Realistic Reaction Engineering Experiments for the Undergraduate Curriculum

Kevin D. Dahm, Stephanie Farrell, Robert P. Hesketh and Mariano J. Savelski
Department of Chemical Engineering, Rowan University

Introduction

The pedagogy of teaching chemical reaction engineering is continually advancing through the use of new computational tools such as POLYMATH and MATLAB; interactive computer applications; and a new emphasis in textbooks on relating theory to industrially relevant chemical reactions. What is currently lacking in this area are chemical reaction engineering experiments that employ realistic reaction engineering systems. Nearly all of the reaction engineering experiments, reported in the literature, employ simple systems that can be described using a single overall reaction. In addition most laboratory experiments do not examine the process fluid mechanics of the reactor and how this effects the product distribution. As a result, students only visualize reactors through theory and do not experience realistic reactor systems in their undergraduate courses. This lack of experience eliminates a major engineering challenge in designing and troubleshooting a reactor in which the yield and selectivity are optimized along with the process economics.

Using funding obtained through an NSF-CCLI grant, the Rowan University department of chemical engineering is developing apparatus and procedures for several reaction engineering experiments that go beyond the traditional single-reaction PFR or CSTR. These experiments will introduce undergraduate students to such topics as biological reacting systems, by-product formation, micromixing and its affect on product distributions, and the effects of scale-up. The students will be exposed to these concepts in an inductive manner through hands-on laboratory experience and then examine the theory behind the systems and why the traditional ideal models do not apply. This paper will describe the progress in the development of two experiments: biological reactors and micromixing.

Bioreaction Engineering Experiments

Several universities have introduced biochemical engineering courses and laboratories into their chemical engineering curricula, primarily at the senior level as elective courses. Nam Sun Wang at the University of Maryland has developed an extensive biochemical engineering laboratory, and has introduced several experiments that explore in depth free and immobilized enzyme kinetics, as well as a continuous bioreactor. The experiments developed at Rowan have been adapted from those described by Dr. Wang[1].

The objectives of the experiments are to:

1) investigate enzyme kinetics

2) to compare the performance of immobilized enzymes and cells to that of their free counterparts in batch bioreactors

3) to investigate the performance of two continuous bioreactors

4) examine the product distribution obtained from these reactors.

Students can collect and analyze kinetic data, obtain values of kinetic parameters, and evaluate the performance of immobilized enzyme systems and cells using criteria established for heterogeneous catalyst systems (effectiveness factors). Procedures for each of the experiments described below have been devised, and some sample results are included. The next step will be integrating the experiments into undergraduate courses.

Substrate conversion using immobilized enzymes

In this experiment students explore the kinetics of the enzymatic degradation of potato starch as it is hydrolyzed into sugars such as dextrin, maltoriose and maltose. The primary reaction of interest is the conversion of amylase to maltose:

$$(C_6H_{10}O_5)n \rightarrow C_{12}H_{22}O_{11} \qquad (1)$$

The experiment involves a simple batch reactor and alpha-amylase enzyme immobilized in calcium alginate beads. These beads are produced by pumping a solution of enzymes in sodium alginate through a syringe, into a calcium chloride solution. The bead size is controlled by choice of needle gauge.

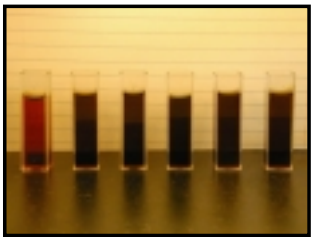

Figure 1. Color change associated with starch conversion using iodine test.

Starch conversion is measured using spectrophotometric determination at 620 nm with an iodine indicator. Figure 1 shows the color change associated with the extent of the starch hydrolysis reaction. Typical student results for the effect of pH on enzyme activity in a batch experiment are shown in Figure 2. From these results students determine the optimal pH for immobilized amylase-catalyzed starch hydrolysis. The effects of parameters such as bead size, temperature and substrate concentration on enzyme activity and ultimate conversion to maltose can also be investigated.

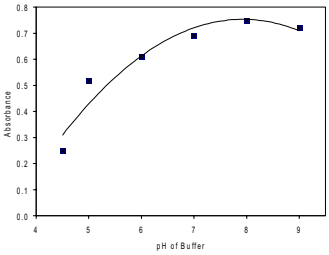

Figure 2. Effect of pH on starch conversion in a batch immobilized enzyme reactor.

The cost of supplies for five experimental set-ups is approximately $200. This includes the enzyme and substrate, reagents, and syringes. Standard laboratory supplies such as beakers and pipettes are assumed to be available and are not included in this cost. A spectrophotometer (visible wavelength) and plastic cuvettes are also required.

Substrate conversion using immobilized cells

As with enzyme immobilization, whole cell immobilization permits the recovery and re-use of cells from bioreactors. Mass transfer limitations are often significant in gel-entrapped cell systems, and oxygen limitations are often most severe due to the low solubility of oxygen in the aqueous phase surrounding the beads. This can be an important concern with aerobic reactions. In this experiment, students investigate the use of free and immobilized cells in batch and fed-batch bioreactors. *Saccharomyces cerevisiae* is a robust yeast that anaerobically converts glucose to ethanol according to the reaction

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 6CO_2 \qquad (2)$$

The yeast, however, are also capable of aerobic respiration which produces carbon dioxide as an end product, and organic acids as intermediates. Both free cells and cells entrapped in alginate beads will be used. Students will monitor the substrate and product concentrations, as well as the free cell concentration in the bioreactor. The apparent reaction kinetics will be compared with the intrinsic kinetics of free cells in a continuous bioreactor. They will investigate the effect of oxygen concentration and pH on intermediate and by-product formation. Typical results for the conversion of glucose to ethanol using immobilized yeast in a batch reactor are shown in Figure 3.

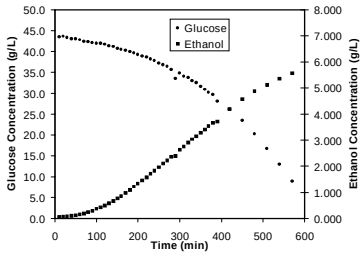

Figure 3. Conversion of glucose to ethanol using immobilized yeast

The experiment duration is approximately ten hours, and the cost for five set-ups is about $200. This includes the yeast and glucose, reagents, and syringes.

Packed bed and fluidized bed immobilized enzyme bioreactors

Continuous bioreactors offer several advantages over their batch counterparts. Automation and control lead to lower cost and more consistent product quality. As mentioned previously, enzyme immobilization can be used in continuous bioreactors to retain the enzyme within the bioreactor. In this experiment, students will study the conversion of starch to sugar in a continuous immobilized enzyme bioreactor. Two reactor configurations will be studied: a packed bed and a fluidized bed. Students will investigate the effect of external mass transfer resistance by varying the flowrate through the column. They will determine the effect of flow rate on conversion, and they will compare the apparent kinetic constant with the intrinsic kinetic constant. The continuous packed column used in these experiments is shown in Figure 4. The color in the column changes from blue to brown to clear, representing unconverted starch, partially converted starch, and total conversion in the presence of iodine solution.

Figure 4. Immobilized enzymes in a continuous packed column reactor.

The glass columns are liquid chromatography columns with adjustable end fittings (flow adaptors), and the total cost for the column set-up is approximately $200.

Micromixing

In practice the issue of mixing and chemical reactions is very important in economic aspects of chemical reaction engineering. A major priority in industrial reactors is to optimize the yield of desired products. This optimization is a function of reactor geometry, the chemical and physical characteristics of the reacting system, the degree of mixing and the mode of supplying the reactor with reagents. Bourne and Gablinger[2] have shown how process chemistry developed in the laboratory can go awry when scaled to industrial reactors. An excellent example of the classic series-parallel reaction using an azo dye chemistry is presented by Bourne and Gholap.[3] The chemist will optimize the reaction to obtain very high reaction rates for the desired reaction. However, in the industrial reactor, micro-mixing is a limiting factor, negatively impacting the process chemistry.[4] However, as explained by Etchells[5], a typical undergraduate reactor design course focuses on ideal reactors and would overlook the impacts of mixing on the reaction chemistry and the formation of trace byproducts. The goal of the experiments described here is to demonstrate to the student the practical limitations of the idealized models.

The experiments developed at Rowan are adapted from Guichardon and Falk[6,7], and involve this pair of parallel competitive reactions:

$$H_2BO_3^- + H^+ \leftrightarrow H_3BO_3 \quad (3)$$

$$5I^- + IO_3^- + 6H^+ \leftrightarrow 3I_2 + 3H_2O \quad (4)$$

The main reaction (3) is essentially instantaneous. The rate of the side reaction (4), in the forward direction, is fast but orders of magnitude slower than that of the first.[6,7] Thus, when H^+ is added as the limiting reagent, a perfectly mixed system would produce essentially no I_2. Production of a significant quantity of I_2 is attributed to a local excess of H^+; a condition in which all $H_2BO_3^-$ in a region is consumed and H^+ remains to react with I^- and IO_3^-.

Any I_2 formed in solution will react further with I^-:

$$I_2 + I^- \leftrightarrow I_3^- \quad (5)$$

The concentration of the I_3^- ion can be measured accurately with spectrophotometry and Beer's law. Thus, the yield of reaction 4 is readily determined.

A team of undergraduate students assembled apparatus and developed an experimental procedure as an Engineering Clinic[8] project. The total cost of the setup was under $500. In the experiment, all reagents except the acid are mixed with a Lightnin' mixer in a 2 L baffled vessel. The acid is then added slowly with a syringe pump, and the rate of addition is one of the parameters that can be studied for its effect on reaction selectivity. The full procedure has been described previously.[9]

Guichardon and Falk characterize the system by dividing the total volume of the reactor into a "perfectly mixed volume" V_{PM} and a "totally segregated volume" V_{TS}. The "micromixedness ratio" α, is defined as V_{PM}/V_{TS}. Details of calculating α for this system are given in their paper.[6]

Figure 5 illustrates the relationship between α and the impeller speed in revolutions per second for both experimental setups. Data produced by the Reaction Engineering class should be similar. Note that α increases with increasing impeller speed. Thus, the influence of improved mixing on product distribution is both demonstrated and quantified.

The experiment, as described here, will be integrated into the Spring 2003 offering of Chemical Reaction Engineering. In addition, a second Engineering Clinic team is retrofitting a specialty chemical pilot plant with a 20-liter reactor to conduct this experiment. This will allow a demonstration of the effect of scale on mixing.

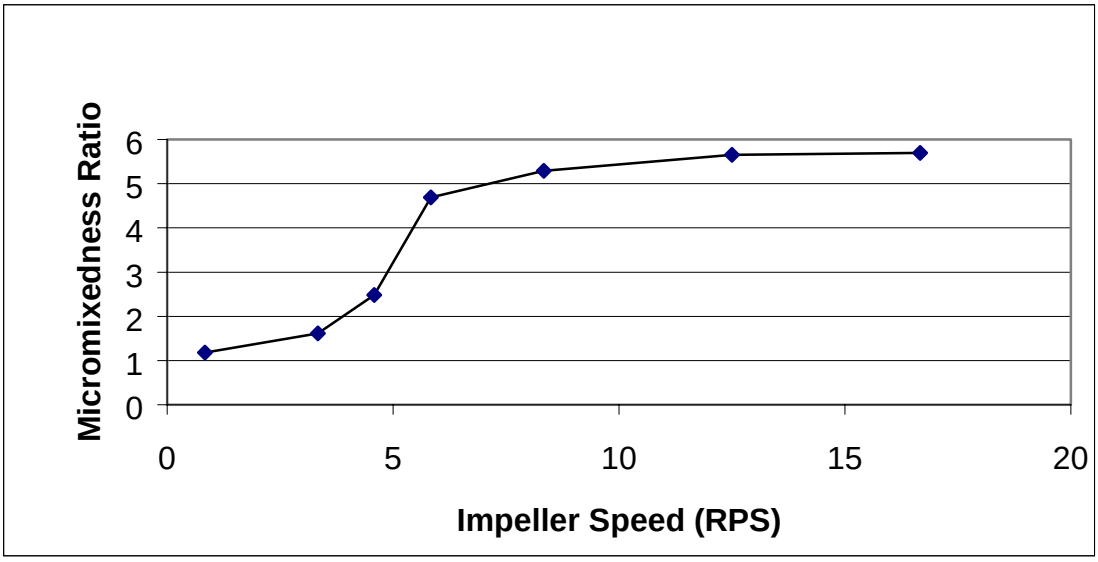

Figure 5: Experimental Results – Effect of Impeller Speed on Micromixedness Ratio (α)

Conclusion

Experiments intended to introduce students to realistic chemical reaction engineering experiments have been developed at Rowan University, and over the next year, will be integrated into undergraduate courses. Among the purposes of these experiments are to expose students to a breadth of chemical reaction applications and techniques, demonstrate practical experimental considerations and challenges, and point out the limitations of the idealized models typically studied in undergraduate chemical reaction engineering coursework.

Acknowledgements

Support for the laboratory development activity described in this paper is provided for by a grant (DUE- 0088501) from the National Science Foundation through the Division for Undergraduate Education.

Bibliographic Information

[1] Wang, Nam Sun, Course Website for Biochemical Engineering Laboratory at University of Maryland, Spring 2000, http://www.glue.umd.edu/~nsw/ench485/ench485.htm

[2] Bourne, J.R.; Gablinger, H., "Local pH gradients and the selectivity of fast reactions. II. Comparisons between model and experiments." *Chemical Engineering Science* **44** (6) p. 1347-1352 (1989).

[3] Bourne, J.R.; Gholap, R.V, "Approximate method for predicting the product distribution of fast reactions in stirred-tank reactors," *Chemical Engineering Journal and Biochemical Engineering Journal* **59**(3) 293-296 (1995).

[4] Baldyga, J.; Bourne, J. R.; Hearn, S.J., "Interaction between chemical reactions and mixing on various scales," *Chemical Engineering Science* **52** (4) p 457-466 (1997).

[5] Etchells, A., "Notes on Mixing in the Process Industries, lecture and short course material," DuPont USA, Wilmington, DE, 1998.

[6] Guichardon, P., Falk, L., "Characterization of micromixing efficiency by the iodide-iodate reaction system. Part I: Experimental procedure," *Chem. Eng. Sci.* **55**, 4233-4243 (2000).

[7] Guichardon, P., Falk, L., Villermaux, J., "Characterization of micromixing efficiency by the iodide-iodate reaction system. Part II: Kinetic Study," *Chem. Eng. Sci.* **55**, 4245-4253 (2000).

[8] J. Schmalzel, A. Marchese, and R. Hesketh, What's Brewing in the Engineering Clinic?. *Hewlett Packard Engineering Educator*. **2(1)**, 6 (1998).

[9] K. D. Dahm, R. P. Hesketh and M. J. Savelski, "Micromixing Experiments in the Undergraduate Curriculum," *ASEE Annual Conference and Exposition*, June 2002, Montreal.

Biographical Information

Kevin Dahm in an Assistant Professor of Chemical Engineering at Rowan University. He received his B.S. from Worcester Polytechnic Institute in 1992 and his Ph.D. from Massachusetts Institute of Technology in 1998. His primary technical area is in chemical kinetics and mechanisms. His current primary teaching interest is integrating process simulation throughout the chemical engineering curriculum, and he is receiving the 2003 Joseph J. Martin Award for work in this area.

Stephanie Farrell is Associate Professor of Chemical Engineering at Rowan University. She received her Ph.D. (1996) from NJIT. Stephanie has developed innovative classroom and laboratory materials in biomedical, food, and pharmaceutical engineering areas. She is the recipient of the 2000 Dow Outstanding Young Faculty Award, the 2001 Joseph J. Martin Award, and the 2002 Ray W. Fahien Award.

Robert Hesketh is a Professor of Chemical Engineering at Rowan University. He received his B.S. in 1982 from the University of Illinois and his Ph.D. from the University of Delaware in 1987. After his Ph.D. he conducted research at the University of Cambridge, England. Robert's research is in reaction engineering, novel separations including supercritical fluids and ultrafiltration, green engineering, and the chemistry of gaseous pollutant formation and destruction related to combustion processes. Robert has presented his educational innovations in national meetings and workshops. Robert's dedication to teaching has been rewarded by receiving several educational awards including the 2002 Robert G. Quinn Award, 1999 Ray W. Fahien Award, 1998 Dow Outstanding New Faculty Award, the 2001, 1999 and 1998 Joseph J. Martin Awards, and four teaching awards.

Mariano Savelski is Assistant Professor of Chemical Engineering at Rowan University. He received Ph.D. in 1999 from the University of Oklahoma. His research is in the area of process design and optimization with over seven years of industrial experience. His prior academic experience includes two years as Assistant Professor in the Mathematics Department at the University of Buenos Aires.