

## EXPERIMENTS IN UNDERGRADUATE REACTION ENGINEERING: Startup And Transient Response Of CSTR's In Series

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**L**ABORATORY WORK HAS been integrated into most of the undergraduate chemical engineering courses at Idaho for the past 5 or 6 years. There are mixed feelings on the part of the faculty as to whether or not this has been a positive change from the concept of a separate course in experimentation or unit operations. It does however allow the students to get "hands-on" experience with the subject matter considered in each course as they are learning it. This article deals with the laboratory portion of the senior level course in chemical reaction engineering.

The experimental portion of the course encompasses two laboratory sessions, each requiring 4-5 hours of work for a team of three students. Class lectures are usually cancelled during the week of the lab. The first lab deals with batch reactions and is intended to generate kinetic data which will yield reaction rate expressions and rate constants. This information is then utilized to determine the least time consuming method of startup of a series of two continuous stirred tank reactors (CSTR's) and also the transient response of these reactors to a sudden change in flow rate after the initial steady state operation has been achieved. These predictions, or approximations, are then compared to the actual data generated from the reactors while operated in the above manner.

The purpose of the particular experimental se-

quence is severalfold, one of the most important being that the student develops an appreciation of the concept of steady state. In classroom discussions it often seems that steady state operation is rather trivial (sometimes magical) and it is important to leave the student with the impression that bringing reactors up to steady state and keeping them there requires a certain amount of thought and effort. Other benefits of this lab sequence are that it provides for an application of unsteady state material balances to flow reactors, it involves elementary process and experimental design, as well as data and mathematical model evaluation, interpretation and comparison.

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**This type of lab allows for development of rate expressions and rate constants; treatment of startup, steady state and transient behavior of CSTR's, and use of mathematical model predictions via computer simulation to guide the development of experimental procedures.**

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### REACTION SYSTEM

**T**HE REACTION STUDIED in these experiments is the saponification of ethyl acetate by sodium hydroxide in water solution. This system has been discussed in the literature [1-4] and has been used as an example of irreversible second order kinetics in physical chemistry texts [5,6]). The reaction does appear to follow second order irreversible kinetics throughout the reaction when the initial concentration of the base is significantly higher than that of the acetate. When the two



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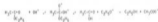


years in the U.S. Army. He currently holds the rank of captain in the U.S. Army Reserve. Prior to entering graduate school, he spent five years with the Elmer Division of Envirotech, with the last two years serving as laboratory manager for pilot plant testing.

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initial concentrations are equal, the apparent second order rate constant decreases as the reaction continues. This has clearly been shown in our laboratory efforts and has been noted by others [2,4]. Tsujikawa and Inoue claim that this can be explained by a sequential reaction mechanism passing through an addition complex.



Here, the reverse rate of the addition complex becomes more apparent as the sodium hydroxide level decreases to low values and results in a lowering of the apparent second order rate constant. Although this variation in performance with choice of starting conditions may seem too complicated for a short laboratory experience, it is actually a useful tool in developing laboratories of varying complexity with the same reaction system. In this paper we have chosen to discuss the results of a laboratory session which deals with the more complicated case using equal concentrations of sodium hydroxide and ethyl acetate in the feed stream.

#### EXPERIMENTAL METHODS

**T**HE REACTION BETWEEN sodium hydroxide and ethyl acetate is quite fast and necessitates the use of low concentrations of these

reactants in order to generate a reasonable laboratory exercise. We have chosen to work with 0.05 Molar feed streams which, when mixed in equal portions, yield initial reactant concentrations of 0.025 moles/liter. This level of dilution, combined with a 10-20°C reaction temperature, allows the students about 3 hours over which to gather data in the range of 0.80% conversion.

The reactions are carried out in one (for batch runs) or two (for CSTR operation) 30 liter reactors which are equipped with agitators, heat exchangers for temperature control, and level control devices for CSTR operation. The size of the equipment presents no problem and serves to give the engineering student a "pilot plant" feeling versus a chemistry lab impression.

Samples are withdrawn directly from the reactor and quenched in prepared quantities of HCl solution. The strength of the acid solution is predetermined such that the HCl is in excess of any possible quantity of NaOH contained in the sample. In our work we used 0.05 Molar HCl and used 25 ml. of this acid solution to quench ~25 ml. of reactor solution. The excess HCl is then back titrated with 0.05 Molar NaOH solution using phenolphthalein\* indicator. The concentration of NaOH in the sample is then calculated from stoichiometry and a simple material balance. The speed of the acid-base reaction is so fast that essentially none of the titrating NaOH is allowed

to react with the remaining ethyl acetate in the sample.

## RESULTS AND DISCUSSION

THE EMPHASIS OF THIS paper is on startup and transient response of a series of CSTR's and as such, discussion of the batch reactor results will be limited. In order to avoid the complexities of the mechanism suggested by Tsujikawa and Inoue, the students are allowed to work with a simple bimolecular reaction mechanism and allow the apparent rate constant to vary with time if necessary. Raw data is converted to fractional degree of conversion of NaOH,  $X$ , and then plotted in the form suggested by the integrated reaction rate expression. For irreversible, second order kinetics this takes the form of  $X/(1-X)$  versus time, and the slope of the curve is proportional to the apparent rate constant. The results for batch runs at 10 and 20°C are plotted in Figure 1 and show two distinct sections, each of which is pretty well characterized by a constant, but different, value of the rate constant. For the 20°C case this procedure yielded rate constants of 1.90 liters/(mole, min.) for conversions less than 53% and 0.46 liters/(mole, min.) above 53% conversion.

Some students endeavor to account for the drop off in rate at higher conversions by assuming a reversible, second order reaction mechanism. The data plot up much better with this assumption but a check on the equilibrium constant calculated from standard free energies ( $K = 10^{11}$ )

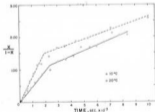


FIGURE 1. Rate constant determination by method of integration.

\*We chose phenolphthalein instead of bromothymol blue because of the clarity of the end point.

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Student response:  
"A good learning experience was achieved as the problem under consideration was a more true to life situation than usually encountered in laboratory situations."

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quickly persuades them that this is not at all probable.

The purpose of the second lab is to develop a startup method for two CSTR's in series which will minimize startup time and off-grade (not at desired conversion level) product production. This coupled with the requirement of analyzing the response of both reactors to an upset in flow conditions after initial steady state operation has been achieved. Both goals are accomplished by applying unsteady state material balances to the reactor sequence. Since these differential equations are coupled (input to second reactor equal to output of first reactor), they are solved via a canned computer program called Continuous System Modeling Program (CSMP) which is available from IEM. This provides a simple and handy way of integrating computer usage into the course and does not involve very much program debugging at all. The procedural section of this program has to be written in such a way as to handle different values of the rate constant depending upon the level of conversion reached in each reactor. During the startup period, the second reactor is required to reach a conversion level of about 70% so that at steady state it will be operating in the area of the lower rate constant. This means that the first reactor in the series will be operating in the conversion range characteristic of the higher rate constant. After operating at steady state for a period of time, the flow conditions are changed to such an extent that the new steady state operating level of the second reactor will be 50%, thus requiring a shift in rate constants during the transient period. Although this may sound complex for the student, it is very easily handled within the computer program with an IF statement, and all students readily accomplish this.

Two alternative startup procedures are quickly arrived at without any assistance from the instructor. These are: 1) batch startup with onset of flow when the conversion level reaches that required for steady state operation and 2)

continuous flow startup with the startup period being assessed for a 95% approach to final steady state conversion. Although the choice between methods is an obvious one, it is good to have the students calculate the anticipated time difference between the two. For the system of interest here, this comes out to be a factor of two in favor of batch startup, which in itself takes about 1-1/2 hours. This time difference coupled with no off-grade product production causes all of the students to choose the batch startup method. Each reactor in the series must now be started at different times to assure that each is at its own steady state conversion level at the same point in time so that flow operation can begin. With this method there is the added opportunity of collecting two more sets of batch rate data to check reproducibility of the first lab session and to provide a better estimate of the rate constant. However, not all the students take advantage of this unannounced opportunity.

Having started up the reactor system and commenced continuous flow, the system is allowed to operate at steady state for 30-45 minutes. At that time the students are asked to make a change in the flow conditions which will result in a new steady state conversion of 50% in the second reactor. The CSMP program is used to predict the time necessary to reach the new steady state levels for both reactors and to help plan the sampling times from both reactors during the transient period. The use of theoretical concepts as aids in determining approximate experimental procedures is a positive point to be worked into the overall lab experience.

Figure 2 is a plot of the transient and steady state operating data for the second reactor at 20°C. Predicted behavior, based on rate constants determined from the first lab, is shown to be in fairly good agreement with the actual results. However not all student groups obtain such a match. The majority of groups that experience a significant lack of agreement actually assess their own problems as being either poor estimations of rate constants from the first lab, or simple errors of coordinating activities of starting up two reactors in the sequence. Other sources of error are incorrect calculations of flow rates for the two steady state cases and simple equipment failure during the transients. In general, good preparation on the part of both student (careful calculations, well defined procedures and good group communications) and instructor (readi-

ness of materials and proper equipment maintenance) leads to a successful laboratory experience.

#### STUDENT FEEDBACK

**T**YPICAL OF INDIVIDUAL responses from a group, the feedback from students on this lab sequence has ranged from "It doesn't strike me that the learning experience is enhanced when a reaction that should be second order just isn't," to "A good learning experience was achieved as the problem under consideration was a more true to life situation than usually encountered in laboratory situations." In general about 70% of

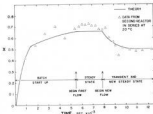


FIGURE 2. Transient and steady-state operation of the second reactor.

the students felt that the lab was a positive experience. Most of them thought it was a difficult set of labs and it is the instructor's opinion that this was because of the open ended nature of the second lab. Those students having had previous industrial experience liked the fact that they were treating a non-ideal system (more typical of their experience) while those with purely academic backgrounds felt somewhat uncomfortable in this situation.

From an instructor's viewpoint, this type of a lab allows for the integration of several features of reaction engineering R&D into one activity: 1) development of rate expressions and rate constants, 2) treatment of startup, steady state and transient behavior of CSTR's, and 3) use of mathematical model predictions via computer simulation to guide the development of experimental procedures. Another positive point is

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## CHEMICAL ENGINEERING DIVISION ACTIVITIES

### Annual Lectureship Award to Robert Reid

The 1977 ASEE CHE Division Lecturer is Dr. Robert Reid of Massachusetts Institute of Technology. Bestowed annually on a distinguished engineering educator who delivers the Annual Lecture of the Chemical Engineering Division, the award consists of \$1,000 and an engraved certificate. These will be presented to Dr. Reid at the ASEE Summer School for Chemical Engineering Faculty July 31-August 5, 1977 at Snowmass, Colorado. Dr. Reid's lecture is entitled "Superheated Liquids: A Laboratory Curiosity and An Industrial Curse". A paper based on his lecture will be published in CEE. During the 1975-76 academic year, Dr. Reid will visit three universities yet to be selected to speak on topics related to the subject matter of his award lecture. The 3M Company is supporting this activity in addition to the award itself.

Professor Reid spent his youth in Denver, Colorado and attended the Colorado School of Mines. After a four-year

interruption during the second world war, he transferred to Purdue University where he obtained both a B. S. and M. S. in chemical engineering. His doctoral studies were carried out at M. I. T. after which he joined the faculty as Director of the Engineering Practice School at Oka Ridge, Tenn. He has been active in the AIChE and served as a Director from 1965-71 and as editor of the AIChE Journal from 1970 to 1976. He was the Institute Lecturer in 1968 and received the Warren K. Lewis award in 1976.

His research interests have covered a wide range of subjects including kinetics, boiling heat transfer, life support systems, crystallization, properties of materials, cryogenics and thermodynamics. Books include texts on crystallization growth rates from solution, thermodynamics and the estimation and correlation of the properties of gases and liquids.

### BOOK REVIEW

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There are some disadvantages to using this book as a text. There are no problems besides the examples. This is not an unsurmountable problem in that the notational format is quite standardized and clear and problems are readily formulated in a consistent context. To offset this, the use of the book as a reference text in an area that brings together classical chemical engineering and process metallurgy could be quite advantageous. The techniques of process analysis are applied to standard chemical process problems but can be carried over nicely to Part III, Metallurgical Reaction Systems.

This most certainly is a valuable book to have as a reference text and quite useable as a supplementary advanced text. I think it would have to be carefully used in any course based on a quarter system. If it were used in successive quarters, the book would be an excellent introductory text to bridge the technique of chemical engineering and process metallurgy. □

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that the reaction system employed is quite flexible and allows the instructor to vary the degree of complexity of the lab without changing the materials, equipment or method of analysis. □

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