<u>May/June 2008 RAE - Start time: 9:00 a.m., Thursday, May 22.</u>

There are three problems shown below, each on a separate page. Each student has to choose one and let Kathy Lopresti (lopresti@umd.edu) know by e-mail by **<u>1 p.m. today.</u>** You have until **<u>Friday, May 30, at 3:00 p.m.,</u>** to complete and submit a written report. The written report should be e-mailed to Kathy Lopresti and a hard copy delivered to her by the due time.

The requirements for the written report, as explained on the ChBE website (http://www.chbe.umd.edu/grad/phd-aptitude.html) are:

The solution to the exam problem is to be in the form of a document not exceeding 10 double-space pages using a 12pt font. The 10 pages must include the title page, proposal body, and all figures; the number of pages used for references is unlimited.

The report **must** follow the following format:
1. It should include a single title page with a project summary.
2. It should include at most 5 pages dedicated to background information relevant to the particular RAE problem (including the figures of this section).
3. The remainder of the 10 page report must focus on proposed approach to solving the stated problem, any preliminary calculations or research results, the expected outcomes of the project, and a summary of the laboratory equipment and computational resources necessary to carry out the project.
The 10 page limit will be strictly enforced.

You are reminded that students are not allowed to consult with anyone during the RAE, including with faculty members. For procedural questions, you may contact the Graduate Director (Dr. Zafiriou) or any other member of the graduate committee (Drs. Adomaitis, Dimitrakopoulos, Raghavan).

The oral examinations will take place on **<u>Monday, June 2</u>**. Each student should plan on a brief (under 30 minutes) oral presentation. The presentation file can be brought to the examination room by the student on a memory stick. If this is not possible, please contact Kathy Lopresti prior to the examination time for alternate arrangements for transfering the file. A schedule with the exact times for each student is given below. If unforeseen factors necessitate any changes, you will be informed by e-mail.

All oral examinations will take place in the ChBE conference room at the main office.

Zhu, Yujie: 9:00 a.m. - 10:30 a.m.
Chen, Xilin: 10:30 a.m. - 12:00 noon.
Arana Chavez, David: 1:00 p.m. - 2:30 p.m.

<u>Problem 1</u>

Background

Free radical polymerization is the most common of all addition polymerization mechanisms. When free radicals are generated in the presence of unsaturated monomers, the radical adds to the double bond and another radical is generated by the resultant unpaired electron. This radical is free to react with another monomer unit, and in this way the polymer molecule grows by adding monomer units while maintaining a free radical at the reactive end of the live (growing) chain. Chain growth continues until the radical is terminated or transferred to another chain. Each radical chain has a growing lifetime of one to ten seconds. The distribution of the lengths of the polymer chains is described by the *Molecular Weight Distribution.* Free radical polymerizations are highly exothermic, since the addition of each monomer unit involves the opening of a carbon-carbon double bond. Removal of the heat of polymerization is one of the most significant challenges in the design of the reactor system.

The simultaneous polymerization of two or more monomers results in a macromolecule in which the two or more types of monomer units are distributed in some fashion throughout the polymer structure. The degree of distribution of the monomer units may range from a strictly alternating structure to a graft copolymer in which chains of polymer B are grafted onto chains of polymer A. The various monomer units must, however, appear within the same polymer molecule. Copolymers are thus distinguished from physical blends of polymers. The ability to create a macromolecule containing two or more types of monomer units gives the polymer chemist a greatly-increased ability to custom-design a polymer to yield specific end-use properties. The distribution of composition (with regard to the two monomers) of a copolymer is described by the *Copolymer Composition Distribution.*

Solution free racial polymerization can be done in batch, semibatch or continuous (tube or CSTR) reactor systems. Semibatch reactions are done in order to control the copolymer composition distribution. If the two monomers polymerize at significantly different rates, the faster monomer will be consumed first in a batch reactor, then the slower monomer will polymerize. This results in a poor copolymer composition distribution, or in the extreme, it a blend of homopolymers (since each chain is active for less than ten seconds). Adding the more reactive commoner over time (semibatch) is a way of controlling copolymer composition.

Problem Statement

A solution free radical copolymerization (two monomers) is current done in a semibatch reactor. Management wishes to evaluate the possibility of converting to a continuous process.

(problem continued on the next page)

Discuss the important considerations in the choice of reactor system for this case. Describe the choice of reactor or reactor train (CSTR, PFR, etc.). Describe the procedure for sizing the reactor system, and for specifying the heat removal system. Consider the copolymer composition distribution and the molecular weight distribution, and how the design of the continuous reactor may be adjusted to keep these polymer properties as similar as possible to those in the semibatch reactor. Describe the experiments necessary to provide proof-of-concept for the system you have chosen.

Background information for this problem may be found in

Polymerization Reaction Engineering
Kyu-Yong Choi and F. Joseph Schork (unpublished manuscript)

Relevant portions of this manuscript can be found at:

http://www.chbe.umd.edu/grad/RAE_Supplemental_Reference.pdf

Problem 2

The reduction of the dependence of transportation systems on petroleum is a major challenge for energy research. Batteries are a key enabling technology for the development of fuel-efficient hybrid, electric vehicles. Fuel cells are the key enabling technology for a future hydrogen economy.

You are asked to consider the following issues for fuel cells and batteries:

1. Start by discussing the calculation of the theoretical open-circuit voltage of hydrogen/oxygen fuel cell at 80^{o}C. Why is the real open-circuit potential of proton exchange fuel cell (PEMFC) at 80^{o}C lower than the theoretical value?
2. Explain how to calculate the theoretical efficiency of PEMFC.
3. Discuss the differences between PEM fuel cells and Li-ion batteries?
4. Propose at least three innovative ideas on **the materials, components, and structures of PEM fuel cells and Lithium ion batteries**. Back up your proposals quantitatively and suggest theoretical and/or experimental tasks that can be used to ascertain whether your ideas will work in practice.

Problem 3

Bioreactors are reactors in which *microorganisms* convert a carbon source to a product of interest (e.g. a pharmaceutical, a specialty polymer, or a renewable fuel). The overall reaction that occurs in a bioreactor can be represented as

cells + carbon source + trace nutrients + O_2 → more cells + product + organic acids + CO_2.

In many cases, the microorganism may be the only possible route for conversion of the carbon source to the product.

Consider a bioreactor that uses a microorganism M to convert glucose into a specialty polymer P. This is done in a fed-batch manner: cells are added to a solution of the carbon source (glucose) and trace nutrients, and oxygen is supplied by sparging air into the *broth* (the liquid in the bioreactor). The microorganism requires oxygen for respiration and this oxygen must be *dissolved* in the liquid phase in order for the cells to be able to use it. Therefore, the lack of sufficient dissolved oxygen (DO) in the bioreactor will compromise both the survival of the microorganism cells and the production rate of the polymer P.

However, the polymer P is highly viscous in solution. Thus the broth becomes highly viscous soon after the bioreaction begins. This causes reduction in the mass transfer of oxygen from the gas phase to the liquid phase, and thereby, reduced availability of dissolved oxygen to the cells.

You are asked to use *chemical engineering principles* to investigate oxygen transfer to the viscous bioreaction described above and look at methods to improve the oxygen transfer. Answer the following questions:

1. How would you measure or estimate DO, the volumetric gas-liquid oxygen mass transfer coefficient (k_La), the gas-liquid oxygen transfer rate in the bioreactor, and the oxygen uptake rate by the microorganism cells?

2. Design experiments to find a relationship between

(a) the viscosity of a solution of the polymer P and the oxygen gas-liquid mass transfer coefficient k_La in that solution,

(b) the effect of oxygen transfer rate on the rate of growth of cells or the rate of product formation.

For both parts, explain the principles involved and adequately describe the experimental methodology.

3. Describe *two* techniques that have the potential to improve the oxygen availability to the cells. You may search the literature or come up with your own ideas. Discuss any disadvantages of these techniques.

Suggested reading

Gomez, E., Santos, V., Alcon, A., Garcia-Ochoa, F., 2006. Oxygen transport rate on *Rhodococcus erythropolis* cultures: Effect on growth and BDS capability. *Chemical Engineering*

(problem continued on the next page)

Science 61, 4595-4604.

Amaral, P.F., Freire, M.G., Rocha-Leão, M.H., Marrucho, I.M., Coutinho, J.A., Coelho, M.A., 2008. Optimization of oxygen mass transfer in a multiphase bioreactor with perfluorodecalin as a second liquid phase. *Biotechnology and Bioengineering* 99, 588-598.