ChE laboratory

*Kinetics**

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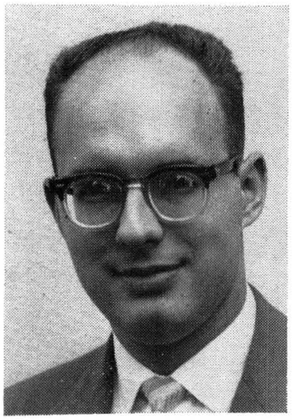
The background of the current extent of chemical engineering kinetics laboratory work is briefly discussed along with some observations on laboratory operation. The statistical results of a survey on this topic are presented and indicate that although many departments have laboratory work, there are a number that do not. As an aid to the introduction of more experiments, a list of successfully used reactions is given. Finally, a detailed example of an experiment used at the University of Texas is discussed.

It is realized that some type of formal chemical engineering kinetics course is a vital part of chemical engineering education. Utilizing the aspects of applied chemistry through reactor design is a unique feature which differentiates chemical engineers from other engineers.

In the 1940's Hougen and Watson began to systematically treat chemical reactor design, which resulted in their well-known textbook. Even then, it was felt that this was essentially graduate level material. It was not until the late 1950's that many chemical engineering departments had undergraduate courses dealing with reactor design. During the last decade this seems to have changed in that now most departments have some sort of undergraduate lecture course in this area. Although the trend had started, the Dynamic Objectives Report[1] of AIChE, with its recommendation that more emphasis be placed upon the chemical content of the curriculum, undoubtedly also had an effect.

In recent years with the introduction of courses on transport phenomena, process dynamics and control optimization, along with kinetics into the curriculum, the time available for extensive laboratories has been steading decreasing.



Dr. Bischoff was educated at the Illinois Institute of Technology. He has written many articles in the fields of chemical reaction engineering and bioengineering and has recently written a textbook (with D. M. Himmelblau) on "Process Analysis and Simulation."

The major aims of this paper will be to first discuss what is currently done in the chemical engineering departments of the U.S. and Canada concerning chemical engineering kinetics laboratories and to list some examples of chemical reactions which could be used by other departments to introduce kinetics experiments into their curriculum. The final part of the paper will describe in detail an experiment used with success at the University of Texas.

Survey of Chemical Engineering Kinetics Laboratory Work

A survey of the North American departments was conducted to obtain data on the extent of chemical engineering kinetics laboratories. Re-

TABLE I

Extent of Kinetics Laboratory Work*

Topic	Number of Departments
Separate chemical engineering kinetics laboratory course and/or taught in conjunction with chemical engineering kinetics lecture course.	8
Experiments in other chemical engineering laboratory courses.	41
No chemical engineering kinetics experiments.	28

* Note: 76/145 replies were received.

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TABLE II.

Type of Chemical Reaction

Type	Number of Departments
Homogeneous	38
Heterogeneous, non-catalytic	6
Catalytic	20
Reaction engineering/design study	16

plies were received from 76 of 145 surveys mailed. The results are shown in Table I from which it is seen that very few departments have either a separate kinetics laboratory course or have one taught in conjunction with the chemical engineering kinetics lecture coures. These two categories from the survey have been lumped together, since there is not a clear distinction between them. Most of the present work is designed as a part of other existing laboratory cources. In other words, the term "unit operations laboratory" quite often seems to be something of a misnomer since things other than this topic are studied. Thus, about half of the replies indicated that they had some work dealing with kinetics and, in fact, several departments had more than one experiment of this type.

Perhaps the most interesting figure in Table I is the fact that 28 departments indicated that they had essentially no work at all. This seemingly large lack does need some qualifications, since most students do get some exposure to kinetics in physical chemistry. However, it does seem that chemical engineering kinetics laboratory experience is lacking in a substantial fraction of chemical engineering departments. Several departments are presently in the process of adding kinetics experiments, but many are not.

Table II indicates various types of reactions that have been used for the laboratories. It can be seen that the major emphasis has been with homogeneous reactions, probably because they are the easiest to perform and obtain consistent results. Heterogeneous catalytic reactions are also fairly extensively used, probably because of their great practical interest. Very few non-catalytic heterogeneous reactions were reported. The final category of reaction engineering design study seems to have a relatively small amount of work, but this may be somewhat ambiguous. Many of the homogeneous and heterogeneous reactions are run for "engineering" purposes and could possibly be included here also. Many of the departments out of the 16 indicated that an important part of this topic was the use of analog or digital computers to simulate chemical reactor operation. Also, the various reactions were run in a variety of reactors such as tubular, stirred tank, as well as batch.

TABLE III.

Examples of Reactions Used for Kinetics Experiments

Homogeneous

1. Ethyl acetate saponification
2. Acetic anhydride hydrolysis
3. Methyl acetate hydrolysis
4. Ethyl acetate hydrolysis
5. Acetone bromination
6. Isopropanol oxidation to acetone
7. Acetic acid + ethanol esterification
8. Benzaldehyde oxidation to benzoic acid
9. Permanganate reduction with dissolved hydrogen
10. Crystal violet hydrolysis
11. Methyl acetate saponification
12. Phthalic anhydride + butanol esterification (pilot plant scale)
13. Ethylene glycol + periodate
14. Hydrogen peroxide + iodide (iodine clock reaction)
15. Ethylene-propylene polymerization
16. Formaldehyde + methanol esterification
17. N.N-dimethylaniline + ethyl iodide (by DTA)

Heterogeneous, non-catalytic

1. Coke oxidation on cracking catalyst
2. Corrosion kinetics
3. Cyclohexane hydrogenation
4. Cu^{++}-H^{+} ion exchange
5. Cottonseed oil hydrogenation
6. Pyrolysis of plastics

Catalytic

1. Ammonia decomposition, iron oxide
2. Cumene cracking, silica-alumina
3. Ammonia oxidation, platinum gauze
4. Toluene hydrogenation, Raney nickel
5. Isopropanol (liq.) dehydrogenation, nickel
6. Propylene oxidation, copper oxide
7. Acetaldehyde decomposition, copper gauze
8. Benzene alkylation, acid catalyst
9. Propylene disproportionation to ethylene + 2-butene, cobalt oxide-molybdena-alumina
10. Sulfur dioxide oxidation
11. n-Propanol dehydrogenation
12. Cumene hydrogenation
13. Styrene hydrogenation
14. 1-Hexanol dehydration
15. Catalytic cracking
16. Permanganate reduction with dissolved hydrogen, Ag^{+}

Table III presents a list of the actual chemical reactions used, which might serve as an aid to those who are trying to find proven reactions for their own laboratories. The saponification of ethyl acetate is the most popular reaction in use, propably because of its good kinetic characteristics, the ease of measuring the results, and the experiment devised by Kendall.[2]

Detailed Example

An example of a chemical engineering reaction kinetics experiment that has worked well in our laboratories at the University of Texas is ethyl acetate saponification in a tubular reactor. Kendall[2] has given a very complete discussion of the system he developed to study the effects of different flow patterns in the reactor. Our system has many features in common with his but the emphasis is somewhat different. A major aspect of our system is to measure and interpret the effects of non-plug flow in the liquid phase tubular reactor and to interpret these results quantitatively in terms of mathematical models.

The fact that the ethyl acetate saponification is a very "clean" second order reaction with no side reactions is given to the student as basic data. The reaction is run in a Tygon tube of 0.615 cm diameter and 810 cm (35 feet) long, looped through baffles in a section of glass pipe which serves as a constant temperature water bath. Gravity feed lines from bottles of ethly acetate and sodium hydroxide are run through the constant temperature water feed tank to attain reaction temperature and joined in a Y section at the reactor tube entrance. Analysis of product samples is by a simple titration method similar to that described by Kendall. Electrical conductivity methods were tried but did not work any better and were somewhat more complicated than simple titration.

In order to have high conversions of 50-90% the reactor is run at a temperature of 100°F, where the rate constant is 0.22 liter/gm mole-second, and with the feed concentrations of both reactants $C_0 = 0.2$ gm mole/liter. Since non-plug flow is most pronounced under laminar conditions, the flow rates range between Reynolds numbers of 100 to 3000. A comparison of the experimental data with theoretical predictions from the axial dispersion model (see Levenspiel[3]) is required, using the established correlations of the axial dispersion coefficients.

Results of some of the recent student data are shown in Figure 1. At the turbulent end of the range, the plug flow equations give good agreement with the experimental data. At the lower flow rates, although there is quite a bit of scatter, it is seen that the plug flow predictions are not very good and the data approach the axial dispersion model line. The data actually fall mostly between the two predictions, but this may be caused by the looped Tygon tube which would lead to less effective axial dispersion than that predicted by the correlations for straight tubes. In any event, the experiment not only gives an example of tubular plug flow reactor results but also illustrates quantitatively the effects of non-plug flow.

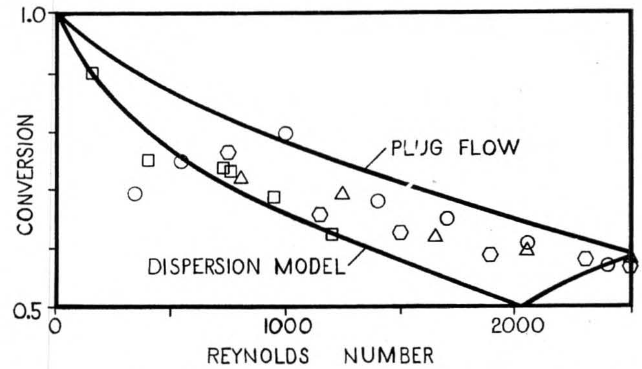

Figure 1.—Student data for ethyl acetate saponification in a tubular reactor.

Conclusions

The survey of chemical engineering kinetics experiments indicated that many departments do have some work in this area, but there are a large number that do not. Very few departments have separate kinetics laboratory or one taught in conjunction with a lecture course.

In addition to the statistical information, the survey produced a rather large selection of chemical reactions that apparently have been successfully used. These have been tabulated to help instructors find experiments that might develop their own laboratories. Finally, an example of an experiment used at the University of Texas was discussed in some detail and the types of results than can be obtained in a student laboratory were indicated.

REFERENCES

1. "Dynamic Objectives for Chemical Engineering," **Chem. Eng. Prog. 57**, (10), 69, 1961.

2. Kendall, H. B., in "Small Scale Equipment for Chemical Engineering Laboratories," ed. R. N. Maddox, **Chem. Eng. Prog. Symp. Ser. No. 70, 63**, 3-15, 1967.

3. Levenspiel, O., "Chemical Reaction Engineering," John Wiley and Sons, Inc., New York, 1962.