

# Energy Balances and Numerical Methods

## Design Project

### Manufacture of Diethyl Ether

Diethyl ether (DEE) is a colorless, highly volatile, flammable liquid with a characteristic odor. It is an important solvent in the production of cellulose acetate and other cellulose-based polymers. Other uses for DEE are as a starter fluid for diesel and gasoline engines, and as a solvent for Grignard and other reactions involving organometallic reagents. Previously, it was used as a general anesthetic.

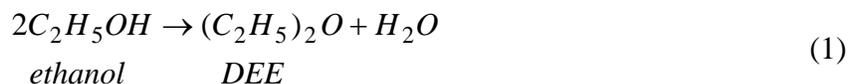
The common production method for DEE is as a by-product from the vapor-phase hydration of ethylene to make ethanol. However, we have an excess of ethanol in our facility. Therefore, the process of interest in this assignment uses the vapor-phase dehydration of ethanol.

We wish to manufacture 50,000 metric tons/year of a liquid containing at least 99.5 mol% DEE, subject to constraints which will be defined later in this document.

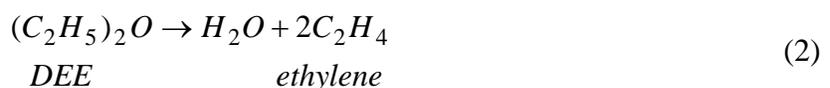
A suggested process flow diagram (PFD) of the unit, termed Unit 1200, is attached as Figure 1. You should use this as a starting point. However, any change that you can justify on economic grounds (and that does not violate the laws of nature) is not only allowed but encouraged. Your assignment is to develop an optimum case based upon an objective function, to be 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

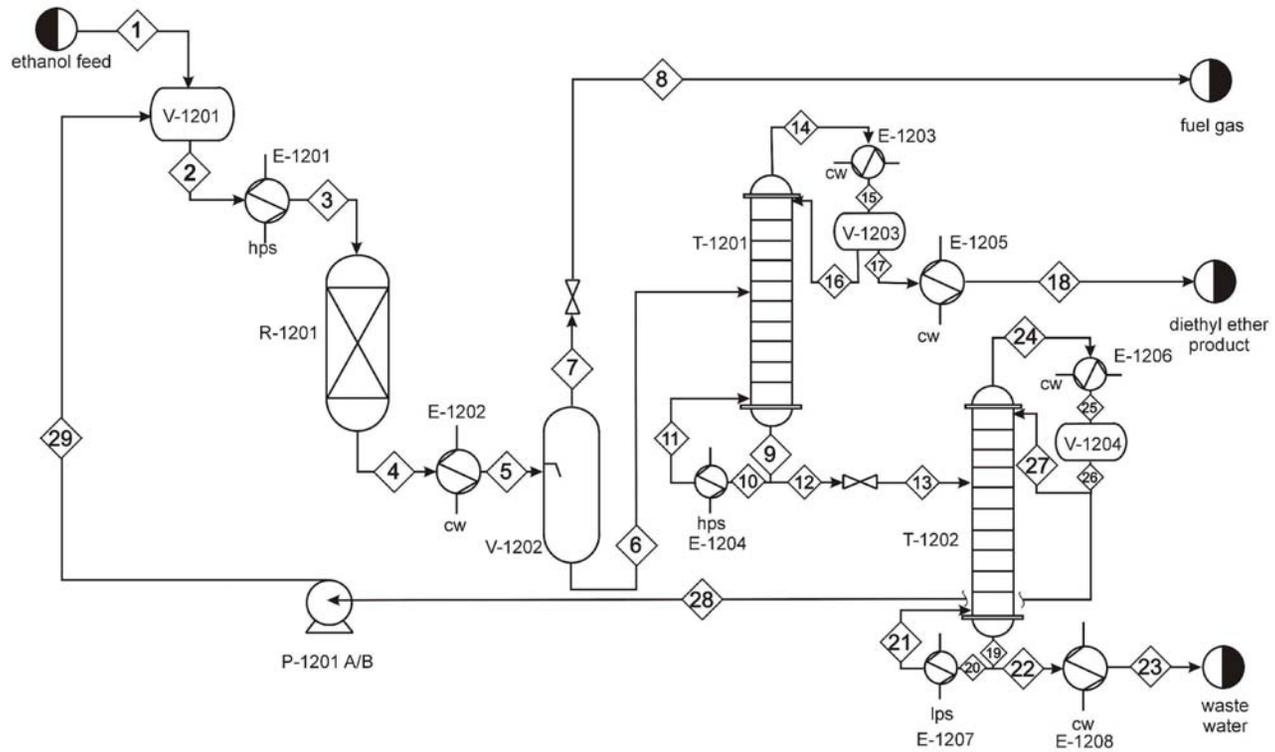
See Figure 1. The fresh feed to the unit, Stream 1, consists of 70 mol% ethanol in water. This stream is pumped from storage and sent to an on-site feed vessel, V-1201, where it is mixed with recycled ethanol, Stream 29. The stream leaving V-1201, Stream 2, is vaporized and heated in heat exchanger E-1201. It is then fed to the packed bed reactor, R-1201. The reactor contains a packed bed of alumina catalyst. The main reaction:



is exothermic, reversible, and limited by equilibrium. The reaction occurs at medium temperatures (400-600 K) and high pressures (1000-1500 kPa). The alumina catalyst minimizes (but does not eliminate) side reactions at higher temperatures. For simplicity, assume that the only side reaction that occurs in R-1201 is the dehydration of DEE to form ethylene:



V-1201	E-1201	R-1201	E-1202	V-1202	P-1201 A/B	T-1201	E-1203	E-1204	V-1203	E-1205	T-1202	E-1206	V-1204	E-1207	E-1208
Feed Drum	Feed Heater	Reactor	Reactor Effluent Cooler	Flash Vessel	Ethanol Recycle Pumps	DEE Column	DEE Condenser	DEE Reboiler	DEE Reflux Drum	DEE Cooler	Ethanol Column	Ethanol Condenser	Ethanol Reflux Drum	Ethanol Reboiler	Waste Water Cooler



**Figure 1: Unit 1200 Diethyl Ether Process**

The primary reaction is limited by equilibrium, and is assumed to approach 80% of equilibrium. The selectivity of the ethylene side reaction is a function of reactor temperature and pressure.

The reactor effluent, Stream 4, is cooled in E-1202 using cooling water and enters a flash vessel, V-1202. The overhead stream from V-1202, Stream 7 (8), contains all of the ethylene that is formed in the undesirable side reaction, along with small amounts of DEE and ethanol. This stream is sent to another process to be used as fuel gas.

The liquid in V-1202 is sent to two distillation towers in series. 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. The liquid stream, Stream 6, enters the DEE purification column, T-1201, where the DEE is separated from the water and ethanol. The overhead product from this column, Stream 17, is then cooled in E-1205. The outlet, Stream 18, is the DEE 99.5+% product stream that is sent to storage.

The bottom product from T-1201, Stream 12, is sent to the second column, T-1202, where the ethanol is purified as the top product to a 70 mol% pure aqueous mixture. This mixture, Stream 28, is pumped back to the feed pressure using P-1203A/B and returned to the front end of the process. The bottom product stream from T-1202, Stream 22, is water with trace amounts of EtOH and DEE. This stream is cooled to 40°C in E-1208 and the wastewater stream is sent to be treated (not shown in Figure 1) prior to discharge to the environment.

## **Process Details**

### **Feed Stream**

Stream 1: Feed: liquid solution of 70 mol% EtOH in water at 30°C and 1500 kPa.

### **Effluent Streams**

Stream 8: Fuel Gas: light-gas stream of ethylene with traces of water vapor, DEE and EtOH in the vapor phase at 40°C and 1100 kPa. Take credit for this stream as a fuel, using the lower heating values of the components of the stream.

Stream 18: Product Liquid: contains at least 99.5 mol% DEE, with the balance being EtOH and water, at 37°C.

Stream 23: Wastewater: contains water with traces of EtOH and DEE, at 40°C. Stream 23 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 29: top product of the EtOH column, T-1202, an aqueous solution of 70 mol% EtOH. Assume that it is pumped back to the feed drum, V-1201, at 1500 kPa and the temperature at the top of T-1202.

## Equipment

Heat Exchangers: Heat exchanger E-1201 heats the feed, Stream 2. The temperature of the exit stream, Stream 3, may not exceed a value that is 5°C lower than the inlet temperature of the appropriate type of steam used for heating.

Heat exchanger E-1202 may be used to cool (or heat) the reactor outlet, Stream 4. If E-1202 is used for cooling, then the temperature of the exit stream, Stream 5, should be at least 5°C greater than the temperature of the outlet cooling water. If E-1202 is used for heating, then the Stream-5 temperature may not exceed a value that is 5°C lower than the inlet temperature of the appropriate type of steam used for heating. The temperature of Stream 5 should be such that the temperatures of Streams 6 and 7 correspond to an optimum separation in the Flash Vessel V-1202 operating adiabatically at the optimum separation pressure.

Heat exchangers E-1205 and E-1208 are used respectively to cool the product liquid, Stream 17, to 37°C and the wastewater, Stream 22, to 40°C. For each of these heat exchangers, the exit temperatures 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-1201: 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 the reactions in Equations (1) and (2) are assumed to occur. The ranges of parameters that can be used are: temperature between 400-600 K and pressure between 1000-1500 kPa. The selectivity  $S$  for DEE formation in R-1201 (relative to ethylene) is dependent on temperature and pressure, and is given by the following:

$$S = S_o \left( \frac{P}{1250} \right)^n \exp \left[ A \left( \frac{1}{T} - \frac{1}{1500} \right) \right] \quad (3)$$

with  $T$  in [K] and  $P$  in [kPa].  $S_o$ ,  $A$  and  $n$  must be obtained by regression of data provided in Table 1 by the company laboratory. 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. The regression should not be extrapolated outside the range 400-600 K.

**Table 1. Selectivity Data for DEE**

Temperature, $T$ [K]	400	400	450	450	500	500	550	550	600	600
Pressure, $P$ [kPa]	1000	1500	1000	1500	1000	1500	1000	1500	1000	1500
Selectivity	24.87	21.48	12.60	10.84	7.43	6.38	4.94	4.23	3.59	3.08

$$S = \frac{\text{change in the molar flow rate of DEE}}{\text{change in the molar flow rate of ethylene}}$$

The catalyst cost in R-1201 may be significant and must be taken into account in the economics and optimization.

Flash Vessel, V-1202: For the purposes of this design project, assume the flash vessel operates adiabatically. Assume that ethylene is insoluble in Stream 6; therefore, all the ethylene present in Stream 5 is present only in Stream 7. Also, assume that water, DEE and EtOH are partitioned between Streams 6 and 7 according to Raoult's Law. You should optimize V-1202 (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 DEE in Stream 6.

Pumps: Pumps increase the pressure of liquids. Figure 1 contains one pair of pumps, P-1201A/B. When you revise Figure 1, you need to add pumps as appropriate, even if they are not currently present in Figure 1. For all pumps, the cost of energy may be neglected for this project.

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:

$$\dot{W}_s [\text{kW}] = 20,000 \dot{m} [\text{kmol/s}] \left[ \left( \frac{P_{out}}{P_{in}} \right)^{0.286} - 1 \right] \quad (4)$$

where  $\dot{m}$  [kmol/s] is the total molar flow rate of the inlet stream. Equation (4) 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:

$$\frac{T_{out}}{T_{in}} = \left( \frac{P_{out}}{P_{in}} \right)^{0.286} \quad (5)$$

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

Distillation Columns T-1201 and T-1202: From V-1202, the liquid product stream (Stream 6) enters the distillation section, columns T-1201 and T-1202.

Stream 17, the top product from the DEE column T-1201, must contain all of the DEE entering the distillation train, and must contain 99.5 mol% DEE, with the rest of Stream 17 being water and ethanol. Note that the compositions of Streams 14-18 must be the same, although temperatures and phases differ. Stream 14, which goes to condenser E-1203, must be a saturated vapor, while Streams 15-17 are saturated liquids. The molar flow rate of Stream 14 must be 10 times that of Stream 17. Stream 17 is cooled to 37°C by E-1205, as noted earlier. Also, the compositions of Streams 9-13 must be the same, although temperatures and phases vary. Streams 9, 10 and 12 must be saturated liquids and Stream 11 must be a saturated vapor. The molar flow rate of Stream 11 must be one-third that of Stream 12. T-1201 must operate at a pressure low enough to make Stream 9 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-1204. Stream 13, the bottoms product from the DEE column (T-1201), is further distilled in the EtOH column (T-1202).

In T-1202, note that the compositions of Streams 24-28 must be the same, although temperatures and phases differ. Stream 24, which goes to condenser E-1206, must be a saturated vapor, while Streams 25-27 are saturated liquids. The molar flow rate of Stream 24 must be 10 times that of Stream 28. The overhead product, Stream 28, contains 70 mol% EtOH in water, and is recycled to mix with Stream 1 in V-1201 before the reactor R-1201. Also, the compositions of Streams 19-23 must be the same, although temperatures and phases vary. Streams 19, 20 and 22 must be saturated liquids and Stream 21 must be a saturated vapor. The bottoms product of T-1202, Stream 22, must be water with a small amount of EtOH, and goes to a wastewater treatment facility after being cooled to 40°C in E-1208. The molar flow rate of Stream 21 must be one-third that of Stream 22. T-1202 must operate at a pressure low enough to make Stream 19 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-1206.

#### Other Equipment Considerations:

- Flow must occur from a higher pressure to a lower pressure.
- Two streams that are to be mixed are required to be at identical pressures.
- Pressure reduction is accomplished by adding a valve.
- 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-1201, T-1201, and T-1202, and to remove material from any towers operating under vacuum conditions.
- A distillation column operates at constant pressure, *i.e.*, the two (or more) streams leaving the column are at the same pressure. The stream(s) entering the column may be at the column pressure, or above. For this design, column pressure is determined by the temperature of the heating source for the bottom product and the composition of the bottom product; see the instructions in the Equipment section. The temperatures of streams entering and leaving the column generally decrease with

height up the column, *i.e.*, the temperature of the top product is the lowest and the temperature of the bottom product is the highest.

- 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

Most data can be found in Reference [1]. Use:

$$C_p^{(liq)}_{DEE} [\text{kJ/kmol K}] = 0.147 \quad (6)$$

$$C_p^{(vap)}_{DEE} [\text{kJ/kmol K}] = 0.02149 + 3.369 \times 10^{-4} T - 1.039 \times 10^{-7} T^2 - 9.387 \times 10^{-12} T^3 \quad (7)$$

with  $T$  in [K] for this year's project only. Any other data can be found from any handbook, *e.g.*, Reference [2].

## Economic Analysis

### Objective Function

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

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

A negative EAOC means there is a profit. It is desirable to minimize the EAOC; *i.e.*, a large negative EAOC is very desirable. Brief descriptions of the various constituents of EAOC follow.

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 (4). 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 1200). These credits are also provided below.

### Raw Material Cost, 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.

**Table 2. Material Prices [3]**

Component	DEE	Ethanol
Price [\$/kg]	1.51	0.98

### 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**

Equipment	Installed Cost [in thousands of dollars]
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 8 used as a fuel source (credit)	\$9.00/GJ

Electricity	\$0.06/kWh
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Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg
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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.

Cooling Water	\$0.354/GJ
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Available at 516 kPa and 30°C

Return pressure  $\geq$  308 kPa

Return temperature should be no more than 15°C above the inlet temperature

Refrigerated Water	\$4.43/GJ
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Available at 516 kPa and 5°C

Return pressure  $\geq$  308 kPa

Return temperature should be no higher than 15°C

### **Waste treatment**

For Stream 23	\$5.00/1000 kg
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### **Catalyst**

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

You have learned, or will learn, optimization methods in ChE 230. The objective function (EAOC) is defined in Equation (8). 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-1201, 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, the liquid formed in V-1202 separates into two phases, which must be added as two streams separately to T-1201. Further, DEE and water could form an azeotrope, a mixture which is difficult to separate by distillation. Finally, a peroxide inhibitor is generally added to the product DEE for safety reasons. These issues are not considered in this design project. Additionally, the selectivity data used may not correspond to the actual kinetics and equilibrium.

## **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, 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 flow rate, total molar flow

rate, and component molar flow rates. 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 20, 2012 by 3:00 pm. Two "originals" must be submitted, one each to Professors Dadyburjor and Stinespring.

### **Oral Report**

Project results will be presented orally in the ChE 202 class on Monday, April 23, 2012. Oral presentations will continue on April 24 and April 25. 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 are also available at the following web site: <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 26, 2012.

### **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. Felder, R.M. and R.W. Rousseau, *Elementary Principles of Chemical Processes (3rd ed. 9<sup>th</sup> printing)*, Wiley, New York, 2005.
2. Perry, R. H. and D. Green, eds., *Perry's Chemical Engineering Handbook (7<sup>th</sup> ed.)*, McGraw-Hill, New York, 1997.
3. <http://www.icis.com/chemicals/channel-info-chemicals-a-z/>