Vertical Integration of an Esterification Reaction in the Chemical Engineering Curriculum

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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. This paper discusses one such experiment, the reaction between ethanol and acetic acid to form ethyl acetate. Students examine this system in their organic chemistry class, and it provides an illustration of the esterification reaction mechanism. The experiment currently under development re-examines this esterification 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 currently under development examines the relationship between residence time and conversion.

The reaction will be carried out in a fixed-bed reactor with Purolite resin 269 acting as a catalyst. An outer shell is used to supply hot water to control the temperature of the bed. The experimental apparatus and procedure are nearing completion and testing of the system and collection of data will begin in the spring of 2004. This paper compares the chemical engineering and organic laboratory versions of the experiments and explains the role of the proposed experiment in the course. The experiment is scheduled to be integrated into the Chemical Reaction Engineering course for the first time in the spring of 2005.
**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 an esterification reaction experiment that is currently being developed, and how it is 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 is to design two experiments that, between them, meet as many pedagogical goals as possible.

**Previous Work**

An experiment investigating the following competitive-parallel reaction scheme has already been developed:

1. \( \text{H}_2\text{BO}_3^- + \text{H}^+ \leftrightarrow \text{H}_3\text{BO}_3 \)
2. \( 5\Gamma^- + 1\text{O}_3^- + 6\text{H}^+ \leftrightarrow 3\text{I}_2 + 3\text{H}_2\text{O} \)

In this system, \( \text{H}^+ \) 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 \( \text{H}^+ \) would be consumed by reaction 1. However, because of mixing limitations, a significant fraction of \( \text{H}^+ \) undergoes the second reaction instead. A detailed description of the experiment was published previously. [9] This experiment has already been incorporated into the chemical reaction engineering course.
Esterification Reaction

The micromixing reaction described in the previous section is used at the end of the semester. The experiment now under development is intended to investigate a simpler reaction to be studied at the beginning of the semester, so that students will see and operate a real reactor before being exposed to simulator models. The reaction chosen is the esterification of ethanol and acetic acid, by the liquid phase reaction:

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

This 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. [10,11]
- 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.

This experiment was also carefully chosen to complement the micromixing reaction:

- The esterification is carried out in a packed bed, the micromixing reaction in a stirred tank.
- The esterification is equilibrium limited, the micromixing reaction proceeds essentially to completion.
- Most importantly, the esterification reaction is readily modeled with the ideal reactor 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.

Apparatus and Procedure

A diagram of the apparatus, which is nearing completion, 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, \( \text{C}_6\text{H}_7\text{NO}_3\text{S} \). The catalyst has pore diameters ranging from 600 to 750 angstroms, with a specific surface of 35 m\(^2\)/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 a mixture of water, ethanol and acetic acid in a 10:1:1 molar ratio. 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. However, the completed apparatus is intended to incorporate the ability to vary the reaction temperature, so an action item for the spring 2004 semester is to build an apparatus allowing the operator to control the temperature of the water entering the shell side of the 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.

**Summary**

This paper describes an esterification reaction that is being developed for Rowan’s Chemical Reaction Engineering course. The experiment will complement lab activities currently included in the course and builds upon the student’s prior experience in organic chemistry. In the spring of 2004, the apparatus will be completed, operating procedures will be finalized, and sample data will be collected. All of this information will be included in the conference presentation in June 2004.

**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. We also gratefully acknowledge the donation of 2 kg of catalyst from Purolite.

**References**


**Biographical Information**

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**Figure 1: Diagram of Apparatus**