

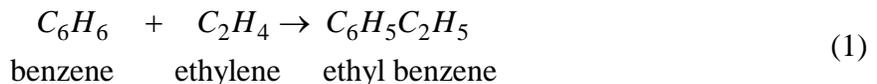
# Separation Processes and Reaction Engineering Design Project

## Production of Ethylbenzene

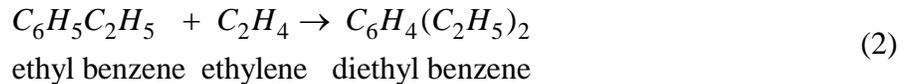
We continue to investigate the feasibility of constructing a new, grass-roots, 80,000 tonne/y, ethylbenzene (EB) facility (99.8 mol%), using benzene and ethylene as raw materials. As the final part of the feasibility study, we would like you to study the details of the reactor and separation section 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 ethyl benzene.

### Ethyl Benzene Production Reactions

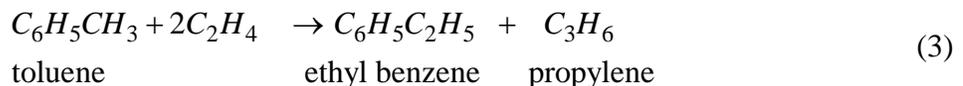
The production of EB takes place via the direct alkylation reaction between ethylene and benzene by acid catalysis:



The reaction between EB and ethylene to produce diethyl benzene (DEB) also takes place:



The incoming benzene contains a small amount of toluene impurity (2 mole %). The toluene reacts with ethylene to form ethyl benzene and propylene:



The rate laws for the reaction kinetics are discussed in Appendix 3. A new  $\beta$ -zeolite catalyst is available as a cylindrical extruded pellet with diameter 2 mm and length 6 mm. For the sake of calculations, you may assume that the catalyst behaves like a spherical particle with packed bed voidage of 0.60. Effective diffusivity of catalyst (from catalyst manufacturer) is equal to  $8 \times 10^{-8}$  m<sup>3</sup>-gas/m-catalyst/s. You should assume that the maximum allowable catalyst temperature = 450°C.

## Specific Assignments

### *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 ethylbenzene 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. 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<sup>1</sup>, p. 336, is that for Raschig rings (ceramic). Assume the HETP for the structured packing to be 0.6 m (see the definition of HETP in Wankat<sup>1</sup>, p. 332, and the relationship between HETP and  $H_{OG}$  in Equation 15.36 in Wankat<sup>1</sup>), and that the pressure drop is 0.2 kPa/m (0.245 inch water/ft).

### *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.

### **General**

The entire ethylbenzene 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, and 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

$$\text{EAOC} = -(\text{product value} - \text{feed cost} - \text{utility costs} - \text{waste treatment cost} - \text{capital cost annuity})$$

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:

$$\text{capital cost annuity} = FCI \frac{i(1+i)^n}{(1+i)^n - 1} \quad (5)$$

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**

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. An appendix should be attached that includes sample calculations. These calculations should be easy to follow.

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.

### **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 optimum 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 once. Reports exceeding this time limit will be stopped. 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 18, 2007, starting at 11:00 a.m. and running until approximately 3:00 p.m. 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 18, 2007. Late projects will receive a minimum deduction of one letter grade.

*In order to evaluate each team members writing skills, the results and discussion sections for each specific assignment should be written by a different team member. The authorship of each of these specific assignments should be clearly specified in the report. If a team has four members, the member not authoring a specific assignment should author the cover memorandum, abstract, introduction, and conclusion.*

### **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 might be forthcoming.

### **References**

1. Wankat, P., *Equilibrium Staged Separation Processes*, Prentice Hall, Upper Saddle River, NJ, 1988.

## 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, use the minimum attribute value to compute the cost. For a piece of equipment with a larger attribute value, extrapolation is possible, but inaccurate.

Pumps	$\log_{10}(\text{purchased cost}) = 3.4 + 0.05\log_{10} W + 0.15[\log_{10} W]^2$ $W = \text{power (kW, 1, 300)}$ assume 80% efficiency
Heat Exchangers	$\log_{10}(\text{purchased cost}) = 4.6 - 0.8\log_{10} A + 0.3[\log_{10} A]^2$ $A = \text{heat exchange area (m}^2\text{, 20, 1000)}$
Compressors	$\log_{10}(\text{purchased cost}) = 2.3 + 1.4\log_{10} W - 0.1[\log_{10} W]^2$ $W = \text{power (kW, 450, 3000)}$ assume 70% efficiency
Compressor Drive	$\log_{10}(\text{purchased cost}) = 2.5 + 1.4\log_{10} W - 0.18[\log_{10} W]^2$ $W = \text{power (kW, 75, 2600)}$
Turbine	$\log_{10}(\text{purchased cost}) = 2.5 + 1.45\log_{10} W - 0.17[\log_{10} W]^2$ $W = \text{power (kW, 100, 4000)}$ assume 65% efficiency
Fired Heater	$\log_{10}(\text{purchased cost}) = 3.0 + 0.66\log_{10} Q + 0.02[\log_{10} Q]^2$ $Q = \text{duty (kW, 3000, 100,000)}$ assume 80% thermal efficiency assume can be designed to use any organic compound as a fuel
Vertical Vessel	$\log_{10}(\text{purchased cost}) = 3.5 + 0.45\log_{10} V + 0.11[\log_{10} V]^2$ $V = \text{volume of vessel (m}^3\text{, 0.3, 520)}$
Horizontal Vessel	$\log_{10}(\text{purchased cost}) = 3.5 + 0.38\log_{10} V + 0.09[\log_{10} V]^2$ $V = \text{volume of vessel (m}^3\text{, 0.1, 628)}$
Catalyst	\$2.25/kg
Packed Tower	Cost as vessel plus cost of packing

Packing	$\log_{10}(\text{purchased cost}) = 3 + 0.97 \log_{10} V + 0.0055 [\log_{10} V]^2$ $V = \text{packing volume (m}^3, 0.03, 628)$
Tray Tower	Cost as vessel plus cost of trays
Trays	$\log_{10}(\text{purchased cost}) = 3.3 + 0.46 \log_{10} A + 0.37 [\log_{10} A]^2$ $A = \text{tray area (m}^2, 0.07, 12.3)$
Storage Tank	$\log_{10}(\text{purchased cost}) = 5.0 - 0.5 \log_{10} V + 0.16 [\log_{10} V]^2$ $V = \text{volume (m}^3, 90, 30,000)$
Reactors	For this project, the reactor is considered to be a vessel.

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.

### Equipment Cost Factors

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

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

### Utility Costs

Low Pressure Steam (618 kPa saturated)	\$7.78/GJ
Medium Pressure Steam (1135 kPa saturated)	\$8.22/GJ
High Pressure Steam (4237 kPa saturated)	\$9.83/GJ
Natural Gas (446 kPa, 25°C)	\$6.00/GJ
Fuel Gas Credit	\$5.00/GJ
Electricity	\$0.06/kWh
Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg
Cooling Water available at 516 kPa and 30°C return pressure $\geq$ 308 kPa return temperature is no more than 15°C above the inlet temperature	\$0.354/GJ
Refrigerated Water available at 516 kPa and 10°C return pressure $\geq$ 308 kPa return temperature is no higher than 20°C	\$4.43/GJ
Deionized Water available at 5 bar and 30°C	\$1.00/1000 kg
Waste Treatment of Off-Gas	incinerated - take fuel credit
Refrigeration	\$7.89/GJ
Wastewater Treatment	\$56/1000 m <sup>3</sup>

Any fuel gas purge may be assumed to be burned elsewhere in the plant at a credit of \$2.50/GJ. Steam produced cannot be returned to the steam supply system for the appropriate credit. Steam produced in excess of that required in this process is purged with no credit.

### Feed and Product Prices

Benzene feed	\$ 1.038 per kg
Ethylene feed	\$ 0.737 per kg
Ethyl benzene	\$ 1.38 per kg

## Appendix 2 Other Design Data

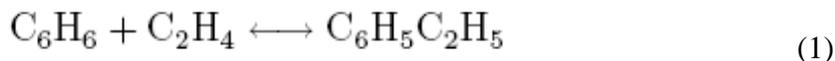
### Heat Exchangers

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

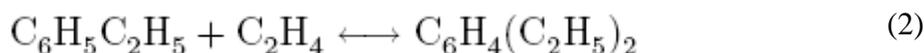
<b>situation</b>	<b><math>h</math> (W/m<sup>2</sup>°C)</b>
condensing steam	6000
condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60

### Appendix 3 Reaction Kinetics

The production of ethyl benzene (EB) takes place via the direct alkylation reaction between ethylene (E) and benzene (B) by acid catalysis:

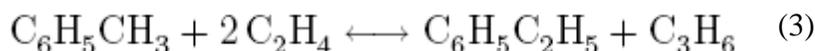


The reaction between EB and ethylene to produce diethyl benzene (DEB) also takes place:



Additional reactions between DEB and ethylene yielding tri- and higher ethyl benzene are also possible. However, in order to minimize these additional reactions, the molar ratio of benzene to ethylene is kept high, at approximately 8:1. The production of diethyl benzene is undesirable, and its value as a side product is low. In addition, even small amounts of DEB in EB cause significant processing problems in the downstream styrene process. Therefore, the maximum amount of DEB in EB is specified as 2 ppm. Excess poly-substituted benzene may be directed towards a waste stream or combusted to reclaim the energy value. In other EB facilities, the early generations of solid acid catalysts were highly corrosive and had a relatively short life, e.g.  $\text{AlCl}_3$ ,  $\text{H}_3\text{PO}_4$  on clay,  $\text{BF}_3$  on alumina, and others require periodic regeneration. More recently, solid acid catalysts based on zeolites have been demonstrated to have superior properties. Studies in our research division have shown that a  $\beta$ -zeolite catalyst (FX-02) is an active and selective catalyst for the alkylation of benzene with ethylene. FX-02 can be used with polymer-grade ethylene as well as ethylene from fluid catalytic-cracking unit off-gas with concentrations as low as 10-20%. FX-02 also operates at lower temperature and lower pressure than existing catalysts.

The incoming benzene contains a small amount of toluene impurity. The toluene (T) reacts with ethylene to form ethyl benzene and propylene (P):



The rate law is based on a Langmuir-Hinshelwood absorption-reaction model, whereby absorbed ethylene reacts with absorbed benzene and ethylbenzene. In addition, absorbed ethylene also reacts with absorbed toluene and ethylbenzene. Reactions described by Equations 1-3 are reversible reactions, where the rate laws correspond to Equations 4-6, respectively.

$$-r_{1B} = \frac{k_1 p_B p_E - k_{-1} p_{EB}}{(1 + K_{BPP} + K_{EPE} + K_{EBPEB} + K_{DEBPDEB} + K_{TPPT} + K_{PPP})^2} \quad (4)$$

$$-r_{2EB} = \frac{k_2 p_{EB} p_E - k_{-2} p_{DEB}}{(1 + K_{BPP} + K_{EPE} + K_{EBPEB} + K_{DEBPDEB} + K_{TPPT} + K_{PPP})^2} \quad (5)$$

$$-r_{3T} = \frac{k_3 p_{TP} p_E - k_{-3} p_{EBP}}{(1 + K_{BPP} + K_{EPE} + K_{EBPEB} + K_{DEBPDEB} + K_{TPPT} + K_{PPP})^2} \quad (6)$$

$$k_j = k_{oj} \exp(-E_{aj}/RT) \quad (j = 1, 2, 3, -1, -2, -3) \quad (7)$$

$$K_i = K_{oi} \exp(E_{ai}/RT) \quad (i = E, B, EB, DEB, T, P) \quad (8)$$

The reaction rate constants and the equilibrium constants are shown in Tables 1, where  $r$  is the rate law in mol/(g min),  $k$  is intrinsic rate constant,  $p$  is pressure in MPa,  $K$  is reaction equilibrium constant,  $E_a$  is reaction activation energy in J/mol,  $R$  is the gas constant, and  $T$  is temperature in Kelvin. The units of  $k$  vary depending on the form of the rate law.

Table 1: Reaction rate constants and equilibrium constants for rate laws.

Rate Constant	$k_{oj}$	$E_{aj}$ J/mol	Equilibrium Constant	$K_{oi}$	$E_{ai}$ J/mol
$k_1$	255.3	42,496	$K_E$	0.457	7,769
$k_{-1}$	5.13	68,741	$K_B$	$6.77 \times 10^{-3}$	12,436
$k_2$	52.41	53,148	$K_{EB}$	$3.19 \times 10^{-3}$	10,173
$k_{-2}$	2.667	73,491	$K_{DEB}$	$8.58 \times 10^{-4}$	14,059
$k_3$	44.32	50,132	$K_T$	$4.63 \times 10^{-3}$	11,768
$k_{-3}$	3.233	69,303	$K_P$	$2.12 \times 10^{-2}$	8,354