

# Design Project

## Energy Balances and Numerical Methods

### Styrene Manufacture

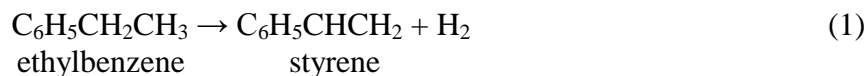
Styrene is the monomer used to make polystyrene, which has many uses [1]. In the current process, styrene is produced by the dehydrogenation of ethylbenzene. There is very little ethylbenzene sold commercially: most ethylbenzene manufacturers convert it directly into styrene in the same manufacturing complex.

We wish to manufacture 100,000 metric tons/year of a liquid containing at least 99% styrene, subject to constraints which will be defined later in this document. The project is a continuation (of sorts) of the project you completed last semester for ChE 201. However, there are important differences in the two, including production rate, assumptions and products.

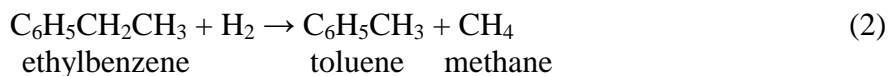
A suggested process flow diagram (PFD) of the unit, termed Unit 500, is attached as Figure 1. You should use this as a starting point. However, any change that you can justify on economic grounds (and that does not violate the laws of nature) is not only allowed but encouraged. Your assignment is to develop an optimum case based upon an objective function defined later. It is your job to define the decision variables, and to choose and implement a method to arrive at an optimum design.

### Process Description

See Figure 1. The raw material is ethylbenzene, and steam is fed as an inert. In the suggested process, ethylbenzene is preheated in E-501 to a saturated vapor. This is then mixed with steam produced from the fired heater H-501. The steam provides the heat of reaction and serves as an inert diluent to help shift the reaction to the right. Steam also tends to limit side reactions and helps to extend catalyst life by reducing coke formation on the catalyst. The ratio of steam to ethylbenzene entering reactor R-501 in Stream 6 ranges between 6 and 12. The main reaction:



is endothermic, reversible, and limited by equilibrium. The reaction occurs at high temperatures (800 - 950 K) and low pressures (0.4-1.4 bar) in order to shift the equilibrium to the right to favor styrene production. In 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:



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	feed	styrene	product	waste	three-	toluene	condenser	reboiler	reflux	styrene	condenser	reboiler	reflux	styrene	toluene
heater	preheater	reactor	cooler	water	phase	column			drum	column			drum	pump	pump
				pump	separator										

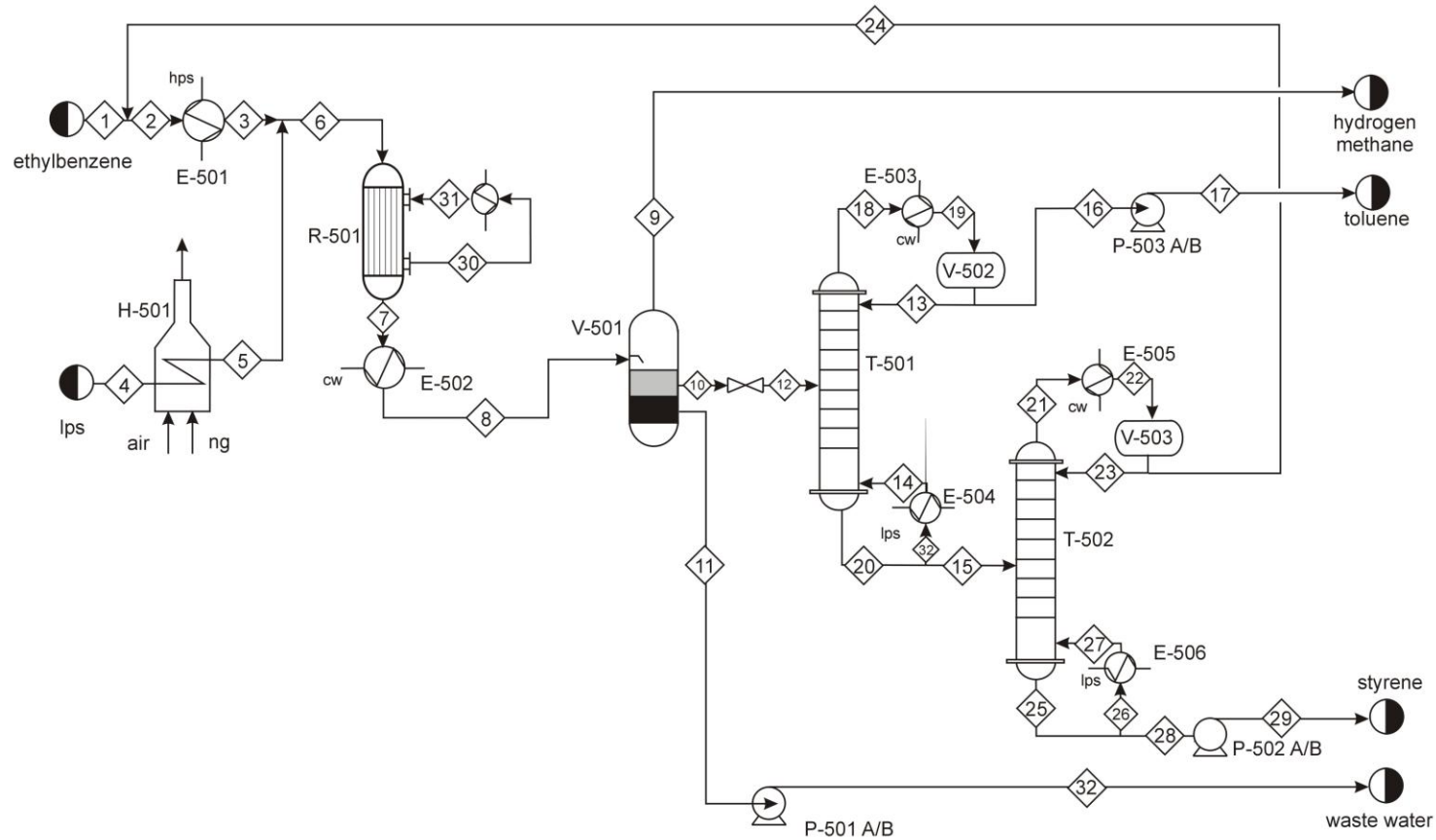


Figure 1: Unit 500 Production of Styrene from Ethylbenzene

The primary reaction is limited by equilibrium, 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 11). This must be decanted and sent for further processing before discharge. This treatment is not shown in the PFD, but it is an expense which must be included in the economic analysis. 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). The distillation columns operate at (different) constant pressures, the values of which are governed by the properties of the heating steam and cooling water used, and the composition of the top and bottom products, as described later. Most of the toluene is removed at the top of first column (T-501) in Stream 16. The remaining toluene, ethylbenzene and styrene leaving the bottom of this column in Stream 15 enter the second column (T-502). From T-502, Stream 24 (containing ethylbenzene, toluene and styrene) is recycled and mixed with fresh ethylbenzene before the reactor. The bottom product of T-502 leaving in Stream 28 constitutes the styrene (with small amounts of ethylbenzene and toluene) leaving Unit 500.

## **Process Details**

### **Feed Streams**

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

Stream 4: low-pressure process steam, available from elsewhere in the plant, to be superheated in H-501 and used as diluent and heat source for mixture entering reactor in Stream 6.

### **Effluent Streams**

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

Stream 17: 99.0% 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 Stream 29.

Stream 29: styrene crude product of at least 99.0 wt% purity, 100,000 metric tons/yr, with small amounts of ethylbenzene. The styrene in Stream 29 is at least 98% of the styrene entering the distillation train in Stream 10.

Stream 32: waste water stream from the three-phase separator, V-501. Stream 32 must be processed at the associated waste-water treatment cost given below. For this design project, assume the properties of this stream to be those of pure water.

### Recycle Stream.

Stream 24: primarily ethylbenzene with some toluene and styrene; assume this stream leaves the top of T-502 as a saturated liquid at 60 kPa.

### Equipment

Fired Heater H-501: The fired heater heats the low-pressure steam to any temperature. H-501 is fueled with natural gas (ng) and/or Stream 9.

Heat Exchangers: Heat exchanger E-501 heats the ethylbenzene feed, Stream 2. The temperature of the exit stream, Stream 3, may not exceed a value which is 5°C lower than the inlet temperature of the appropriate type of steam used for heating.

Heat exchanger E-502 may be used to cool the reactor outlet, Stream 7. The temperature of the exit stream, Stream 8, should be at least 5°C greater than the temperature of the outlet cooling water.

Temperature constraints of heat exchangers, condensers and reboilers associated with other pieces of equipment are provided separately below.

Catalytic Reactor R-501: This may be either an isothermal fixed-bed reactor with a heat-transfer jacket, or two (or more) adiabatic fixed-bed reactor stages with a heat exchanger between stages. (Figure 1 shows only the isothermal option but you should consider both in your optimization.)

Only Reactions (1) and (2) are assumed to occur. The ranges of parameters that can be used are: temperature between 800-950 K, pressure between 0.4-1.4 bar, steam-to-ethylbenzene ratio between 6 and 12. Reaction (1) is assumed to run at a fractional conversion corresponding to 80% of the value at thermodynamic equilibrium at the exit temperature. The mole fractions of styrene, hydrogen and ethylbenzene at equilibrium are given by the relationship:

$$K_{eq} = \frac{y_{S,e} y_{H_2,e} P}{y_{EB,e}} \quad (3)$$

where  $y_{S,e}$ ,  $y_{H_2,e}$ , and  $y_{EB,e}$  are equilibrium mole fractions of styrene, hydrogen, and ethylbenzene, respectively, and P is the reactor total pressure. (Note that the three mole fractions do not sum to unity, as there are other species present as well.) The reaction equilibrium constant  $K_{eq}$  is a nonlinear function of temperature only, and is given as:

$$\ln K_{eq} = 15.5408 - \frac{14852.6}{T} \quad (4)$$

where  $K_{eq}$  is in [bar] and T is in [K]. The fractional selectivity  $S$  for toluene formation in R-501 (relative to all the products in Reactions (1) and (2)) is dependent on temperature and is given by the following:

$$S = S_o T^n \quad (5)$$

where  $S_o$  and  $n$  must be obtained by regression of data provided in Table 1 below by the company laboratory.

The catalyst cost in R-501 may be significant and must be taken into account in the economics and optimization. Cost parameters are provided below.

**Three-Phase Separator V-501:** For the purposes of this design project, assume the methane and hydrogen are insoluble in Streams 10 and 11. So all methane and hydrogen present in Stream 8 is present only in Stream 9. Also assume that water is immiscible in the organic phase, Stream 10. Trace amounts of water vapor may be present in the methane/hydrogen gas mixture, Stream 9, and must be accounted for; but most goes to Stream 11. However, after decanting pure liquid water from V-501 in Stream 11, and removing methane and hydrogen in Stream 9, the styrene, ethylbenzene, and toluene are partitioned between Streams 9 and 10 according to Raoult's Law. Although Stream 11 contains trace amounts of waste components, assume that it has the properties of pure water but with the treatment costs associated with waste water as shown below. 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. 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 100°C.

**Pumps:** Pumps increase the pressure of liquids. Figure 1 contains three pairs of pumps: when you revise Figure 1, you need to add pumps as appropriate, even if they are not present currently in Figure 1. For all pumps, the cost of energy may be neglected.

**Compressors:** Compressors increase the pressure of vapor phases. If you use one or more compressors, they may be assumed to be adiabatic. In that case, the compressor power may be calculated as:

$$\dot{W}_s [\text{kW}] = 20,000 \dot{m} [\text{kmol/s}] \left\{ \left( \frac{P_{out}}{P_{in}} \right)^{0.286} - 1 \right\} \quad (6)$$

where  $\dot{m}$  [kmol/s] is the total molar flow rate of the inlet stream. Equation (6) includes the compressor efficiency. In general, the ratio of outlet to inlet pressure (compression ratio) in a compressor is between 3 and 5. If a compression ratio greater than 5 is needed, compressors are usually staged, with cooling between the compressor stages ("intercooling"), but not after the last

stage. If you choose to do this, the compression ratio for each stage should be identical, and the intercooling should be to 50°C. The PFD that you draw should accurately represent the chosen compressor configuration.

The compressor increases the temperature of the stream being compressed according to:

$$\frac{T_{out}}{T_{in}} = \left( \frac{P_{out}}{P_{in}} \right)^{0.286} \quad (7)$$

where  $T$  is absolute temperature. The cost of electricity to run the compressor is a utility cost and is given below.

Distillation Columns T-501 and T-502: From the three-phase 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. Stream 16, the top product from the toluene column T-501, must contain at least 95% of the toluene entering the distillation train, and must contain 99% toluene, with the rest of Stream 16 being ethylbenzene.

Relating to the toluene column, Stream 18, which goes to Condenser E-503, must be a saturated vapor. The molar flow rate of Stream 18 must be 10 times that of Stream 16. Stream 13 re-enters the distillation column as a saturated liquid. Stream 20 must be a saturated liquid and Stream 14 must be a saturated vapor. The molar flow rate of Stream 14 must be one-third that of Stream 15. T-501 must operate at a pressure low enough to make Stream 20 vaporize at a temperature that has a value no higher than 5°C lower than the temperature of the steam used as the heat source for E-504.

Stream 15, the bottoms product from the toluene column (T-501), is further distilled in the ethylbenzene-recycle column (T-502). The overhead ethylbenzene product, Stream 24, contains small amounts of toluene and styrene and is recycled to mix with Stream 1 before the reactor. The bottoms product of T-502, Stream 28 must be 99% pure styrene, with at least 98% recovery of the styrene entering the distillation train and the remainder ethylbenzene.

Relating to the ethylbenzene-recycle column, Stream 21, which goes to Condenser E-505, must be a saturated vapor. The molar flow rate of Stream 21 must be 10 times that of Stream 24. Stream 23 re-enters the distillation column as a saturated liquid. Stream 25 must be a saturated liquid and Stream 27 must be a saturated vapor. The molar flow rate of Stream 27 must be one-third that of Stream 28. T-502 must operate at a pressure low enough to make Stream 25 vaporize at a temperature that has a value no higher than 5°C lower than the temperature of the steam used as the heat source for E-506.

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.
- 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 design, it is assumed that valves are available as needed at no cost. 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.

## Physical Property Data

Use data from Reference [2] or from any handbook, e.g., Reference [3].

## Kinetic Data

Selectivity data are given in Table 1. These data are approximate and are to be used only for this design project this semester, not for more complex versions to be completed in subsequent semesters. These data should be regressed to fit Equation (5), and the regression used for the optimization. The regression should not be extrapolated outside the range 800-950 K.

**Table 1. Fractional Selectivity Data for Toluene**

Temperature, $T$ [K]	800	850	900	950
Fractional Selectivity, $S$	0.01	0.03	0.06	0.13

$$S = \frac{\text{change in the molar flow rate of toluene}}{\text{(change in the molar flow rates of styrene, hydrogen, toluene and methane)}}$$

## Economic Analysis

### Objective Function

When evaluating alternative cases, the following objective function should be used. The equivalent annual operating cost (*EAOC*) is defined as:

$$EAOC = - (\text{value of product and byproduct}) + (\text{feed cost}) + (\text{capital cost annuity}) + (\text{other operating costs}) - (\text{operating credits}) \quad (8)$$

A negative *EAOC* means there is a profit. It is desirable to minimize the *EAOC*; i.e., a large negative *EAOC* is very desirable. Below are brief descriptions of the various constituents of *EAOC*. More details are given later.

Historic values of styrene (the product) and toluene (the byproduct), and the historic cost of ethylbenzene (the reactant) are given in Table 2. These values should be updated by referring to a current issue of Reference [4].

The capital cost annuity is an annual cost associated with the one-time costs for plant construction (like a car payment). A list of capital costs for each piece of equipment is provided below in Table 3. These can be added to obtain the total installed cost ( $C_{FI}$ ). Then the capital cost annuity is related to  $C_{FI}$  as follows:

$$\text{capital cost annuity} = C_{FI} \frac{i(1+i)^n}{(1+i)^n - 1} \quad (9)$$

where  $i$  is the interest rate (as a fraction) and  $n$  is the plant life, in [y]. For the purposes of this project, take  $i = 0.15$  and  $n = 10$ .

Other operating costs are for utilities (steam, cooling water, natural gas, electricity, etc.), for catalyst replacement, and for waste treatment. The power needed for compression is provided in Equation (6a). The costs of utilities, catalysts and waste treatment are provided below.

Operating credits are for streams sold for their fuel content (if they are not used within Unit 500). These credits are also provided below.

### Raw Material Costs/Product Value

These are provided in Table 2. When using these numbers, you should be aware that they may be modified later, so write programs, spreadsheets, etc. with this in mind. The values in Table 2 should be updated by referring to a current issue of Reference [4].

**Table 2. Material Prices (ca. 2010)**

Component	Ethylbenzene	Styrene	Toluene
Price [\$/kg]	0.50	0.62	0.44

### Equipment Costs

Preliminary equipment costs for the plant are given in Table 3. More up-to-date costs may be provided later. Each cost is for an individual piece of equipment, including installation.



**Table 3. Equipment Costs**

<b>Equipment</b>	<b>Installed Cost [in thousands of dollars]</b>
Isothermal packed-bed reactor	5,000
Adiabatic packed-bed reactor, per stage	100
Vessel	100
Distillation column	500
Heat exchanger	300
Compressor	Larger of {4,000 and $0.0189 (\dot{W}_s [\text{W}])^{0.8}$ }
Fired Heater	$11 \times 10^A$ where $A = 0.8 \log_{10}[Q] - 0.5$ and $Q$ is the heat duty [kW]

**Utility Costs/Credits**

Low-Pressure Steam (618 kPa, saturated, cost or credit)	\$13.28/GJ
Medium-Pressure Steam (1135 kPa, saturated, cost or credit)	\$14.19/GJ
High-Pressure Steam (4237 kPa, saturated, cost or credit)	\$17.70/GJ
Natural Gas (446 kPa, 25°C, cost)	\$11.00/GJ
Waste Stream 9 used as a fuel source (credit)	\$9.00/GJ
Electricity	\$0.06/kW-h
Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg
<p>There is a cost for boiler feed water only if the steam produced enters process streams. If, on the other hand, the steam produced does not enter a process stream and is subsequently condensed, then it can be made into steam again. In that case, there is no net cost for boiler feed water.</p>	
Cooling Water	\$0.354/GJ
<p>Available at 516 kPa and 30°C Return pressure <math>\geq</math> 308 kPa Return temperature should be no more than 15°C above the inlet temperature</p>	
Refrigerated Water	\$4.43/GJ
<p>Available at 516 kPa and 5°C Return pressure <math>\geq</math> 308 kPa Return temperature should be no higher than 15°C</p>	

**Waste treatment**

For Stream 32	\$5.00/1000 kg
---------------	----------------

**Catalyst**

Cost	\$1.00/kg
Load	40 metric ton
Replacement Time	21 months

**Optimization**

You have learned, or will learn, optimization methods in ChE 230. The objective function (*EAO*C) is defined above. You should consider both topological and parametric optimization.

Topological optimization involves considering different process configurations (such as location of process equipment, whether or not to add or remove equipment). You may alter the process configuration in any way that improves the economic performance as long as it does not violate the laws of nature. Determining the type of reactor used is an example of a topological optimization.

Parametric optimization involves determining the best operating parameters for the chosen process topology. It is your responsibility to define appropriate decision variables. It is suggested that you look carefully at the efficient use of raw materials and the three-phase separator V-501, and correlate the reactor type and temperature with separation costs. If there are too many decision variables to do a reasonable parametric optimization, it is your responsibility to determine, with appropriate justification, which ones most significantly affect the objective function. Then you should focus on only those decision variables. This is called a Pareto analysis.

**Other Information**

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

During the actual process, inhibitors must be added (about 10-50 ppm) to reduce polymerization, but this will not be considered in this design. Also, Stream 16 is pumped to another unit that makes toluene available for external sale at market prices. That unit is not considered in this design project. Finally, styrene is further prepared for sale in another unit. That process too is not considered in this design project.

## Groups

You will work on this project in groups of four. More details of group formation and peer evaluation will be discussed in class.

## 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. You are advised to start working on this problem as soon as possible, so that your questions may be asked, and clarifications made, sooner rather than later.

## Deliverables

### Written Report

Each group must deliver a word-processed report that is clear and concise and adheres to the prescribed format. The format is explained in the Written Report Guidelines, provided as a separate document (also available at <http://www.che.cemr.wvu.edu/publications/projects/index.php> ). A brief summary is provided here.

The body of the report should be short, emphasizing only the results and explaining why the results presented are optimal. The report must contain a labeled PFD and a stream table. 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 often superior to tables (but see discussion in the Guidelines).

The report appendix should contain details of calculations. These calculations should be annotated so that they are easy to follow -- calculations that cannot be followed easily will lose credit. Computer output without detailed explanations is not appropriate; neatly hand-written calculations are best.

Reports not adhering to the prescribed format will receive significant deductions and may have to be rewritten.

The written report is due on Friday, April 22, 2011 by 3:00 pm.

### Oral Report

Project results will be presented orally in the ChE 202 class on Monday, April 25, 2011. Oral presentations will continue on April 26 and April 27. 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 each oral report.

Oral Presentation Guidelines are also provided. These should be followed in your presentations. These guidelines too are available at

<http://www.che.cemr.wvu.edu/publications/projects/index.php>

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.

### **Project Review**

There will be a project review in the ChE 230 class on Thursday, April 28, 2011.

### **Grading**

Anyone not participating in this project will be subject to actions as noted in the syllabi for ChE 202 and ChE 230.

Generally, the grades for the oral presentation and written report will be composite grades for the entire team. Therefore, group preparation and feedback are recommended.

The report grade for each course will be based on the technical content pertinent to that course (including the response to questions during the oral presentation), the overall technical content (including that pertinent to the other class), the oral presentation, and the written report. The grades for the oral presentation and written report will take into account the quality of the writing or the oral presentation and the adherence to the prescribed format.

The documents on the following web site provide an indication of the expected attributes of a written design report and an oral presentation:

<http://www.che.cemr.wvu.edu/ugrad/outcomes/rubrics/index.php>

### **References**

1. Kent, James A., Ed. *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology*, Volumes 1 & 2 (11th Edition). Springer – Verlag, 2007.
2. Felder, R.M. and R.W. Rousseau, *Elementary Principles of Chemical Processes (3rd ed., 9<sup>th</sup> printing)*, Wiley, New York, 2005.
3. Perry, R. H. and D. Green, eds., *Perry's Chemical Engineering Handbook (7<sup>th</sup> ed.)*, McGraw-Hill, New York, 1997.
4. <http://www.icis.com/StaticPages/a-e.htm>