A Grass Roots Facility to Produce Mixed Ethers

Background

During the past few years, production of dimethyl ether (DME) at Drift Engineering facilities has been steadily increasing due to increased sales in the aerosol business. We now find ourselves in the position that we are operating at full capacity, and our business group is turning down contracts with new customers due to lack of capacity. For this reason, we are considering building a new facility to supply both DME and diethyl ether (DEE) to a growing customer base. The location of this new facility has not been finalized, but all cost estimates will be done based on Gulf Coast prices.

Product and Feed Specifications

The object of your new assignment is to design a grass roots facility to produce a mixture of pure DME and pure DEE using a mixed feed stream of ethanol (EtOH) and methanol (MeOH). The composition of this feed stream is the same as given previously, namely:

Methanol	88 mol%
Ethanol	11 mol%
Water	1 mol%

This feed stream is available at a cost of $0.70 per gallon. Refined methanol and/or ethanol may also be purchased to supplement this feed if you deem it necessary. The Chemical Market Report (Sept 18, 2000) gives that the current prices for these raw materials as follows:

- The price of 190-proof ethanol (95 vol%) varies from $1.35 to $ 2.10 per gal - use a value of $ 1.80 per gal
- The price of methanol varies from $0.66 to $0.69 per gal – use a value of $ 0.675 per gal

The specifications for the products are as follows:

- Dimethyl Ether >99.5 wt% purity with less than 0.1 wt% alcohol – current price is $0.43 per lb
- Diethyl Ether >99.5 wt% purity with less than 0.1 wt% alcohol– current price is $0.575 per lb
- Ethylene >95 wt% purity with less than 1 wt% water

You may sell the ethylene for twice its fuel value based on the equivalent value for natural gas of $2.50 per GJ. If you cannot make this specification, then you may sell the ethylene as a fuel gas substitute at $2.50 per GJ, however, the water content cannot exceed 2 wt% (in other words the fuel gas must contain at least 98 wt% organics). Note that current natural gas prices are much higher than this, but we expect these prices to come down in the long term.

Capacity of New Facility

The new plant should produce 100,000 tonnes/yr of DME and 15,000 tonnes/yr of DEE. The facility will have a stream factor of 0.94.

Economic Parameters

The fixed capital investment for this project should be based on the grass roots facility cost given by CAPCOST. The following economic parameters should be used to determine the economic viability of your optimized process.

Objective Function – Net Present Value
Internal hurdle rate = 9% p.a.
Time for Construction of Plant – 2 years
Distribution of Fixed Capital Investment – 60% at the end of year 1
– 40% at the end of year 2
Cost of Land - $ 1 million (taken at the end of year 0 – the start of the project)
Working Capital – use 6 months of the cost of manufacturing COM_d
Depreciation Method – use MACRS for 5 years (20%, 32%, 19.2%, 11.52%, 11.52%, 5.76%)
Taxation Rate = 45%
Life of the project = 10 years after startup (at the end of year 2)

You may use the utility costs given in Table 3.4 of your textbook (1). Also note that the cost of cooling water is $0.16 per GJ of heat removed, and the cost of cooling water does not depend on the return temperature! You may take the cost of refrigerated water (available at 5°C and returned at 15°C) as $20 per GJ of energy removed.

New Catalyst

Several processing schemes to produce the mixed ether products are possible. The catalyst used for the dehydration reactions is high purity γ-alumina. There are several reactions that can take place (2,3) and these are described below:

$$2CH_3OH \xrightarrow{k_1} (CH_3)_2O + H_2O$$
methanol *DME*

$$(CH_3)_2O + H_2O \xrightarrow{k_2} 2CH_3OH$$
DME *methanol*

$$C_2H_5OH \xrightarrow{k_3} C_2H_4 + H_2O$$
ethanol *ethylene*

$$2C_2H_5OH \xrightarrow{k_4} (C_2H_5)_2O + H_2O$$
ethanol *DEE*

$$(C_2H_5)_2O \xrightarrow{k_5} C_2H_5OH + C_2H_4$$
DEE *ethanol* *ethylene*

$$(C_2H_5)_2O \xrightarrow{k_6} 2C_2H_4 + H_2O$$
DEE *ethylene*

The forms of the rate equations for these reactions are taken from references 2 and 3, and are given below:

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 activation energy for reaction 1, given in the numerator, 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 activation energy. 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, namely that as the temperature increases the reaction rates also increase.

Due to the complexity of these equations, a CHEMCAD file has been placed on the desktop of the computers in the undergraduate room. This file gives a simulation for a packed bed, plug-flow, isothermal reactor using the above kinetic expressions. The active reactor volume is 1 m^3 (the volume that CHEMCAD gives is the volume of voids and catalyst) and the operating temperature is 320°C. The feed to the reactor is 100 kmol/h of the mixed alcohol feed described previously. The results of this simulation are included in Appendix 1 of this assignment. This simulation will help you get started in this project. Note that the reactor configuration given in this file is not optimized. The purpose of providing this file is to give a working kinetic model as a starting point. Adiabatic packed beds, staged beds with inter-cooling/heating, near isothermal beds with heat transfer, fluidized beds, and many other reactor configurations are all possible. You are expected to consider several alternative reactor configurations in this project.

In order to prevent catalyst deterioration and sintering, a maximum temperature for the catalyst of 400°C should be used. 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 capital investments for reactors are not included in the Capcost program. These may be entered as user added equipment. The following cost estimates are for the Bare Module Costs for different reactor types:

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

Packed Bed Reactor (cooling fluid in Shell and Catalyst in Tubes) =
$\$2.25\times10^4\left[Heat\ Transfer\ Area\ (m^2)\right]^{0.5}$

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

Thermodynamic Model for CHEMCAD Simulation

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

Assignment

Your assignment is to prepare a written and oral report summarizing your findings and recommendations. The written report is due on Monday, February 19th, 2001 at 9:00 am. You should read carefully the guidelines for written and oral reports and Chapters 22 and 23 in the your textbook (1). These chapters cover the required guidelines for written and oral presentations. A cover memorandum should accompany the report, the report must contain a table of contents, and all relevant calculations should be included in a well-indexed appendix. These calculations should be neat and legible but may be hand written. The form of the report should follow the guidelines for a standard design report, using standard headings, etc. The following information must appear in the main body of the report:

a. A computer-generated process flow diagram (PFD) showing the configuration of equipment for your recommended optimum case (the one that maximizes the Net Present Value).
b. A flow summary table showing the amounts and conditions of all the streams that are numbered on the PFD.
c. A clear summary of all cases for which you obtained solutions. These should be clearly labeled and explained. For example, Case A – two fixed bed reactors with inter-cooling and three towers operating in series, etc.
d. Figures must be provided that clearly illustrate why the chosen optimum case is the best case considered.
e. A list of all new equipment with installed costs and the bare module costs for the optimum process.
f. A summary table of the utilities consumed, by each piece of equipment, for the optimum process.
g. A signed copy of the confidentiality statement. This should be the very last page of the written report.

Please provide the written report in a 3-ring, spiral or riveted binder (not oversized). You must bring a hard copy of your slides to leave behind after the oral presentation. These should be distributed to your audience prior to the start of your presentation.

Late Written Reports

Late written reports are unacceptable. The following severe penalties will apply:

- Late reports on the due date after 9:00 am but before noon (February 19, 2001): one letter grade.
- Late reports after noon on the due date (February 19, 2001): two letter grades.
- Late report one day late (February 20, 2001): three letter grades.
- More than one day late (after February 20, 2001): one additional letter grade for every day after the 20th of February.

References

1. Turton, R., R.C. Bailie, W.B. Whiting, and J.A. Shaeiwitz, Analysis, Synthesis, and Design of Chemical Processes, Prentice Hall, Upper Saddle River, NJ (1998).
2. 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).
3. 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).

Appendix

CHEMCAD Output for Kinetic Reactor Example

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Equip. No.                      2
Name
Reactor type:                   2
Reaction phase                  1
Thermal mode:                   1
Pressure In  kPa          1300.0000
Pressure Drop  kPa         100.0000
Tout  C                    320.0000
Q  MJ/h                   -238.2742
Vol                          1.0000
Concentration Flag              1
No. of Reactions                6
Molar Flow Unit                 1
Activ. E/H of Rxn Unit          4
Volume Unit                     1
Overall Ht of Rxn         -492.5226
 (MJ/h)

Reaction Stoichiometrics and Parameters for unit no. 2

 Reaction   1
 Rate const =   3.5910e+001  Act. E =  -7.8670e+003  Hrxn  = 0.0000e+000

Comp    Stoich.    Exp.factor    Adsorb Fac.   Adsorb E      Adsorb Exp.
   1   -2.00e+000   2.0000e+000   3.9471e-004  -3.7835e+004   5.0000e-001
   3    1.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
   5    1.00e+000   0.0000e+000   5.6057e-006  -4.7468e+004   1.0000e+000

 Reaction   2
 Rate const =   6.5110e+002  Act. E =   1.4652e+004  Hrxn  =  0.0000e+000

Comp    Stoich.    Exp.factor    Adsorb Fac.   Adsorb E      Adsorb Exp.
   3   -1.00e+000   1.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
   5   -1.00e+000   1.0000e+000   5.6057e-006  -4.7468e+004   1.0000e+000
   1    2.00e+000   0.0000e+000   3.9471e-004  -3.7835e+004   5.0000e-001

 Reaction   3
 Rate const =   8.3450e-002  Act. E =   1.7700e+003  Hrxn  =  0.0000e+000

Comp    Stoich.    Exp.factor    Adsorb Fac.   Adsorb E      Adsorb Exp.
   2   -1.00e+000   1.0000e+000   1.2185e-006  -4.1060e+004   1.0000e+000
   6    1.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
   5    1.00e+000   0.0000e+000   3.5730e-005  -2.6200e+004   1.0000e+000
   4    0.00e+000   0.0000e+000   5.2950e-006  -3.3010e+004   1.0000e+000




 Reaction   4
 Rate const =   2.9050e+000  Act. E =   2.3090e+004  Hrxn  =  0.0000e+000
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Comp	Stoich.	Exp.factor	Adsorb Fac.	Adsorb E	Adsorb Exp.
2	-2.00e+000	2.0000e+000	1.2185e-006	-4.1060e+004	1.0000e+000
4	1.00e+000	0.0000e+000	5.2950e-006	-3.3010e+004	1.0000e+000
5	1.00e+000	0.0000e+000	3.5730e-005	-2.6200e+004	1.0000e+000

Reaction 5
Rate const = 1.7876e+005 Act. E = 7.2210e+004 Hrxn = 0.0000e+000

Comp	Stoich.	Exp.factor	Adsorb Fac.	Adsorb E	Adsorb Exp.
4	-1.00e+000	1.0000e+000	5.2950e-006	-3.3010e+004	1.0000e+000
2	1.00e+000	0.0000e+000	1.2185e-006	-4.1060e+004	1.0000e+000
6	1.00e+000	0.0000e+000	0.0000e+000	0.0000e+000	0.0000e+000
5	0.00e+000	0.0000e+000	3.5730e-005	-2.6200e+004	1.0000e+000

Reaction 6
Rate const = 3.1440e+001 Act. E = 3.1763e+004 Hrxn = 0.0000e+000

Comp	Stoich.	Exp.factor	Adsorb Fac.	Adsorb E	Adsorb Exp.
4	-1.00e+000	1.0000e+000	5.2950e-006	-3.3010e+004	1.0000e+000
6	2.00e+000	0.0000e+000	0.0000e+000	0.0000e+000	0.0000e+000
5	1.00e+000	0.0000e+000	3.5730e-005	-2.6200e+004	1.0000e+000
2	0.00e+000	0.0000e+000	1.2185e-006	-4.1060e+004	1.0000e+000

Plug Flow Profile for unit no. 2

Vol m3	Temp C	Press kPa	Total kmol/h	Mole frac Methanol	Mole frac Ethanol
0.00	320.02	1300.01	100.00	8.800E-001	1.100E-001
0.05	320.02	1294.97	100.23	7.593E-001	3.331E-002
0.10	320.02	1290.01	100.46	7.013E-001	2.131E-002
0.15	320.02	1284.98	100.66	6.603E-001	1.629E-002
0.20	320.02	1280.01	100.84	6.282E-001	1.354E-002
0.25	320.02	1274.98	101.02	6.017E-001	1.181E-002
0.30	320.02	1270.01	101.19	5.792E-001	1.063E-002
0.35	320.02	1264.98	101.35	5.595E-001	9.786E-003
0.40	320.02	1260.02	101.50	5.421E-001	9.155E-003
0.45	320.02	1254.98	101.65	5.265E-001	8.668E-003
0.50	320.02	1250.02	101.80	5.123E-001	8.283E-003
0.55	320.02	1244.99	101.94	4.994E-001	7.973E-003
0.60	320.02	1240.02	102.07	4.875E-001	7.719E-003
0.65	320.02	1234.99	102.20	4.764E-001	7.507E-003
0.70	320.02	1230.03	102.33	4.661E-001	7.327E-003
0.75	320.02	1224.99	102.45	4.566E-001	7.174E-003
0.80	320.02	1220.03	102.57	4.475E-001	7.041E-003
0.85	320.02	1214.99	102.69	4.391E-001	6.925E-003
0.90	320.02	1210.03	102.80	4.311E-001	6.822E-003
0.95	320.02	1205.00	102.92	4.235E-001	6.730E-003
1.00	320.02	1200.03	103.02	4.163E-001	6.648E-003

Vol m3	Temp C	Press kPa	Total kmol/h	Mole frac Dimethyl Ether	Mole frac Diethyl Ether
0.00	320.02	1300.01	100.00	0.000E+000	0.000E+000
0.05	320.02	1294.97	100.23	5.933E-002	3.703E-002

0.10	320.02	1290.01	100.46	8.738E-002	4.183E-002
0.15	320.02	1284.98	100.66	1.070E-001	4.324E-002
0.20	320.02	1280.01	100.84	1.222E-001	4.359E-002
0.25	320.02	1274.98	101.02	1.347E-001	4.349E-002
0.30	320.02	1270.01	101.19	1.452E-001	4.316E-002
0.35	320.02	1264.98	101.35	1.544E-001	4.271E-002
0.40	320.02	1260.02	101.50	1.624E-001	4.219E-002
0.45	320.02	1254.98	101.65	1.696E-001	4.163E-002
0.50	320.02	1250.02	101.80	1.761E-001	4.105E-002
0.55	320.02	1244.99	101.94	1.820E-001	4.047E-002
0.60	320.02	1240.02	102.07	1.873E-001	3.988E-002
0.65	320.02	1234.99	102.20	1.923E-001	3.929E-002
0.70	320.02	1230.03	102.33	1.969E-001	3.870E-002
0.75	320.02	1224.99	102.45	2.012E-001	3.813E-002
0.80	320.02	1220.03	102.57	2.052E-001	3.756E-002
0.85	320.02	1214.99	102.69	2.089E-001	3.700E-002
0.90	320.02	1210.03	102.80	2.125E-001	3.645E-002
0.95	320.02	1205.00	102.92	2.158E-001	3.592E-002
1.00	320.02	1200.03	103.02	2.190E-001	3.539E-002

Vol m3	Temp C	Press kPa	Total kmol/h	Mole frac Water	Mole frac Ethylene
0.00	320.02	1300.01	100.00	1.000E-002	0.000E+000
0.05	320.02	1294.97	100.23	1.087E-001	2.365E-003
0.10	320.02	1290.01	100.46	1.437E-001	4.531E-003
0.15	320.02	1284.98	100.66	1.667E-001	6.519E-003
0.20	320.02	1280.01	100.84	1.841E-001	8.370E-003
0.25	320.02	1274.98	101.02	1.982E-001	1.011E-002
0.30	320.02	1270.01	101.19	2.100E-001	1.176E-002
0.35	320.02	1264.98	101.35	2.203E-001	1.333E-002
0.40	320.02	1260.02	101.50	2.293E-001	1.484E-002
0.45	320.02	1254.98	101.65	2.373E-001	1.628E-002
0.50	320.02	1250.02	101.80	2.446E-001	1.767E-002
0.55	320.02	1244.99	101.94	2.512E-001	1.900E-002
0.60	320.02	1240.02	102.07	2.573E-001	2.030E-002
0.65	320.02	1234.99	102.20	2.629E-001	2.155E-002
0.70	320.02	1230.03	102.33	2.682E-001	2.276E-002
0.75	320.02	1224.99	102.45	2.730E-001	2.394E-002
0.80	320.02	1220.03	102.57	2.776E-001	2.508E-002
0.85	320.02	1214.99	102.69	2.819E-001	2.619E-002
0.90	320.02	1210.03	102.80	2.859E-001	2.727E-002
0.95	320.02	1205.00	102.92	2.898E-001	2.832E-002
1.00	320.02	1200.03	103.02	2.934E-001	2.935E-002

Overall Material Balance for Kinetic Reactor Example

Stream No.	1	2
	Input	Output
Temp C	320.0000*	320.0000
Pres kPa	1500.0000*	1200.0000
Enth MJ/h	-19191.	-19430.
Vapor mole fraction	1.0000	1.0000
Total kmol/h	100.0000	103.0236
Total kg/h	3344.4701	3344.4688
Total std L m3/h	4.1771	4.4628
Total std V m3/h	2241.36	2309.13
Flowrates in kmol/h		
Methanol	88.0000	42.8866
Ethanol	11.0000	0.6849
Dimethyl Ether	0.0000	22.5567
Diethyl Ether	0.0000	3.6458
Water	1.0000	30.2261
Ethylene	0.0000	3.0236