Two Experiments for the Introductory Chemical Reaction Engineering Course

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Abstract

The Rowan University Department of Chemical Engineering has received an NSF-CCLI grant to develop realistic chemical reaction engineering experiments for the undergraduate curriculum. Two of these experiments were an esterification reaction carried out in a packed bed, and a competitive reaction in which the kinetics were influenced by micromixing.

The first experiment is the esterification of ethanol and acetic acid to form ethyl acetate. The reaction is carried out in a fixed-bed reactor with Purolite resin 269 acting as a catalyst. Students first examine this esterification reaction in their organic chemistry class, and the focus is on the esterification reaction mechanism. The packed bed experiment developed in this project re-examines this reaction from a chemical engineering perspective. For example, the reaction is reversible and equilibrium-limited, but in the organic chemistry lab, there is no examination of the kinetics. The complementary chemical engineering experiment examines the relationship between residence time and conversion.

The second experiment is a competitive system involving these two reactions:

\[
\begin{align*}
\text{H}_2\text{BO}_3^- + \text{H}^+ & \leftrightarrow \text{H}_3\text{BO}_3 \\
5\Gamma^- + \text{IO}_3^- + 6\text{H}^+ & \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}
\end{align*}
\]

The first reaction is essentially instantaneous, the second fast but orders of magnitude slower. 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\(_2\)BO\(_3^-\) in a region is consumed and H\(^+\) remains to react with \(\Gamma^-\) and IO\(_3^-\). This experiment gives the students an example of the limitations of the idealized reactor models upon which most of the introductory course is based.

Apparatus and procedures for each of these experiments have been completed and presented in previous NSF Grantee’s Poster sessions. In the spring of 2005, for the first
time, both experiments will be integrated into the undergraduate chemical reaction engineering course. This paper will describe the use of the experiments in the classroom.

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 [1,2] on relating theory to industrially relevant chemical reactions. There is an ongoing effort at Rowan University to integrate these new tools and ideas into the chemical reaction engineering course. This paper describes reaction experiments that have been developed, and how they are intended to complement other activities in the course.

The Rowan chemical reaction engineering class has a weekly 3-hour laboratory period, which, until recently, has been devoted to virtual experiments conducted using POLYMATH, HYSYS and ASPEN. These computer laboratories are valuable because they illustrate many of the same concepts as wet-lab experiments with less substantial time, cost and space requirements. Students can use a simulation to explore many variations on a reactor very quickly, allowing them to investigate cause-effect relationships in the process such as the effect of temperature, pressure or initial concentration on conversion. The literature contains much discussion on pedagogically sound uses for process simulators throughout the curriculum. [3-6]

However, these computer laboratories have limitations. One point is that they are abstract, and a natural learning progression requires that students have some tactile experience with the equipment and the process before they are asked to use abstract models. [7,8] Another point is that simulators lack practical insights. For example, using a process simulator, one can create a detailed model of an isothermal reactor and use it to solve many textbook problems, but never realize how difficult it is to design and build a reactor that is truly isothermal. For these reasons, we are developing wet-lab experiments that complement the computer experiments.

Since time, space and money limit the number of wet-lab experiments that can be included, the intent of this project was to design two experiments that, between them, meet as many pedagogical goals as possible. The following sections describe the two experiments and how they are intended to complement each other.

Esterification Reaction

This experiment is intended to be used early in the semester, so that students will see and operate a real reactor before being exposed to abstract models. The reaction chosen is the esterification of ethanol and acetic acid, by the liquid phase reaction:

\[ \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \]

This system was chosen for several reasons:
• The reactants are familiar, inexpensive and not overly hazardous.
• The reaction has been studied and kinetics and equilibrium relationships are known. [9,10]
• The reaction can be carried out at low temperatures of 40-50 °C.
• The reaction here uses a heterogeneous catalyst but has also been studied with homogeneous catalysts and no catalyst, making it an interesting case study.

In addition, the Rowan organic chemistry course includes this esterification reaction as a laboratory. Thus, this experiment is an opportunity to re-examine a reaction from a chemical engineering perspective. In organic chemistry, the reaction was carried out in a beaker. Here, the students carry out the same reaction in a continuous, steady-state process. In organic chemistry, students carried out the reaction to equilibrium, with no discussion or examination of kinetics. Here, the reaction will not reach equilibrium and conversion is a function of initial concentration and residence time, as well as temperature. Finally, in organic chemistry, the students quantified the yield with a destructive test. Here, the students analyze the liquid product with gas chromatography.

A diagram of the apparatus is shown in Figure 1. It is constructed entirely from basic lab equipment; the only new items purchased were two micro-pumps costing less than $100 total. The heat exchanger and reactor are both glass shell-and-tube heat exchangers. However, the tube side of the reactor is packed with 37 grams of Purolite 269 catalyst. This catalyst is a zeolite base that has been impregnated with a sulfonic acid group, C₆H₇NO₃S. The catalyst has pore diameters ranging from 600 to 750 angstroms, with a specific surface of 35 m²/g and a void fraction of 0.3.

The water bath and feed tank are 10 L buckets. The bath is filled with water and heated to 76 °C while the feed is being prepared. The feed tank is filled with 8 L of water, ethanol and acetic acid in the desired feed concentrations. Once the contents of the feed tank are fully mixed, both pumps are started and the tap water is turned on. Water from the 76 °C bath enters the shell side of the heat exchanger and the feed is pre-heated to 40 °C. This is both the desired reaction temperature and the temperature of the hot tap water. Consequently, in the current design, the shell side of the reactor simply uses hot tap water to maintain an approximately isothermal reactor.

Samples of the liquid product are analyzed using an HP 6890 Gas Chromatograph with TCD and FID, and helium acting as the carrier gas. The column is 30 m long with a diameter of 0.25 mm coated with 0.25 µm film of polyethylene glycol.

Figures 2 and 3 show sample results from the experiment. Figure 2 shows a very intuitive result, in which the conversion increases linearly with an increased concentration of ethanol in the feed. Figure 3 shows a result that novices find counter-intuitive, but one that can be understood through the kinetics of the reaction. The rate of the reaction is ½ order in concentration of acetic acid, so when one doubles the concentration of acetic acid in the feed, the rate of reaction increases but does not double. The number of moles of ethyl acetate leaving the reactor is in fact increasing as the feed
concentration of acetic acid increases, but the conversion, which is a measure of the fraction of entering acetic acid converted to ethyl acetate, decreases.

**Micromixing Reaction**

The second experiment is an investigation of the following competitive-parallel reaction scheme:

1. \[ H_2BO_3^- + H^+ \leftrightarrow H_3BO_3 \]
2. \[ 5I^- + IO_3^- + 6H^+ \leftrightarrow 3I_2 + 3H_2O \]

In this system, H+ is the limiting reagent, and the kinetics of reaction 1 are essentially instantaneous, such that micro-mixing limits reaction 1. If the reactor were perfectly mixed, essentially all of the H+ would be consumed by reaction 1. However, because of mixing limitations, a significant fraction of H+ undergoes the second reaction instead.

This specific reaction system was chosen for several reasons:

- The reagents are readily available, cheap and reasonably safe, with water acting as the solvent.
- Quantitative results can be obtained with a fairly simple analytical method.
- The kinetics of both reactions have been studied. [13-15]
- Imperfect mixing has an effect on product distribution that is straightforward to quantify and explain.
- Finally, the iodine formed in solution has a striking yellow color. This is a perk compared to a solution that remains transparent throughout the reaction because the solution appears to be homogeneous. The yellow color grows darker as the reaction progresses but appears uniform at any given time. The fact that something can be well mixed macroscopically but poorly mixed on a molecular level is an important take-home message of this experiment.

The experimental apparatus consists of a 2 liter baffled vessel with a Lightnin mixer. For comparison, the experiment has also been carried out in a simple unbaffled beaker with a magnetic stir bar. Boric acid, iodate and iodine are added to the reactor and mixed, and then 10 mL of 0.5 M sulfuric acid, the limiting reagent, is added gradually with a syringe pump. Analysis is carried out with a Spec220. A more detailed description of the experimental apparatus and procedures was published previously. [11,12]

Sample results from this reaction are shown in Figure 4. The selectivity is defined as the quantity of the added acid that reacted by pathway 1, divided by the quantity of the added acid that reacted by pathway 2. The selectivity is on the order of 20-40, so reaction 1 is favored, but this observed selectivity is several orders of magnitude lower than would be expected in a perfectly mixed reactor. The fact that the selectivity increases as the impeller speed increases helps demonstrate that poor mixing is indeed the reason for the strong departure from the ideal case. The fact that the Lightnin mixer provides higher selectivity than the simple beaker and magnetic stir bar is further evidence of this fact.
Pedagogical Goals of Experiments

The micromixing experiment was incorporated into the chemical reaction engineering course in 2003, but at that time the esterification apparatus was not yet available. The micromixing and esterification experiments are intended to complement each other:

- The esterification is carried out in a packed bed, the micromixing reaction in a stirred tank.
- The esterification reaction is continuous, the micromixing reaction semi-batch.
- The esterification reaction uses heterogeneous catalysis, the micromixing reaction is carried out in a single phase with no catalyst.
- The esterification is single reaction, and the challenge in making the desired product is that the reaction is slow and equilibrium limited. By contrast the micromixing reaction is fast and proceeds essentially to completion, but making the desired product is challenging because of a competing undesired side reaction.

Thus, with only two wet-lab experiments, students receive a broad exposure to the variety of challenges presented in chemical reaction engineering and the variety of reactor configurations one has to choose from in addressing these challenges. In addition, the pair of experiments is chosen to complement the use of idealized reactor models. The usual strategy in an introductory chemical reaction engineering course, used in texts such as Fogler’s [1] which was used for this course, is to start by presenting a handful of idealized reactor models, such as the plug flow reactor and the perfectly mixed CSTR. These are used repeatedly throughout the book and course in exploring the principles of reaction engineering. The esterification reaction is readily modeled with the idealized models presented in the Fogler text [1], and is therefore a useful introduction to these methods. The micromixing experiment, by contrast, is used late in the semester to demonstrate the limitations of these idealized reactor models.

Summary

This paper describes a pair of experiments that have been developed for the introductory chemical reaction engineering course at Rowan University. The experiments build upon the student’s prior experience in organic chemistry and are designed to complement each other. The two experiments described here will be used in the Chemical Reaction Engineering course for the first time in the spring of 2005. The spring 2004 offering of this course included no wet-lab experiments at all. At the conclusion of the spring 2005 semester, an assessment of the effect of the two labs on student learning will be completed.

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References


Biographical Information

Kevin Dahm in an Associate 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. He has received the 2002 PIC-III Award and the 2003 Joseph J. Martin Award from ASEE.
Figure 1: Diagram of Esterification Apparatus

Figure 2: Conversion acetic acid to ethyl acetate vs. feed concentration of ethanol, with feed acetic acid concentration constant at 1 mol/L.
Figure 3: Conversion of acetic acid to ethyl acetate vs. feed concentration of acetic acid, with feed concentration of ethanol held constant at 1 mol/L.

Figure 4: Selectivity vs. impeller speed for micromixing reaction carried out in Lightnin mixer, and in beaker with stir bar.