Appendix G for Essentials of CRE is the same as Appendix H from 4/e Elements of CRE, which is given below

CD-ROM Appendix H: Open Ended Problems

CDH.1 AIChE National Student Chapter Competition

This exercise was given as an open-ended problem to 160 students (working in groups of 4) in the University of Michigan Chemical Reaction Engineering class Winter Term 1997. However, the students were to only design the experiment and not build the experiment as is the case with the national competition. Each group of students presented its design on poster boards to an outside panel of judges. The same judging criteria applied for the posters as for the national competition.

MEMORANDUM
TO: Student Chapters
RE: National Student Chapter Competition

For the past several years we have all seen the esprit de corps, excitement, and learning that has been generated among undergraduates from engineering disciplines engaging in national competitions. The civil engineers have the "concrete canoe race," the mechanical engineers the "egg-drop competition," and there is the interdisciplinary "solar car race." Many students, faculty, and practicing engineers would like to give chemical engineers a similar experience, one that would educate others about our profession and receive similar publicity (e.g., newspapers, perhaps even TV coverage). It has been suggested that the latter would be more probable if the competition involved topical issues: environment, energy reduction, worldwide food production, and the like. In any case, safety should be a primary concern (e.g., no explosive or toxic chemicals).

To celebrate the newest division of the American Institute of Chemical Engineers, the Chemical Reaction Engineering Division, the first competition will be concerned with chemical reaction engineering.

THE 1998 COMPETITION

Design, build, and operate an apparatus for an undergraduate laboratory experiment that demonstrates chemical reaction engineering principles and that is novel or perhaps strives to do the improbable (e.g., won't a concrete canoe sink?).

The experiment should be bench scale and of the type currently found in undergraduate laboratory courses. It is also possible that the experiment could be used for a lecture demonstration. The experiment should cost less than $500 in purchased parts to build.

The first year's competition could include experiments that would either produce a product (e.g., yogurt or something that would fffind use in the feeding of starving nations) or demonstrate how an environmental problem might be solved (e.g., wetlands to degrade toxic chemicals). The winners (perhaps second place also) of the regional competition will be invited to bring their experiments to the annual AIChE meeting, where the national winners will be selected. General Mills has agreed to sponsor the competition and the following prizes will be awarded to the student chapters:

1st prize	$2,000
2nd prize	$1,000
3rd prize	$500

In addition, a description of the winning experiment will be published in *Chemical Engineering Education*. The first regional competition will be held at the 1998 Student Chapter Regional Conferences and the finals at the 1998 annual meeting in Miami Beach, Florida. The rules and judging criteria are attached.

Rules

1. Design, build, and operate an apparatus for an undergraduate laboratory experiment that demonstrates the principles of reaction engineering principles and that is novel or perhaps strives to do the improbable (e.g, won't a concrete canoe sink?). The experiment should be bench scale and of the type currently found in most undergraduate laboratory courses. It is also acceptable that the experiment be of the type that would be used for a lecture demonstration.
2. The experiments should encompass "simplicity/ease of communication to nontechnical people." The process should be one easily understood by people outside the profession. Either the object of the process, such as the manufacture of yogurt, the importance of the project, such as feeding many people from increasingly scarce resources, or the process itself should be easily communicated to people without a background in chemical engineering. Media coverage (newspapers/television/radio) is one way to show success.
3. The competition will be conducted on the honor system. The faculty and graduate students can act only as sounding boards to student queries. The faculty *cannot be idea generators* for the project. The student chapter advisor or department chair must write a cover letter

stating to the best of his or her knowledge that students have abided by the rules. Students who work on the project must also sign a statement stating that they have abided by the rules.

4. The competition is to be a team competition with at least 20% of the team being composed of members from each of the junior and senior chemical engineering classes. The minimum number of participants is 5 and the maximum is 15 per university.
5. Associated measuring equipment (e.g., pH meter) must be of the type that is readily available at most universities through department ownership or borrowing from other departments in the university.
6. Purchased parts must cost less than $500. This price does not include a PC for data acquisition, or associated measuring or other (e.g., pumps, fittings, vessels) equipment that exists in most chemical engineering undergraduate laboratories.
7. The experiments will be displayed at the regional meeting. A poster board should accompany the apparatus as well as a 5- to 10-page report describing how the idea for the experiment was generated, the underlying principles, the experimental procedure, and sample results. In the event that the apparatus may not be physically brought to the meeting, videotape or other means may be used to assist understanding of the experiment. The top one or two winners of the regional student chapters will be eligible to compete in the finals to be held at the annual meeting.
8. Safety regarding assembling and operating the experiment must be addressed.
9. The student chapter advisor or department chair at the host chapter at the regional conference will select a panel of three judges. The judges can be from industry or be faculty or students. The judges cannot be affiliated with any organization that has an entry.

   The number of winners selected to go to the finals will depend on the number of regional entries. If there are six or fewer entries, one winner will be selected to advance to the national competition. If there are seven or more entries, two winners will be selected. The decision of the regional and national judges shall be final.

Judging Criteria

1.	Creativity/novelty/originality	40 points
2.	Statement of the principle to be demonstrated and clarity in demonstrating that principle	30 points
3.	Proper description of the safety issues associated with building and operating the experiment	15 points
4.	Simplicity/ease of communication/media coverage	15 points
5.	Quality of communication	10 points
	Introduction: How was the idea generated? What principle does the experiment demonstrate and why is it important?	

	Discussion: Explain the fundamentals.	
	Procedure: Discuss safety concerns.	
	Results: Describe what you found.	
6.	Opportunity for subsequent laboratory groups to study different variables or outcomes using the same apparatus	10 points
7.	Ease, desirability, and feasibility of being replicated by another student chapter	10 points
8.	Physical appearance	10 points
9.	Participation (more than 16 hours) by someone who is not a chemical engineering major (3 points for each non-chemical engineering major) and/or participation by chemical engineering sophomores (2 points for each sophomore) (10 points maximum)	10 points
		150 points

CDH.2 Effective Lubricant Design[1]

Background

Lubricants are often applied at the interface between rubbing surfaces to reduce friction and prevent wear by disallowing direct surface-to-surface contact. An automobile engine has many contacting metal parts, such as the pistons and cylinders, and the cam lobes and cam followers. Without adequate lubrication, the sliding metal parts within the engine would wear appreciably, leading to engine failure. A typical consumer may expect to drive more than 100,000 miles before experiencing severe engine problems resulting from wear within the engine. To meet this expectation, lubricant manufacturers, in close collaboration with automobile manufacturers, continue to develop improved lubricant formulations.

Lubricants are formulated by blending a base oil with additives to yield a mixture with the desirable physical and chemical properties dictated by the application environment. Base oils are typically derived from petroleum and are complex mixtures of aliphatic and aromatic hydrocarbons. However, some lubricants are blended using synthetic base oils. Examples of synthetic base oils include esters, polyphenyl ethers, polyalphaolefins, and perfluoroalkylethers. Lubricant additives are classified according to their function, including antioxidants, viscosity index (VI) improvers (to maintain desired viscosity over a wide temperature range), antiwear additives, friction modifiers, dispersants, detergents, pour point depressants, and antifoaming agents. A fully formulated lubricant typically consists of 80–90% base oil and 10–20% additives.

Lubricant development requires an understanding of the specific problems and needs associated with lubrication such as: the need for automotive lubricants with enhanced oxidation stability, antiwear properties, and physical

[1] Problem provided by General Motors Research Laboratories, Warren, Michigan.

properties under severe operating condition. A kinetics model may be used to try to predict the oxidative degradation behavior of lubricants under differing conditions.

Lubricant Degradation Model: A fresh lubricant may have physical properties ideally suited to its application, but as the lubricant degrades its physical properties can change markedly. This transformation can lead to increased friction and wear at lubricated surfaces. After significant degradation takes place, sludge and varnish deposits may form on lubricated surfaces to further hinder the smooth operation of lubricated components. There is general agreement in the literature that under normal service conditions a major portion of lubricant degradation is due to oxidation of the lubricant base oil. Consequently, a great deal of lubricant research has focused on base oil degradation and the inhibition of oxidation through the use of antioxidant additives. The oxidation of a lubricant base oil follows the hydroperoxide chain mechanism for hydrocarbon oxidation. Some of the major steps of this mechanism are listed in Reactions (1)–(10).

Low Temperatures, No Antioxidants

$$\left.\begin{array}{l}(1)\ \mathrm{I_2} \xrightarrow{k_0} 2\mathrm{I}\bullet \\ (2)\ \mathrm{I}\bullet + \mathrm{RH} \xrightarrow{k_1} \mathrm{R}\bullet + \mathrm{HI}\end{array}\right\} \text{INITIATION}$$

$$\left.\begin{array}{l}(3)\ \mathrm{R}\bullet + \mathrm{O_2} \xrightarrow{k_{P_1}} \mathrm{RO_2}\bullet \\ (4)\ \mathrm{RO_2}\bullet + \mathrm{RH} \xrightarrow{k_{P_2}} \mathrm{ROOH} + \mathrm{R}\bullet\end{array}\right\} \text{PROPAGATION}$$

$$(5)\ \mathrm{RO_2}\bullet + \mathrm{RO_2}\bullet \xrightarrow{k_t} \text{Inactive products} \Big\} \text{TERMINATION}$$

High Temperatures, No Antioxidants

$$(6)\ \mathrm{ROOH} \xrightarrow{k_{i_3}} \mathrm{RO}\bullet + \bullet\mathrm{OH} \Big\} \text{INITIATION}$$

$$\left.\begin{array}{l}(7)\ \mathrm{RO}\bullet + \mathrm{RH} \xrightarrow{k_{P_4}} \mathrm{RO_2H} + \mathrm{R}\bullet \\ (8)\ \bullet\mathrm{OH} + \mathrm{RH} \xrightarrow{k_{P_5}} \mathrm{HOH} + \mathrm{R}\bullet\end{array}\right\} \text{PROPAGATION}$$

Low and High Temperatures with Antioxidants

$$(9)\ \mathrm{RO_2}\bullet + \mathrm{AH} \xrightarrow{k_{\mathrm{A1}}} \mathrm{ROOH} + \mathrm{A}\bullet$$

$$(10)\ \mathrm{A}\bullet + \mathrm{RO_2}\bullet \xrightarrow{k_{\mathrm{A2}}} \text{Inactive products}$$

Also hydroperoxide decomposing antioxidants can transform hydroperoxides to stable products as shown in Reaction (11):

$$(11)\ \mathrm{ROOH} + \mathrm{A}\bullet \xrightarrow{k_{A3}} \text{Inactive products}$$

This antioxidant is effective provided the products are stable, and the rate is much faster than reaction (6).

An example of a hydroperoxide-decomposing antioxidant is phenothiazine. In the absence of an antioxidant (or after antioxidant additive depletion), significant quantities of hydroperoxides may accumulate as a result of extensive base oil oxidation. Resulting secondary oxidation reactions may occur, leading to the formation of alcohols, ketones, carboxylic acids, and esters. Extensive oxidation can also lead to the formation of high-molecular-weight material, which may form deposits on lubricated surfaces. A dramatic increase in viscosity generally results from extensive oxidation of a lubricant, which may also lead to poor lubricant performance. Clearly, extensive lubricant oxidation leads to a rapid deterioration of lubricant effectiveness, and at the point of antioxidant depletion, an automobile engine lubricant should generally be considered ineffective and should be replaced with fresh lubricant.

Problem Statement

1. Consider the possible attributes of currently available, general-purpose engine lubricants. List them in what you consider their order of importance. (You may wish to examine sales displays, advertisements, cans/bottles of motor oil, etc., for help with this information.)
2. If you could design an ideal engine lubricant to totally dominate the marketplace, what characteristics would you give it?
3. In the future, a priority will most likely be to make automobile maintenance easier for the owner. What kind of creative ideas/inventions can you conceive of for streamlining oil change maintenance for the consumer? After you've generated some ideas (by brainstorming perhaps), critique them from the standpoint of practicality, cost, availability of technology, and so on.
4. Degradation by oxidation is a major cause for having to replace engine lubricants. Using your knowledge of reaction kinetics, analyze the degradation of engine lubricants due to oxidation using the reactions shown in the introduction (i.e., find an expression for the rate of degradation).
   Consider the following four cases.
   In the absence of antioxidants, examine base oil (RH) degradation
   (a) at low temperatures (25°C)
   (b) at high temperatures (100°C)
   In the presence of antioxidants, examine base oil (RH) degradation

(c) at low temperatures (25°C)
(d) at high temperatures (100°C)

$[RH]_0 = 3$ M $\quad [I_2]_0 = 0.10$ M $\quad k_0\ 10^{-6}$ ($E_{act} = 7.5$)

$k_{A1} = 10^3$ ($E_{act} = 10$) $\quad k_{P_2} = 1.58$ ($E_{act} = 8.5$) $\quad k_{i_3} = 10^{-6}$ ($E_{act} = 9$)

$k_t = 10^7$ ($E_{act} = 0$) $\quad k_{A2} = 10^3$ ($E_{act} = 9$) $\quad k$A3 3.33×10^{-3} ($E_{act} = 10$)

The units on the preceding rate constants are sec^{-1} for first order and dm^3/mole • sec for second order. The units for the activation energies are kcal/mole. You may assume for the purposes of this investigation that 10% conversion of the base oil (RH) is the point at which the lubricant will have to be replaced. From your analysis, what kind of recommendations can you make for the improvement of the engine lubricants? If you were making suggestions to the R&D division of a lubricant manufacturer, what would you have them investigate to make the most impact on the retardation of oil degradation by oxidation? What kind of experiments should they do? What are the drawbacks of this type of kinetic model for oil degradation? Do you have a better modeling suggestion?

5. Some suggestions that have been turned in to the suggestion box of Synthoil, an up and coming, newly formed lubricant manufacturer, follow:
   (a) New cars should be equipped up with a feed-and-bleed system for the oil. Every so often, a quart of used oil should be drained and a quart of new oil should be added to the automobile. This should lengthen the necessary time between complete oil changes and save the consumer money
   (b) We should design and market an inhibitor feed system for automobiles that would allow us to maintain a minimum inhibitor concentration in the engine oil, thereby protecting it from excessive oxidative breakdown.

   As head of the R&D division of this progressive company, it is your job to investigate the technical feasibility of these suggestions and report on them at the next Board of Directors meeting. Investigate one of these suggestions, or substitute an equally good one of your own and investigate it. Be creative!

Problem Information

Synthoil Cost Data for Evaluation Purposes:
Complete oil change: $29.95 (includes 5 qts. oil, filter, and labor)
Quart of oil: $1.50 (typical engine = 5 qt. capacity)
Inhibitor (antioxidant, AH): $0.10/gram, approx. MW = 100 g

Additional Information

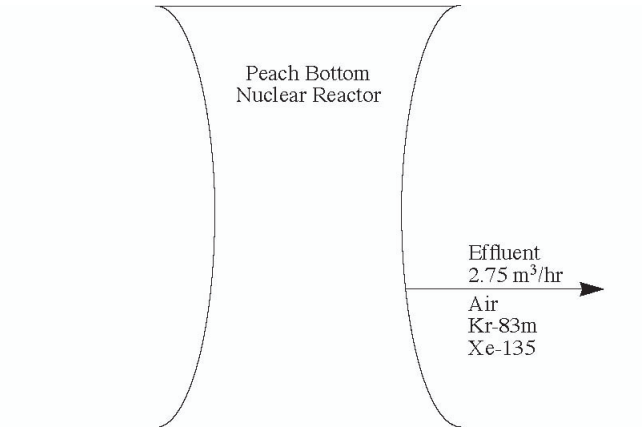
H. Scott Fogler, *Elements of Chemical Reaction Engineering*, 2nd ed. Englewood Cliffs, N.J.: Prentice-Hall, 1992. Given as an OEP at The University of Michigan, Winter 1991.

CDH.3 Peach Bottom Nuclear Reactor[2]

Background

The Peach Bottom Nuclear Reactor, located in Georgia, has been built and is almost operational. The reactor is a boiling water nuclear reactor that produces 1,100 MW of power and cost approximately $2 billion to build. The effluent from the reactor contains cooling air and isotopes of krypton and xenon. The major constituents of the stream are Kr-83m and Xe-135, which are present in the exit gas at concentrations of 3.19×10^{6} mCi/dm^3 and 1.4×10^{-3} mCi/dm^3, respectively. The volumetric gas flow rate exiting the reactor is 2.75 m^3/hr at a temperature of 3C.

The Nuclear Regulatory Commission (NRC) issued emission limits for Kr-83m and Xe-135 in the *Federal Register*, (Vol. 56, No. 98, Part VI, dated Tuesday, May 21, 1991). The emission standards as issued are .05 mCi/dm^3 for Kr-83m and 7.0×10^{-5} mCi/dm^3 for Xe-135.



Problem Statement

Propose two or more solutions that will enable the Peach Bottom Nuclear Reactor to go on line with the 2.75 m^3/hr of exit gas meeting the NRC emission standards. Please show all calculations and include any diagrams necessary to thoroughly explain your solutions. Additional information and

[2] Problem developed by Susan Stagg, University of Michigan, from a problem suggested by Octave Levenspiel, Oregon State University.

properties for Kr-83m and Xe-135 can be obtained from the *Handbook of Chemistry and Physics*.

Problem Information

Ci is the symbol for a curie. A curie is the unit of radioactivity equivalent to 3.70×10^{10} disintegrations per second. This unit is named after Marie Curie.

Effluent data:

Constituent in Effluent	Concentration (mCi/dm^3)	NRC Emission Standard (mCi/dm^3)
Kr-83m	3.19×10^{6}	0.05
Xe-135	1.4×10^{-3}	$7.0 \times 10^{—5}$

Additional Information

H. SCOTT FOGLER. *Elements of Chemical Reaction Engineering*. 2nd ed. Englewood Cliffs, N.J.: Prentice-Hall, 1992.

DAVID R. LIDE. *CRC Handbook of Chemistry and Physics*. Ann Arbor, Mich.: CRC Press, 1993.

Given as an OEP at The University of Michigan, Winter 1994.

CDH.4 Underground Wet Oxidation[3]

Background

Several of your company's chemical processes generate aqueous waste streams containing a large number of hazardous compounds that are presently being destroyed by incineration. The Chief Executive Officer (CEO) of your company saw the attached article in a local journal. He asked the Director of the Engineering Service Division (ESD) if the technology would be useful for treating the aqueous waste streams from your plant. After assuring the CEO that he would investigate the possibilities, the ESD Director asked the Manager of the Reaction Engineering Group to check it out. The manager, who is also your supervisor, handed the assignment to you.

Problem Statement

Your mission is to evaluate the technology, size a reactor system, and specify appropriate operating conditions for oxidizing the components of the aqueous waste streams. The Engineering Economics group will then compare the costs of your artesian with incineration to assess the relative financial merits of using the new technology.

---

[3] Problem developed by Professor Phillip E. Savage, University of Michigan.

A few questions to provide some initial direction in your evaluation follow:

- At what temperature and pressure should the reactor operate?
- Is an underground reactor better than the conventional above-ground reactor?
- What safety considerations do you need to include in your design for this high-temperature, high-pressure process involving hazardous chemicals?
- Can you ethically recommend this technology to your management? Is it sufficiently proven?
- How confident are you that your reactor will be able to destroy the hazardous chemicals and meet the design specifications?
- Are the products of incomplete oxidation also hazardous?
- What material should be used to construct the reactor? Will corrosion be a problem?
- Should the reactor operate isothermally, adiabatically, or with heat transfer?

Problem Information

To complete your work, you will need more information than the article provides. Fortunately, your company's Technical Service Division can conduct experiments for you (for a fee, of course). To request their services, you need only send the Technical Services Manager a written memo explaining what you want them to do. They will let you know the cost and time required to do the work. Then, if you still want the work done, they will provide the results.

Additional Information:

H. SCOTT FOGLER. *Elements of Chemical Reaction Engineering*. 2nd ed. Englewood Cliffs, N.J.: Prentice-Hall, 1992.
Given as an OEP at The University of Michigan, Winter 1994.

(*Note:* The following journal article is based upon one found in the December 7, 1988, edition of the *New York Times*.)

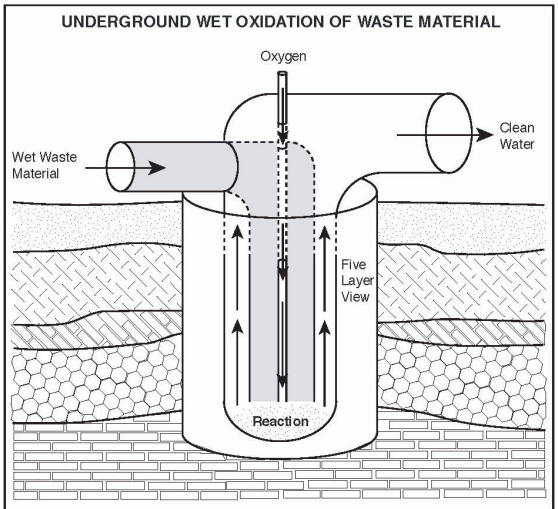
CDH.5 Hydrodesulfurization Reactor Design[4]

Background

Just as you arrive at work one morning, your supervisor, Dr. Jones, says he needs to speak with you and your design group. He seems concerned about something, so you locate your group members and hurry into his office. As the last member of your group shuffles in, you turn to your supervisor and ask, "okay, we are all here. What did you want to talk to us about?"

"Well, one of the processes recently proposed by the Process R& D group produces a by-product stream consisting of nearly pure benzothiophene.

[4] Problem developed by John T. Santini, Jr., University of Michigan.



When wet waste material is mixed with oxygen under high pressures, the wet oxidation process produces sterile ash and clean water. The process is ideal for degrading sewage sludge and other waste material. However, frequently the high pressure requires special equipment and large process plants.

It has been suggested that gravity might provide the high pressures, as indicated by this setup. The reaction is carried out 5,000 ft underground. The waste material and oxygen are transported by pipes to the bottom of the vessel. Falling waste material provides the needed excess pressure. The reaction typically occurs at approximately 550°F and 2,000 psi. The products are drawn to the surface via a third pipe.

Because benzothiophene contains sulfur and an aromatic ring, we cannot vent this stream into the atmosphere. The engineers in Catalyst Development believe that we can use a hydrodesulfurization reaction to convert benzothiophene into ethylbenzene with a cobalt-molybdenum catalyst supported on alumina. If we can design a reactor to do this efficiently, we could sell the ethylbenzene as a commodity chemical. The other product, hydrogen sulfide, could be sent to the sulfur treatment facilities in Building 12.

"I know that your group's specialty is reactor design, so I'm assigning the hydrodesulfurization reactor project to you. I would like a progress report in three weeks and a final design report four weeks after that. I've compiled a list of items that you should include in each of these reports. I know it has been a while since most of you designed a reactor from start to finish, so I've included a partial list of references that may help you. They will be especially helpful with the selection of the materials of construction. I know this assignment is open-ended and requires a lot of engineering judgment, but just remember to use your common sense and BE CREATIVE! Any questions?"

"No. We'll get started right away," you reply as you and your group leave the office.

Problem Statement

As your supervisor told you, the engineers in Catalyst Development think that benzothiophene could be converted to ethylbenzene by a hydrodesulfurization

reaction. Before you commit the company's time and money to design a reactor for this reaction, you may want to attempt to verify that the production of ethylbenzene is economically feasible. In other words, are the products worth more than the reactants and energy required to make them? If you discover the answer is no, you may have saved your company thousands of dollars in design fees. Research this issue and discuss your findings in your progress report. (See the Additional Information section for some references that may help in answering these questions.) If you knew that your supervisor supported the design of the new reactor and you discovered that producing ethylbenzene from benzothiophene was not cost effective, how would you inform your supervisor of this?

The progress report may consist of a maximum of five pages, excluding figures and appendices. In the progress report, be sure that your group provides support for your choice of

- Reactor (i.e., PER, PER, fluidized CSTR, etc.)
- Adiabatic vs. isothermal reactor operation
- Reactor temperatures and pressures (*Hint*: Single-phase reactions are less complicated than multiple-phase reactions)
- Feed ratio of hydrogen to benzothiophene
- Effluent conditions and compositions
- The weight of catalyst required

Also include

- A qualitative discussion of the effect that operating conditions and the method of operation have on capital and operating costs
- Justification for any assumptions made
- Appendices summarizing your calculations

The final design report may consist of a maximum of ten pages, excluding figures and appendices. In the final design report, you should provide support for your choice of

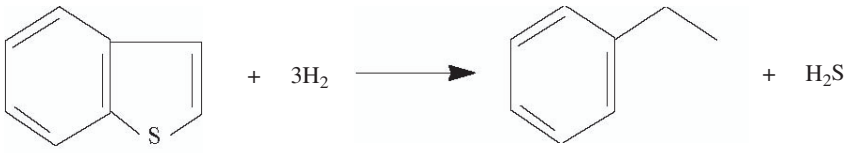
- Materials of construction for the reactor (*Hint*: Is the material susceptible to accelerated corrosion due to the presence of sulfur or hydrogen?)
- Reactor shape and dimensions
- Reactor wall thickness

Also include

- Support for any changes in the initial reactor design presented in your progress report
- Any environmental or safety concerns that may be relevant to your design
- Diagram of the reactor
- Justification for any assumptions made
- Appendices summarizing ALL calculations

Problem Information

The reaction is



Benziothiophene (Thianapthene) Ethylbenzene

In past research studies, the proposed reaction has been run in the vapor phase with reactor temperatures of 240–300°C, total pressures of 2–30 atm, and hydrogen to benzothiophene feed ratios of 4 : 1 to 9 : 1. These experiments resulted in the development of the following rate law. (*Note:* You may assume that the rate law holds for conditions outside this range. Therefore, you are in no way constrained to using these operating ranges and should use them only as guides.)

The rate law is

$$-r_B' = \frac{k_B K_B K_{H_2} P_B P_{H_2}}{\left[1 + (K_{H_2} P_{H_2})^{0.5} + \left(K_{H_2S}\frac{P_{H_2S}}{P_{H_2}}\right) + (K_B P_B)\right]}$$

where

$k_B(260°C) = 6.65 \times 10^{-5}$ mol/gcat • s $\quad k_B(300°C) = 1.80 \times 10^{-4}$ mol/gcat • s

$K_B(260°C) = 19.3$ atm^{-1} $\quad K_B(300°C) = 9.90 \times 10^{-2}$ atm^{-1}

$K_{H_2}(260°C) = 0.358$ atm^{-1} $\quad K_{H_2}(300°C) = 1.84 \times 10^{-3}$ atm^{-1}

$K_{H_2S}(260°C) = 211$ $\quad K_{H_2S}(300°C) = 10.82$

(*Note:* The heat of adsorption was estimated at –80 kcal/mol for all three species.)

Catalyst Properties:

Particle diameter: 0.08 cm

For a packed bed reactor:
ϕ = porosity = 0.30
α = pressure drop parameter = 0.34 kg^{-1}

For a fluidized CSTR:
ϕ = porosity = 0.75
α = pressure drop parameter = 0.005 kg^{-1}

Feed (pure benzothiophene before the addition of hydrogen):

F_{B0} = 20 mol/h

T_0 = entering temperature = 260°C

T_{melt} = melting temperature at 1 atm = 32°C

T_{boil} = boiling temperature at 1 atm = 221°C

References

M. J. GIRGIS and B. C. GATES. "Reactivities, Reaction Networks and Kinetics in High-Pressure Catalytic Hydroprocessing." *Ind. Eng. Chem. Res.*, 30, 2021–2058, (1991).

I. A. VAN PARIJS, L. H. HOSTEN, and G. F. FROMENT. "Kinetics of Hydrodesulfurization on a CoMo/γ-Al_2O_3 Catalyst. 2. Kinetics of the Hydrogenolysis of Benzothiophene." *Ind. Eng. Chem. Prod. Res. Dev.*, 25, 437–443, (1986).

Additional Information

Economic Sources:

Chemical Marketing Reporter. New York: Schnell Publishing Co., Inc.
Oil, Paint, and Drug Reporter. New York: Schnell Publishing Co., Inc.

Reactor Codes:

"Rules for Construction of Pressure Vessels." *A.S.M.E. Boiler and Pressure Vessel Code (Section VIII)*. July 1, 1980.

S. YOKELL. "Understanding the Pressure Vessel Codes." *Chem. Eng.* 75–85 (May 12, 1986).

Selection of Materials:

G. N. KIRBY. "How to Select Materials." *Chem. Eng.* 86–131 (Nov. 3, 1980).

G. N. KIRBY. "Corrosion Performance of Carbon Steel." *Chem. Eng.* 72–84 (March 12, 1979).

M. S. PETERS and K. D. TIMMERHAUS. *Plant Design and Economics for Chemical Engineers*. 4th ed. New York: McGraw-Hill, l99l.

C. M. SCHILLMOLLER, "Solving High-Temperature Problems in Oil Refineries and Petrochemical Plants." *Mat. Eng*. 83–87 (January 6, 1986).

Thermodynamic and Physical Property Data:

DAVID R. LIDE. *CRC Handbook of Chemistry and Physics*. Ann Arbor, Mich.: CRC Press, 1993.

R. H. PERRY, D. W. GREEN, and J. O. MALONEY. *Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill, 1984.

CDH.6 Continuous Bioprocessing[5]

Background

In some biochemical processes, it is desired to use continuous rather than batch processing for economic and efficiency reasons. An example of a continuous process is given in Figure H-1.

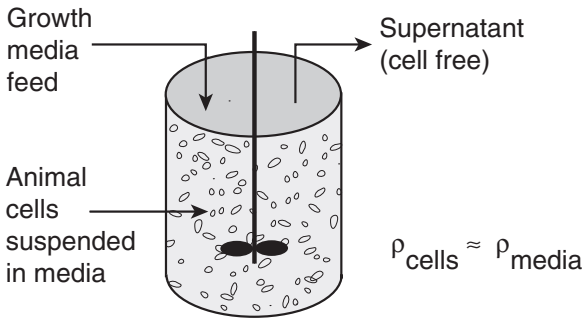


Figure CDH-1 Continuous bioreactor.

The animal cells are in a suspension (they may or may not be on beads) in the reactor unit. When the growth medium is fed in, the cells begin to produce the desired product. The exit stream (supernatant) is composed of this product along with any unused growth media. It is critical that the animal cells are not removed with the supernatant but are retained in solution. It is also important to keep the reactor well-stirred without exerting a large shear stress on the cells, since this may kill or damage them. In addition, the product flow rate from the reactor must not be fast (the space time is of the order of 0.5 to 2 days).

Problem Statement

Your problem is to design a reactor for an actual process of your choice that will meet the preceding specifications (see the following journal references for hints and examples). Consider the aspects of mixing, separation, and kinetics.

Additional Information

C. BECK, H. STIEFEL, and T. STINNETT. "Cell-Culture Bioreactors," *Chem. Eng.* 121–129 (February 16, 1987).

R. MILLER and M. MELICK. "Modeling Bioreactors," *Chem. Eng.* 112–120 (February 16, 1987)

H. SCOTT FOGLER. *Elements of Chemical Reaction Engineering*. 2nd ed. Englewood Cliffs, N.J.: Prentice-Hall, 1992.

M. F. RUBINSTEIN. *Tools for Thinking and Problem-Solving*. Englewood Cliffs, N. J.: Prentice-Hall, 1986.

[5] Problem provided by The Upjohn Company, Kalamazoo, Michigan.

CDH.7 Methanol Synthesis[6]

Background

Kinetic models based on experimental data are being used more frequently in the chemical industry for the design of catalytic reactors, but the modeling process itself can influence the final reactor design and its ultimate performance by incorporating different interpretations of experimental design into the basic kinetic models.

Model Reaction. The reaction for the synthesis of methanol is

$$2H_2 + CO \longrightarrow CH_3OH$$

This reaction is commercially significant and chemically simple, and the thermodynamic properties of the chemical species are well known. The mechanism assumed here is complex enough to make some sophistication necessary for the analysis, but it is too simple to be really true. We assumed a chemical mechanism of medium complexity, comprised of several elementary reaction steps, for the synthesis of methanol. The data were generated for the overall reaction as it would occur in a backmixed, gradientless, experimental reactor at realistic reaction conditions. The final data set is from a statistically designed, central composite set of simulated experiments, to which 5% random error was added. It comprises a total of 27 simulated results (see Table CDH-1).

Problem Statement

The primary purpose of this model is to develop kinetic modeling methods and approaches. We have included the reactor simulation part primarily to afford a realistic basis for the comparison of different kinetic models. The design of the reactor to be simulated; the thermodynamic, transport, and physical properties data to be used; and the reaction conditions to be assumed are specified in Tables CDH-2 and CDH-3. The reactor is a commercially realistic, plant-scale, shell-and-tube reactor, suitable for the synthesis of methanol. However, its actual design, its reaction conditions, and its performance will be different from those of any existing commercial methanol process. Simulate the shell-and-tube reactor at specified conditions, using a simple, one-dimensional, plug-flow, pseudohomogeneous, nonisothermal reactor model. Further, investigate the effect of different coolant temperatures. In all calculations, assume that the ideal gas law applies.

With this in mind, the following tasks should be completed.

1. Develop a kinetic model for the synthesis of methanol from the set of synthetic rate data shown in Table CDH-1.

---

[6] Problem presented by J. Berty, S. Lee, F. Szeifert, and J. Cropley at the International Workshop on Kinetic Model Development, AIChE Meeting, Denver, CO, August 1983. (With Permission)

2. Simulate a plant-scale catalytic reactor at specified reaction conditions, using your kinetic model. The design of the reactor, the reaction conditions, and necessary thermodynamic and physical property data are given in Tables CDH-2 and CDH-3.
3. Summarize your results in the format shown in Table CDH-4. Then plot the results with temperature on the y-axis and distance on the x-axis.
4. Suggest a cooling water temperature to be used.

Problem Information

TABLE CDH-1. DATA FOR KINETIC ANALYSIS

			Partial Pressure (kPa)		
Experiment	*Rate (mol/m3 s)*	*Temp. (K)*	*Methanol*	*CO*	*Hydrogen*
1	6.573	495	1013	4052	8509
2	4.819	495	1013	4052	5906
3	6.27	495	1013	1530	8509
4	4.928	495	1013	1530	5906
5	10.115	495	253	4052	8509
6	7.585	495	253	4052	5906
7	9.393	495	253	1530	8509
8	7.124	495	253	1530	5906
9	1.768	475	1013	4052	8509
10	1.177	475	1013	4052	5906
11	1.621	475	1013	1530	8509
12	1.293	475	1013	1530	5906
13	2.827	475	253	4052	8509
14	2.125	475	253	4052	5906
15	2.883	475	253	1530	8509
16	2.035	475	253	1530	5906
17	4.03	485	507	2533	7091
18	3.925	485	507	2533	7091
19	3.938	485	507	2533	7091
20	10.561	500	507	2533	7091
21	1.396	470	507	2533	7091
22	2.452	485	1520	2533	7091
23	5.252	485	172	2533	7091
24	3.731	485	507	4862	7091
25	3.599	485	507	1276	7091
26	5.085	485	507	2533	9330
27	3.202	485	507	2533	5369

TABLE CDH-2. REACTOR, CATALYST, AND PROCESS CONDITIONS FOR SIMULATION REACTOR CONDITIONS

Reactor

Type: shell and tube
Tubes: 3000, 38.1 mm i.d. × 12 m
Coolant: boiling water is on shell side; assume coolant temperature constant at 483 K
Heat-transfer coefficient (overall): assume 631 $W/m^2 \cdot K$

Catalyst Description

Shape: Approximately spherical
Diameter: 2.87 mm
Effective catalyst bed void fraction: 40%
Diffusional resistance: may be ignored

Process Conditions

Feed gas:
Composition: 70 mol% H_2; 30 mol% CO
Space Velocity: 10,000 standard cubic meters per hour per cubic meter of reactor volume
Reactor inlet pressure: l0.13 MPa
Reactor inlet temperature: 473 K
Reactor coolant temperature: 483 K (constant)

TABLE CDH-3. PHYSICAL PROPERTY AND THERMODYNAMIC INFORMATION

Prandtl number of gas: 0.70 (assume constant)
Heat capacity of gas: 29.31 J/g mol • K (assume constant)
Viscosity of gas: 1.6×10^{-5} Ps • s (assume constant)
Heat of reaction: –97.97 kJ/mol methanol formed
Thermodynamic equilibrium constant: (T in K)

$$\log_{10} K_{eq} = \frac{3921}{T} - 7.971 \log_{10} T + 0.002499\, T$$
$$-(2.953 \times 10^{-7})\, T^2 + 10.2$$

TABLE CDH-4. RESULTS

Authors:					
Shell-side temperature (K)		483			
Maximum tube-side temperature					
Location from inlet of max. temp.					
Outlet temperature					
Outlet methanol concentration					
Same as fraction of equilib. value					
Production rate (kg/h)					

Additional Information

H. SCOTT FOGLER. *Elements of Chemical Reaction Engineering*. 2nd ed. Englewood Cliffs, N.J.: Prentice-Hall, 1992.

CDH.8 Cajun Seafood Gumbo

Most gourmet foods are prepared by batch processes. In this problem, students are challenged to design a continuous process for the production of gourmet-quality Cajun seafood gumbo from an old family recipe. The focus is on reactor design.

Most gourmet foods are prepared by a batch process (actually in a batch reactor). Some of the most difficult gourmet foods to prepare are Louisiana specialities, owing to the delicate balance between spices (hotness) and subtle flavors that must be achieved. In preparing Creole and Cajun food, certain flavors are released only by cooking some of the ingredients in hot oil for a period of time.

We shall focus on one specialty, Cajun seafood gumbo. Develop a continuous-flow reactor system that would produce 5 gal/h of a gourmet-quality seafood gumbo. Prepare a flow sheet of the entire operation. Outline certain experiments and areas of research that would be needed to ensure the success of the project. Discuss how to research these problems. Make a plan for any experiments to be carried out (see Section 5.6).

Following is an old family formula for Cajun seafood gumbo for batch operation (10 quarts, serves 40):

1 cup flour
$1\frac{1}{2}$ cups olive oil
1 cup chopped celery
2 large red onions (diced)
5 qt fish stock
6 lb fish (combination of cod, red snapper, monk fish, and halibut)
12 oz crabmeat
1 qt medium oysters
1 lb medium to large shrimp
4 bay leaves, crushed
$\frac{1}{2}$ cup chopped parsley
3 large Idaho potatoes (diced)
1 tablespoon ground pepper
1 tablespoon tomato paste
5 cloves garlic (diced)
$\frac{1}{2}$ tablespoon Tabasco sauce
1 bottle dry white wine
1 lb scallops

1. Make a roux (i.e., add 1 cup flour to 1 cup of boiling olive oil). Cook until dark brown. Add roux to fish stock.
2. Cook chopped celery and onion in boiling olive oil until onion is translucent. Drain and add to fish stock.
3. Add $\frac{1}{3}$ of the fish (2 lb) and $\frac{1}{3}$ of the crabmeat, liquor from oysters, bay leaves, parsley, potatoes, black pepper, tomato paste, garlic, Tabasco, and $\frac{1}{4}$ cup of the olive oil. Bring to a slow boil and cook 4 h, stirring intermittently.
4. Add 1 qt cold water, remove from the stove, and refrigerate (at least 12 h) until $2\frac{1}{2}$ h before serving.
5. Remove from refrigerator, add $\frac{1}{4}$ cup of the olive oil, wine, and scallops. Bring to a light boil, then simmer for 2 h. Add remaining fish (cut to bite size), crabmeat, and water to bring total volume to 10 qt. Simmer for 2 h, add shrimp, add oysters 10 minutes later, and serve immediately.

CDH.9 Alcohol Metabolism[7]

The purpose of this OEP is for the students to apply their knowledge of reaction kinetics to the problem of modeling the alcohol in humans. In addition, the students will present their findings in a poster session. The poster presentations will be designed to bring a greater awareness to the university community of the dangers associated with alcohol consumption. The project will consist of two memos, a final report, and a poster presentation. The poster presentation will be held in the Media Union atrium during Spring-fest.

Students should choose one of the following four major topics to further investigate:

1. Death caused by acute alcohol overdose
2. Long-term effects of alcohol
3. Interactions of alcohol with common medications
4. Factors affecting metabolism of alcohol

Some general information regarding each of these topics follows.

General Background of Alcohol Metabolism

After alcohol is ingested, some of the ethanol is metabolized in the stomach by an enzyme called alcohol dehydrogenase (ADH). However, the stomach is not the primary site for alcohol metabolism. Any unmetabolized alcohol is absorbed into the bloodstream through the stomach and small intestine. The blood is transported to the liver, where the majority of alcohol metabolism occurs. The liver can only metabolize alcohol at a fixed rate (i.e., it is zero order with respect to ethanol concentration). Therefore, any alcohol that is unmetabolized enters the systemic circulation and travels throughout the body until the liver can metabolize it. The liver metabolized alcohol via multiple enzymes, most notably ADH. Alcohol is water-soluble and therefore is absorbed primarily be water in the body. Absorption sites include the blood and the water fluid inside and surrounding the cells. The alcohol is therefore absorbed by most organs including the brain.

1. Death caused by acute alcohol overdose
   - At blood alcohol levels of 300–400 mg/ml, deep coma occurs, and death may occur due to central nervous system (CSN) and respiratory depression (i.e., you stop breathing).
   - Once in the brain, ethanol binds to an enzyme, GABA. With an ethanol molecule present, this enzyme binds more tightly to its substrate. GABA and other similar receptors are responsible for controlling ion levels of Cl^{-}, Ca^{+2}, and K^{+}. Extremely high or low levels of these ions can cause respiratory problems as well as heartbeat irregularities.
   - Death also can occur due to aspiration. Death occurs most often when a person drinks in excess and passes out. The alcohol still in his or her stomach causes the valve leading to the intestines to spasm causing the person to vomit. Vomiting is essentially a last-

[7] Winter 2001 Chemical Reaction Engineering OEP.

ditch effort by the body to get the alcohol out of the body before it passes into the intestines where it will be absorbed. If the person is unconscious at the time, there is a good chance he or she will essentially choke on his or her own vomit.
- The development of a pharmokinetic model will require estimates (or possibly even guesses) of the rate constants for the mechanisms and reactions discussed here.

2. Long-term effects
   - Chronic use of alcohol can have toxic effects on many organs including: brain damage, liver failure, heart damage (increased risk of coronary heart disease), and gastrointestinal disorders. Models may be constructed showing how long (or how much) a person must drink before damage begins to appear.
   - Enzyme levels in the stomach and liver may be altered, changing the rate of metabolism of alcohol. Metabolism models that take drinking habits into account can be developed (i.e., the alcohol metabolism of a person's first drink will be different from that of a chronic drinker's metabolism).
3. Interactions of alcohol with common mediations
   - Some medications (e.g., Tylenol or acetaminophen) are broken down by the same enzymes that metabolize alcohol. Therefore, if alcohol and Tylenol are consumed at the same time, the alcohol and the acetaminophen both compete for the same enzyme. The ensuing competition for the same enzyme can cause the level of alcohol and acetaminophen to remain at higher than normal levels for a longer period of time and can lead to acute or chronic liver damage.
   - Medications can block the normal enzyme activity of ADH. Lower ADH activity can cause the blood alcohol level to be higher than a person would have otherwise experienced. These ADH-blocking drugs include aspirin and heartburn or ulcer medications.
   - The bacteria in a healthy person's large intestine may also play a role in metabolizing alcohol. A person taking antibiotics that reduce the levels of bacteria in the intestine may have a slower rate of alcohol metabolism.
   - There are many other interactions between alcohol and various drugs (both over-the-counter and prescription) that can be investigated. The development of models and mechanisms for these reactions will require estimates of the kinetic parameters.
4. Factors affecting metabolism of alcohol
   - Women vs. Men: Women have less total body fluid than men. Also, women have lower levels of ADH in their stomachs than men. The ADH enzyme plays a key role inmetabolizing alcohol.
   - In some ethnic groups, a polymorphism in the ADH genes may interfere with alcohol metabolism, causing the facial flushing reaction.

- Chronic drinking seems to increase the level of some enzymes responsible for metabolizing alcohol, specifically CYP2E1. An increase in theses enzymes would increase the rate at which alcohol could be broken down.
- There are many other factors that will influence the metabolism of alcohol.

The suggestions listed here are by no means all inclusive. Students should do research within their groups to look at other possibilities within each group. A brief outline of the assignments follows.

Memo 1: The students should discuss each of the four options presented and briefly mention the key ideas associated with each topic. The students should select one of the categories on which to focus their project. Then, using different brainstorming techniques, the students should make a list of relevant subtopics that could be investigated further. A Gantt chart for the completion of the project should be included. A list of references will be provided to give the students a starting point.

Memo 2: After one of the four project topics has been selected, the students should choose two or three main subtopics to focus on. The groups should perform a literature search and conduct web research to obtain relevant information. The students should come up with a model to illustrate the kinetics behind their topic. Students are encouraged to make realistic assumptions wherever needed and to make educated engineering guesses for specific information they may be lacking. This memo should also describe some of the creative ways in which you plan to display your results.

Final Report: The final report should be a one-page summary of the first and second memos, along with no more than one additional page that discusses which factors are most important and why. In addition, the final report should serve as a supplement to the poster presentation so that, if needed, it can be used as a reference for further information.

Poster Presentation: The students should prepare a poster for display at in the Media Union during Spring-fest. The purpose of this poster is to educate the university community and classmates as to what the groups have found regarding their alcohol research. Posters should be informative and visually appealing. Pamphlets or similar handouts will be encouraged. The posters should be as creative as possible. External judges will evaluate the posters. In the past we have had chemical engineering professors from Michigan State, Wayne State, and the University of Toledo, along with other chemical engineers.

CDH.10 Methanol Ingestion

If methanol is ingested, it can be metabolized to formaldehyde, which can cause blindness if the formaldehyde reaches a concentration of 0.16 g/dm^3 of fluid in the body; a concentration of 0.75 g/dm^3 will be lethal. After all the methanol has been removed from the stomach, the primary treatment is to

intravenously inject ethanol to tie up (competitive inhibition) the enzyme alcohol degydrogenase (ADH) so that methanol is not converted to formaldehyde and is eliminated from the body through the kidney and bladder (k_7). We will assume as a first approximation that the body is a well-mixed CSTR of 40 dm^3 (total body fluid). In Section 7.5, we apply a more rigorous model.
The following reaction scheme can be applied to the body.

$$\text{Ethanol} \xrightarrow{\text{ADH}} \text{Acetaldehyde} + \text{Water} \tag{1}$$

$$\text{Methanol} \xrightarrow{\text{ADH}} \text{Formaldehyde} + \text{Water} \tag{2}$$

First, show

$$r_{P1} = \frac{V_{max1}(S)}{S + K_{M1}\left(1 + \frac{M}{K_{M2}}\right)}$$

$$r_{P2} = \frac{V_{max2}(M)}{M + K_{M2}\left(1 + \frac{S}{K_{M1}}\right)}$$

Methanol has been ingested and after pumping the stomach methanol has a high initial concentration.
Investigate how ethanol should be used to prevent blindness.

The suggestions listed here are by ne means all inclusive. Students should do research within their groups to look at other possibilities within each group.
First, show that for immediate injection of ethanol

$$\frac{d(S)}{dt} = -r_{P1} - k_7(S) \quad t = 0 \quad S = S_0$$

$$\frac{d(M)}{dt} = -r_{P2} - k_7(M) \quad t = 0 \quad M = M_0$$

$$\frac{d(P_2)}{dt} = +r_{P2} - k_7(P_2) \quad t = 0 \quad (P_2) = 0$$

Show that for continuous injection of ethanol

$$\frac{d(S)}{dt} = -r_{P1} - k_7(S) + r_{iv}$$

Emergency room guidelines suggest a 10 volume % of ethanol be administered travenously according to the rate 0.16 g ethanol/kg body weight/h. How does the value compare with your model?

- Use the following values for V_{max1} and K_{M1} for ethanol, neglecting the reverse reaction of acealdehyde to ethanol. As a first approximation, use the same values for methanol. Next, vary V_{max2} the initial metha-

nol concentration (0.1 gm/dm^3 < C_M < 2 gm/dm^3), (0.1 V_{max1} <V_{max2} < 2V_{max1}), k_7, and the intravenous injection rate, r.

- There are 10 mg of methanol per 12 ounce can of diet pop. How many cans and how fast must you need to drink them to cause blindness. Just estimate, no need to modify and run the Polymath program.

Additional Information

The standard reference body weight is 70 kg.

S = Ethanol
M = Methanol
E = ADH
P_1 = Acetaldehyde
P_2 = Formaldehyde
P_3 = Excretion products

Reaction sequence

$$\left.\begin{aligned} S + E &\xrightarrow{k_1} E\ S \\ E\ S &\xrightarrow{k_2} E + S \\ E\ S &\xrightarrow{k_3} P_1 + E \end{aligned}\right\} \text{Metabolism 1}$$

$$\left.\begin{aligned} M + E &\xrightarrow{k_4} M\ E \\ M\ E &\xrightarrow{k_5} M + E \\ M\ E &\xrightarrow{k_6} P_2 + E \end{aligned}\right\} \text{Mettabolism 2}$$

$$\left.\begin{aligned} M &\xrightarrow{k_7} P_3 \\ S &\xrightarrow{k_7} P_3 \\ P_2 &\xrightarrow{k_7} P_3 \end{aligned}\right\} \text{Eliminnation 1}$$

K_{M1} = Michaelis constant for ethanol
K_{M2} = Michaelis constant for methanol
V_{max1} = V_{max} for ethanol
V_{max2} = V_{max} for methanol

Base case parameter values (to be varied)

V_{max1} = 3.1 milligrams/(dm^3 • min)
V_{max2} = 2.16 milligrams/(dm^3 • min)
K_{M1} = 1.53 milligrams/dm^3
K_{M2} = 1.07 milligrams/dm^3
$k_7 = 3.47 \times 10^{-5}$ min (kidney removes 0.0833 liters of fluid per hour)
assume the concentration in the urine is the same as the blood.
M_0 = 0.25 g/dm^3
S_0 = To be found