Separations and Reaction Engineering
Design Project

Production of Ethanol

Your assignment is to continue evaluating the details of a process to produce 30,000 tonne ethanol per year from ethylene. As the final part of the feasibility study, we would like you to study the details of the reactor and separation section of proposed plant and then optimize the complete process. Your final design should be an optimized process and should include all unit operations necessary to produce the desired amount and purity of ethanol.

Chemical Reaction

Most ethanol manufactured in the U.S. is generated using a fermentation process. However, a small amount is manufactured via the catalytic, gas-phase hydration of ethylene. This process is commercially competitive with a fermentation-based process when ethylene streams are readily available. Legacy facilities for the conversion of ethylene to ethanol by direct hydration were based upon a liquid acid catalyst, such as phosphoric or sulfuric acids. Trace amounts of the liquid acid catalyst remaining in the ethanol product stream prohibit the use of ethanol as a transportation fuel due to the corrosive nature of this impurity. In light of new market conditions, you are to consider the direct hydration of ethylene using a tungsta monolayer loaded on titania catalyst.

The reaction that occurs in the reactor is reversible

$$C_2H_4 + H_2O \leftrightarrow C_2H_5OH \tag{1}$$

Ethylene is available from a pipeline at 5000 kPa and 25°C. The ethylene feed specifications are 8 mole % acetylene, 5 mole % ethane, 1 mole % methane and the balance is ethylene. The specifications of the crude ethanol product stream is to have an ethanol content of greater than 96 weight % at a pressure of 200 kPa and as a saturated liquid.

The feed stream contains acetylene that reacts with water to form acetaldehyde.

$$C_2H_2 + H_2O \leftrightarrow CH_3CHO \tag{2}$$

Acetaldehyde in the product stream is acceptable at only very low concentrations (< 1 ppm). Detailed kinetics for the reaction network are shown in Appendix 2.

Specific Assignments

1. Separations Design – (ChE 312)

You are to determine the number of distillation columns required, their locations, their sequence, and enough information for each column to determine their costs. The distillation column that purifies the ethanol 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.

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 factor as defined in Wankat[1], p. 336, is that for Koch Flexipac #2. Assume the HETP for the structured packing to be 0.6 m (see the definition of HETP in Wankat[1], p. 332, and the relationship between HETP and H_{OG} in Equation 15.36 in Wankat[1].), 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. They are 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. The suggested heat-transfer fluid is Dowtherm A™. 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. Properties of the Dowtherm A™ can be obtained from Chemcad..

For your best case, you should include a discussion of the temperature, pressure, and concentration profiles obtained from Chemcad.

Other Information

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

Deliverables

General

The entire ethanol process should be optimized using decision variables of your choosing. Decision variables should be chosen as those most strongly affecting the objective function. There are topological optimization and parametric optimization. In topological optimization, which is usually done first, the best process configuration is chosen. Parametric optimization involves varying operating variables and should be done after topological optimization is complete. Some examples of parameters that can be used as decision variables are reactor temperature, pressure, conversion, and distillation column reflux ratio.

Economic Analysis

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

EAOC = -(product value - feed cost – utility costs – waste treatment cost - 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.

The capital cost annuity is an ***annual*** cost (like a car payment) associated with the ***one-time***, fixed cost of plant construction.

The capital cost annuity is defined as follows:

$$\textit{capital cost annuity} = FCI\,\frac{i(1+i)^n}{(1+i)^n-1} \tag{3}$$

where *FCI* is the installed cost of all equipment; *i* is the interest rate (take *i* = 0.15) and *n* is the plant life for accounting purposes (take *n* = 10).

Report Format

Other Information

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

Deliverables

Written Reports

Each group 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. Wednesday, April 22, 2009. 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 base case. Figure 1 should be used as a template for your PFD. 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 two “mini-designs,” it is suggested that the report be organized as follows. There should be a general abstract and introduction. Then, there should be a results section followed by a discussion section for each of the major components of this design project, namely the design of the reactor and separation strategy. General conclusion and recommendation sections should follow. At a minimum, there should be separate appendices for each class, ChE 312 and ChE 325, each containing detailed calculations that are clearly written, easy to follow, and appropriate for the respective class.

In order to evaluate each group member’s writing skills, the results and discussion sections for each mini-design should be written by a different group member. The authorship of each of these mini-reports should be clearly specified in the report. Although the individual written portions of the reports must be authored by a single group member, it is the intent of the instructors that group 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 group.

The reports will be evaluated as follows:

- course-specific technical content – 50%
- oral presentation – 20%
- written report – 20%
- technical quality of general sections (safety, simulation, etc.) – 10%

For a more detailed set of evaluation criteria that we will use, 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 group 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 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 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. Each group 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 Wednesday April 22, 2009, from 11:00 a.m. to 1:00 pm. 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 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, questions from the class will require revisions and/or clarifications of the problem statement. You should be aware that these revisions/clarifications might be forthcoming.

References

1. Wankat, P., *Separation Process Engineering* (2nd ed.), Prentice Hall, Upper Saddle River, NJ, 2007.

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 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)

Catalyst $2.25/kg

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.
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.

Additional Cost Information

Piping straight pipe $\$/\text{m} = 5.0\,(\text{nominal pipe diameter, in})(1+(\text{sch }\#)/20)^{0.25}$
sch = schedule number for pipe
use the same sch number for fittings and valves

fittings (except valves) $\$/\text{fitting} = 50.0\,(\text{nominal pipe diameter, in})(1+(\text{sch }\#)/20)^{0.25}$

Valves for gate (isolation) valves $\$100\,(\text{nominal pipe diameter, in})^{0.8}\,(1+(\text{sch }\#)/20)^{0.25}$
for control valve use $\$1000\,(\text{nominal pipe diameter, in})^{0.8}(1+(\text{sch }\#)/20)^{0.25}$

Utility Costs

Low-Pressure Steam (618 kPa saturated)	$\$13.28/\text{GJ}$
Medium-Pressure Steam (1135 kPa saturated)	$\$14.19/\text{GJ}$
High-Pressure Steam (4237 kPa saturated)	$\$17.70/\text{GJ}$
Natural Gas (446 kPa, 25°C)	$\$11.00/\text{GJ}$
Fuel Gas Credit	$\$9.00/\text{GJ}$
Electricity	$\$0.06/\text{kWh}$
Boiler Feed Water (at 549 kPa, 90°C)	$\$2.45/1000\ \text{kg}$
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	$\$0.354/\text{GJ}$
Refrigerated Water available at 516 kPa and 10°C return pressure ≥ 308 kPa return temperature is no higher than 20°C	$\$4.43/\text{GJ}$
Deionized Water available at 5 bar and 30°C	$\$1.00/1000\ \text{kg}$
Waste Treatment of Off-Gas	incinerated - take fuel credit
Refrigeration	$\$7.89/\text{GJ}$
Wastewater Treatment	$\$56/1000\ \text{m}^3$

Equipment Cost Factors

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

Pressure (absolute)
< 10 atm, PF = 0.0
10 - 20 atm, PF = 0.6
20 - 40 atm, PF = 3.0
40 - 50 atm, PR = 5.0
50 - 100 atm, PF = 10

does not apply to turbines, compressors, vessels, packing, trays, or catalyst, since their cost equations include pressure effects

Carbon Steel MF = 0.0
Stainless Steel MF = 4.0

Appendix 2 – Information on Reaction Kinetics

The main reaction in the catalytic, gas-phase hydration of ethylene is

$$C_2H_4 + H_2O \underset{r_2}{\overset{r_1}{\longleftrightarrow}} C_2H_5OH \qquad \text{(A2-1)}$$

$$\textit{ethylene} \qquad\qquad \textit{ethanol}$$

where r_1 and r_2 are the forward and reverse rates, respectively. Experimental analysis of the performance of this catalyst [A2-1], gives the following expressions for these reaction rates:

$$r_1 = \frac{k_1 p_W p_E}{\left(1 + K_W p_W + K_E p_E + K_A p_A + K_{DEE} p_{DEE}\right)^2} \qquad \text{(A2-2)}$$

and

$$r_2 = \frac{k_2 p_A}{\left(1 + K_W p_W + K_E p_E + K_A p_A + K_{DEE} p_{DEE}\right)^2} \qquad \text{(A2-3)}$$

where

$$k_1\ [\text{kmol/m}^3\text{cat/h/atm}^2] = 8.342 \times 10^{-13} \exp\left(\frac{121{,}435}{RT}\right) \qquad \text{(A2-4)}$$

$$k_2\ [\text{kmol/m}^3\text{cat/h/atm}^2] = 6.4062 \times 10^{-6} \exp\left(\frac{74{,}311}{RT}\right) \qquad \text{(A2-5)}$$

$$K_w\ [\text{atm}^{-1}] = 1.2328 \times 10^{-17} \exp\left(\frac{162{,}730}{RT}\right) \qquad \text{(A2-6)}$$

$$K_E\ [\text{atm}^{-1}] = 2.0850 \times 10^{-4} \exp\left(\frac{35{,}368}{RT}\right) \qquad \text{(A2-7)}$$

$$K_A\ [\text{atm}^{-1}] = 3.3685 \times 10^{-8} \exp\left(\frac{59{,}150}{RT}\right) \qquad \text{(A2-8)}$$

and the activation energy is given in kJ/kmol, and p_i is measured in atmospheres.

Under typical reactor conditions, the last term in the denominator (*i.e.*, $K_{DEE}p_{DEE}$) is negligible and may be ignored. Also note that the exponential terms in the numerator and denominator of the rate laws (Eqns. A2-2, A2-3, A2-10, and A2-11) are all positive. This is an artifact of the lumping together of reaction rate constants and adsorption equilibrium constants in

Equations A2-2, A2-3, A2-10, and A2-11. However, the net effect of temperature on the overall forward and reverse reactions is that the overall rates increase with increasing temperature, which is consistent with Arrhenius-type behavior.

Along with the desired, forward, reaction shown in Equation (A2-1), ethanol can also dehydrate to form diethyl ether as follows:

$$\underset{ethanol}{2C_2H_5OH} \underset{r_4}{\overset{r_3}{\longleftrightarrow}} H_2O + \underset{diethyl\ ether}{(CH_3CH_2)_2O} \tag{A2-9}$$

where

$$r_3 = \frac{k_3 p_A^2}{\left(1 + K_W p_W + K_E p_E + K_A p_A + K_{DEE} p_{DEE}\right)^2} \tag{A2-10}$$

$$r_4 = \frac{k_4 p_W p_{DEE}}{\left(1 + K_W p_W + K_E p_E + K_A p_A + K_{DEE} p_{DEE}\right)^2} \tag{A2-11}$$

and

$$k_3\ [\mathrm{kmol/m^3cat/h/atm^2}] = 1.7723 \times 10^{-2} \exp\left(\frac{50{,}031}{RT}\right) \tag{A2-12}$$

$$k_2\ [\mathrm{kmol/m^3cat/h/atm^2}] = 1.3865 \times 10^{-13} \exp\left(\frac{194{,}115}{RT}\right) \tag{A2-13}$$

The catalyst used in the process of interest is a tungsta monolayer loaded on a titania support. The bulk density of this catalyst was reported to be 1.8 g/ml.

In addition, any acetylene in the ethylene feed may be converted to acetaldehyde, which is tolerable in the final ethanol product at only very low concentrations (< 1ppm).

$$\underset{acetylene}{C_2H_2} + H_2O \xrightarrow{r_5} \underset{acetaldehyde}{CH_3CHO} \tag{A2-14}$$

The rate for this reaction is given by:

$$r_5 = k_5 p_{Acet} \tag{A2-15}$$

where

$$k_5\ [\text{kmol/m}^3\text{cat/h/atm}] = 1\times10^{-4}\exp\left(-\frac{25{,}000}{RT}\right) \qquad \text{(A2-16)}$$

Reference

A2-1. Momose, H., K. Kusumoto, Y. Izumi, and Y. Mizutani, “Vapor-Phase Direct Hydration of Ethylene over Zirconium Tungstate Catalyst,” *J. Catalysis*, 77, 23-31 (1982).