Separations and Reaction Engineering
Spring 2002

Design Project

Production of Dimethyl Ether and Diethyl Ether

Introduction

Our company currently produces dimethyl ether from methanol and diethyl ether from ethanol. Construction of a new process to meet increased demand appears certain. We are in the midst of evaluating whether a mixed alcohol feed containing 88 mole% methanol, 11 mole% ethanol, and 1 mole% water would be suitable as a feed to produce both ethers, because it is available at a lower price than either pure alcohol. The desired capacities are 100,000 tonne/y dimethyl ether (DME) and 15,000 tonne/y diethyl ether (DEE). Thus far, we have investigated two alternatives. The first is production of both ethers simultaneously in the same reactor followed by separation of all reaction products. The second is separation of the mixed feed followed by two parallel processes, one to produce each ether. With the first alternative, it is very difficult to achieve both production goals simultaneously. With the second alternative, the capital cost is very high due to the amount of equipment needed.

Assignment

Your assignment is to investigate a third alternative: separation of the alcohols followed by production of both ethers in the same equipment in two "campaigns" over the course of the year. For example, while DME is being produced, ethanol would be stored; then, when DEE is being produced, methanol would be stored. Your design should include capital costs only for the storage tanks used to store the alcohols after purification, in addition to the needed equipment for the process.

In order to make this problem tractable, you should do the following. Divide the 8000-hour year into two parts, 6957 hours to make DME and 1043 hours to make DEE. These numbers are obtained by dividing the year in proportion to the amount of each ether to be produced in that time period. Since we are primarily interested in DME, you should design and optimize a process to produce 100,000 tonne of DME in 6957 hours. Then, you should investigate what type of flexibility needs to be introduced into the equipment design and what, if any, additional equipment needs to be added to produce 15,000 tonne of DEE in 1043 hours. If you complete the above assignment and have additional time, you should investigate whether the year could be divided up differently and equipment designed and/or operated differently to improve the profitability. It is assumed that there will be approximately a two-week shutdown (about 380 hours) between campaigns; therefore, minor equipment adjustments are possible during the shutdowns. (Note that one full year is 24×365=8760 hours. So, one full year equals one year of operation at 8000 hours plus 2 shut-down periods of 380 hours each.)

In the process of optimizing this design, it is allowable to purchase small amounts of pure alcohols to supplement the mixed feed if the economic benefits warrant it.

Reaction Kinetics

The reactions involved in the production of ethers from alcohols are listed below. Note that our proprietary catalyst eliminates the production of the asymmetric methyl ethyl ether.

The reaction from methanol to DME is limited by equilibrium. The equilibrium expression for that reaction is

$$\ln K = -2.205 + \frac{2708.6317}{T}$$

The kinetics that follow are only valid if the single-pass conversion of methanol in the reactor does not exceed 80% of the equilibrium conversion.

Several processing schemes to produce the mixed ether products are possible. The catalyst used for the reactions is high-purity γ-alumina. The reactions that take place are [1, 2]:

$$\begin{array}{l} 2CH_3OH \xrightarrow{k_1} (CH_3)_2O + H_2O \\ \textit{methanol} \qquad \textit{DME} \end{array}$$

$$\begin{array}{l} (CH_3)_2O + H_2O \xrightarrow{k_2} 2CH_3OH \\ \textit{DME} \qquad\qquad\qquad \textit{methanol} \end{array}$$

$$\begin{array}{l} C_2H_5OH \xrightarrow{k_3} C_2H_4 + H_2O \\ \textit{ethanol} \qquad \textit{ethylene} \end{array}$$

$$\begin{array}{l} 2C_2H_5OH \xrightarrow{k_4} (C_2H_5)_2O + H_2O \\ \textit{ethanol} \qquad\quad \textit{DEE} \end{array}$$

$$\begin{array}{l} (C_2H_5)_2O \xrightarrow{k_5} C_2H_5OH + C_2H_4 \\ \textit{DEE} \qquad\quad \textit{ethanol} \qquad \textit{ethylene} \end{array}$$

$$\begin{array}{l} (C_2H_5)_2O \xrightarrow{k_6} 2C_2H_4 + H_2O \\ \textit{DEE} \qquad\quad \textit{ethylene} \end{array}$$

The forms of the rate equations for these reactions are taken from references 1 and 2, and are:

Reaction 1

$$r_1 = \frac{71.82\exp\left(\frac{+7,867[kPa.m^3/kmol]}{RT}\right)p_{MeOH}^2}{\left[1+3.9471\times10^{-4}\exp\left(+\frac{37,835}{RT}\right)p_{MeOH}{}^{1/2}+5.6057\times10^{-6}\exp\left(+\frac{47,468}{RT}\right)p_{H_2O}\right]^4}$$

Reaction 2

$$r_2 = \frac{651.1\exp\left(\frac{-14,652[kPa.m^3/kmol]}{RT}\right)p_{DME}\,p_{H_2O}}{\left[1+3.9471\times10^{-4}\exp\left(+\frac{37,835}{RT}\right)p_{MeOH}{}^{1/2}+5.6057\times10^{-6}\exp\left(+\frac{47,468}{RT}\right)p_{H_2O}\right]^4}$$

Reaction 3

$$r_3 = \frac{0.08345\exp\left(\frac{-1770[kPa.m^3/kmol]}{RT}\right)p_{EtOH}}{\left[1+1.2185\times10^{-6}\exp\left(+\frac{41,060}{RT}\right)p_{EtOH}+5.295\times10^{-6}\exp\left(+\frac{33,010}{RT}\right)p_{DEE}+3.573\times10^{-5}\exp\left(\frac{+26,200}{RT}\right)P_{H_2O}\right]}$$

Reaction 4

$$r_4 = \frac{5.81\exp\left(\frac{-23,090[kPa.m^3/kmol]}{RT}\right)p_{EtOH}^2}{\left[1+1.2185\times10^{-6}\exp\left(+\frac{41,060}{RT}\right)p_{EtOH}+5.295\times10^{-6}\exp\left(+\frac{33,010}{RT}\right)p_{DEE}+3.573\times10^{-5}\exp\left(\frac{+26,200}{RT}\right)P_{H_2O}\right]}$$

Reaction 5

$$r_5 = \frac{1.7876\times10^5\exp\left(\frac{-72,210[kPa.m^3/kmol]}{RT}\right)p_{DEE}}{\left[1+1.2185\times10^{-6}\exp\left(+\frac{41,060}{RT}\right)p_{EtOH}+5.295\times10^{-6}\exp\left(+\frac{33,010}{RT}\right)p_{DEE}+3.573\times10^{-5}\exp\left(\frac{+26,200}{RT}\right)P_{H_2O}\right]}$$

Reaction 6

$$r_6 = \frac{31.44\exp\left(\frac{-31,763[kPa.m^3/kmol]}{RT}\right)p_{DEE}}{\left[1+1.2185\times10^{-6}\exp\left(+\frac{41,060}{RT}\right)p_{EtOH}+5.295\times10^{-6}\exp\left(+\frac{33,010}{RT}\right)p_{DEE}+3.573\times10^{-5}\exp\left(\frac{+26,200}{RT}\right)P_{H_2O}\right]}$$

It should be noted that the term in the exponential in the numerator of Reaction 1 (that looks like an activation energy) is negative. This is unusual; however, the term in the numerator is actually the product of a rate constant (with a positive activation energy) and two adsorption constants (with negative adsorption energies). The net result is a negative value for the term in the exponential. This reaction rate form will give a warning in Chemcad, but you can ignore this during the simulation. It should also be noted that the terms in the denominators are adsorption rates with negative adsorption or activation energies. The net result for all reactions is that, as the temperature increases, the overall reaction rates given by the above equations all increase. This is consistent with our intuition.

In order to prevent catalyst deterioration and sintering, a maximum temperature of 400°C should be used for the catalyst. This means that nowhere in the catalyst bed should the temperature exceed 400°C. The form of the catalyst is 3-mm diameter pellets (you may assume that these are spherical) and their bulk density is 940 kg/m^3 (voidage = 0.5). The following cost estimates are for the purchased costs for different reactor types:

Fluidized Bed Reactor = $\$2.29\times10^5[\text{Volume of Catalyst and Voids } (m^3)]^{0.67}$

Packed Bed Reactor (cooling fluid in Shell and Catalyst in Tubes) =
$\$2.24\times10^4[\text{Heat Transfer Area } (m^2)]^{0.5}$

Packed Bed Reactor (Adiabatic Packed Bed with Heat Exchange after the Packed Bed) =
$\$4.57\times10^4[\text{Volume of Catalyst and Voids } (m^3)]^{0.67}$ + Cost of Heat Exchanger

Thermodynamic Model for CHEMCAD Simulation

Use the UNIQUAC thermodynamics package for your K-value option and the SRK model as your enthalpy option.

Chemcad Hints

For heat exchangers with multiple zones, it is recommended that you simulate each zone with a separate heat exchanger. Actual equipment may include several zones, so costing should be based on the actual equipment specifications. On your PFD, only the actual equipment should appear.

For the distillation columns, you should use the shortcut method (SHOR) to get estimates for the rigorous distillation simulation (TOWR or SCDS). The shortcut method may be used until an optimum case is near. It is then expected that everyone will obtain a final design using rigorous simulation of the columns. For an absorber, shortcut calculations are not possible.

When simulating a process using "fake" streams and equipment, it is absolutely necessary that the process flow sheet that you present not included any "fake" streams and equipment. It must represent the actual process.

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:

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

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).

Specific Assignments

General

Optimize the DME process using decision variables of your choosing. Each ether product purity should be 99.5 wt %. You should choose as decision variables the design variables most strongly affecting the objective function. Then, determine what modifications/additions are necessary to produce DEE in the same equipment.

ChE 312

Determine the number of distillation columns required, their location, and enough information for each distillation column to cost them. The distillation column that separates the alcohol feed should be designed in detail. A detailed design of a tray tower includes number of trays, tray spacing, diameter, reflux ratio, active area, 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. You should determine the better choice between packed and tray towers.

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% up to a ratio of 25, and a “penalty” of an additional 100% up to a ratio of 30.

ChE 325

Three reactors may be considered for use in this design. They are an adiabatic packed-bed reactor, an “isothermal” packed-bed reactor, and a fluidized-bed reactor. A fluidized-bed reactor is modeled as an isothermal PFR. Its behavior approaches that of a PFR for the material balance, but the mixing caused by the fluidization creates a constant temperature throughout the bed. An “isothermal” packed-bed reactor is defined here as one with a specified outlet temperature. 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. One suggestion for the heat-transfer fluid is Dowtherm™ A; however, you may make another choice, such as making steam from boiler feed water or using cooling water. If a heat-transfer fluid is used, it is circulated in a closed loop through the reactor where its temperature is increased. Then, heat is removed from the fluid in a heat exchanger. The cooled heat-transfer fluid is then pumped back to the reactor.

For your best case that is a packed-bed reactor, you should include a discussion of the temperature, pressure, and concentration profiles obtained from Chemcad.

Cost Data

Equipment Costs (Purchased)

Pumps	$\$630\ (\text{power, kW})^{0.4}$
Heat Exchangers	$\$1030\ (\text{area, m}^2)^{0.6}$
Compressors	$\$770\ (\text{power, kW})^{0.96} + 400\ (\text{power, kW})^{0.6}$
Turbine	$\$2.18\times10^5\ (\text{power output, MW})^{0.6}$ assume 65% efficiency
Fired Heater	$\$635\ (\text{duty, kW})^{0.8}$ assume 80% thermal efficiency assume can be designed to use any organic compound as a fuel
Vessels	$\$[1.67(0.959 + 0.041P - 8.3\times10^{-6}P^2)]\times10^{z}$ $z = (3.17 + 0.2D + 0.5 \log_{10}L + 0.21 \log_{10}L^2)$ D = diameter, m $0.3\text{ m} < D < 4.0\text{ m}$ L = height, m $L/D < 20$ P = absolute pressure, bar
Catalyst	\$2.25/kg
Packed Tower	Cost as vessel plus cost of packing
Packing	$\$(-110 + 675D + 338D^2)H^{0.97}$ D = vessel diameter, m; H = vessel height, m
Tray Tower	Cost as vessel plus cost of trays
Trays	$\$(187 + 20D + 61.5D^2)$ D = vessel diameter, m
Storage Tank	$\$1000V^{0.6}$ V = volume, m^3

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.

Raw Materials

mixed alcohol feed	\$0.70/gal

pure alcohols	see *Chemical Market Reporter*

Products

dimethyl ether	\$1.00/kg
diethyl ether	see *Chemical Market Reporter*

Utility Costs

Low Pressure Steam (618 kPa saturated)	\$6.62/1000 kg
Medium Pressure Steam (1135 kPa saturated)	\$7.31/1000 kg
High Pressure Steam (4237 kPa saturated)	\$8.65/1000 kg
Natural Gas (446 kPa, 25°C)	\$3.00/GJ
Fuel Gas Credit use this price for fuel gas credit	\$2.50/GJ
Electricity	\$0.06/kW h
Boiler Feed Water (at 549 kPa, 90°C)	\$2.54/1000 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	\$0.16/GJ
Refrigerated Water available at 516 kPa and 10°C return pressure ≥ 308 kPa return temperature is no higher than 20°C	\$20/GJ
Deionized Water available at 5 bar and 30°C	\$1.00/1000 kg
Waste Treatment of Off-Gas	incinerated - take fuel credit
Refrigeration	\$60/GJ
Wastewater Treatment	\$50/1000 m^3

Equipment Cost Factors

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

Pressure (absolute)	< 10 atm, PF = 0.0	does not apply to turbines, compressors, vessels, packing, trays, or catalyst, since their cost equations include pressure effects
	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

Heat Exchangers

For heat exchangers, use the following approximations for heat-transfer coefficients to allow you to determine the heat transfer area:

situation	***h*** **(W/m²°C)**
condensing steam	6000
condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60

Physical Properties of Dowtherm™ A

temperature use range (in liquid phase)	60°F – 750°F
vapor pressure at 750°F	137.8 psig
thermal conductivity (avg. over use range)	0.07 BTU/hr ft°F
heat capacity (avg. over use range)	0.5 BTU/lb°F
viscosity (at max. and min. temp. use range)	0.14 cp, 6.0 cp
density (avg. over use range)	54 lb/ft^3

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

Each group must deliver a report (two identical copies, one for each professor) written using a word processor. The report should be clear and concise. The format is explained in the document *Written Design Reports*. Any report not containing a labeled PFD and a stream table, each in the appropriate format, will be considered unacceptable. PFDs from CHEMCAD are generally unsuitable unless you modify them significantly. 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. There should be separate appendices for each class, ChE 312 and ChE 325, each containing calculations appropriate for the respective class. These may be handwritten if done so neatly. Calculations that cannot be easily followed will lose credit.

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. A 5-10 minute question-and-answer session will follow. Instructions for presentation of oral reports are provided in a separate document entitled *Oral Reports*. The oral presentations will be Wednesday, April 24, 2002, starting at 11:00 a.m. and running until approximately 3:00 p.m. It is possible that some presentations will be on Thursday, April 25, 2002, beginning at 11:00 am. 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.

The written project report is due by 11:00 a.m. Wednesday, April 24, 2002. Late projects will receive a minimum deduction of one letter grade.

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.

References

1. Butt, J. B., H. Bliss, and C. A. Walker, "Rates of Reaction in a Recycling System – Dehydration of Ethanol and Diethyl Ether Over Alumina," *AIChE-J*, **8**, 42-47 (1962).

2. Berčič, G. and J. Lavec, "Intrinsic and Global Reaction Rates of Methanol Dehydration over γ-Al_2O_3 Pellets," *Ind. Eng. Chem. Res.*, **31**, 1035-1040 (1992).