **one-time**, capital cost of plant construction. Capital costs for all pieces of equipment will be provided by Spring Break. The capital cost annuity (CCA) is calculated as:

$$CCA = \text{capcost} \frac{i(1+i)^n}{(1+i)^n - 1}$$

where capcost is the capital cost of the equipment, i is the annual interest rate (use 0.15), and n is the number of years over which the investment is amortized (use 10 years).

Optimization

The objective function (EAOC) is to be used as defined above. It is your responsibility to define appropriate decision variables. If there are too many decision variables to do a reasonable optimization, it is your responsibility to determine with appropriate justification, which ones most significantly affect the objective function and focus on only those decision variables.

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, entitled *Written Design Reports.* Any report not containing a labeled PFD and a stream table will be considered unacceptable. The stream table must include temperature, pressure, phase, total mass flowrate, total molar flowrate, and component molar flowrates. 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. Refer to this document for more detailed information.

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 5-10 minute question-and-answer session will follow. Instructions for presentation of oral reports are explained in a separate document, entitled *Oral Reports.* 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 upperclassmen before you are to present your report. Presentation schedules will be posted in mid-April.

The written report and oral report documents are available for download on the department home page at http://www.cemr.wvu.edu/~wwwche/publications/projects/index.html.

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 24th in ChE 38 class and Wednesday, April 26th in ChE 41 class. Attendance is required of all students during their classmates' presentations. Attendance means you must be seated in the classroom, not in the hall or the lounge. There will be a project review on Friday April 28th in ChE 41 class. In addition, everyone must attend at least one (and preferably both) of the senior design presentations, either Tuesday, April 25th or Thursday, April 27th (substitutes for Thursday ChE 38 class). 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. Finally, anyone not participating in this project will automatically receive an F for ChE 38, regardless of other grades earned in these classes.

Revisions

As with any open-ended problem, that is, 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 (3rd ed.),* Wiley, New York, 2000.

2. Perry, R. H. and D. Green, eds., *Perry's Chemical Engineering Handbook (7th ed.),* McGraw-Hill, New York, 1997.