

AN INTEGRATED REACTOR ENGINEERING LABORATORY

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Chemical Engineering is unique among other engineering specialties in that its basis is in chemistry. Since this is so and since chemical rate phenomena are an important part of chemistry, the body of knowledge including not only chemical rate phenomena but also the coupling of such phenomena with physical processes is worthy of intensive coverage in the training of chemical engineers.

Two pressures familiar to academicians involved in curricula review are the pressures from outside the University (industry) to make the curriculum more relevant and practical, and pressures from inside the university to make the curriculum attractive to interested students. These two pressures are not complementary in that the former results in the addition of new experiments or new laboratories and hence tends to increase the rigor of the curriculum whereas the latter results in just the opposite.

At the University of Arizona we have attempted to compromise these considerations in the area of chemical reaction engineering by integrating as much as possible of relevant principles, concepts, and techniques from the theory course into a one unit laboratory in the semester following the presentation of the theory. As will be brought out, the number of items deemed important for inclusion into the lab necessitates careful selection of experiments such that each covers several of these important items. It is in this sense that the term "integration" is used in this paper and not in the sense that the theory and lab have been integrated time-wise. This paper will first discuss laboratory objectives and then illustrate their implementation by giving specific examples of experiments being conducted.

OBJECTIVES

In 1969 we conducted a poll of 152 departments of chemical engineering, principally in the United States

and Canada. The response to the poll was high (102/152=67%) so that meaningful conclusions may be drawn as to trends across the country. Of the 102 responding departments, 61 stated that they currently had some lab experience in kinetics and 41 did not. Of those who did, only 8 had labs completely devoted to the subject and of those who did not the majority (33/41) anticipated the addition of such experience in the future.

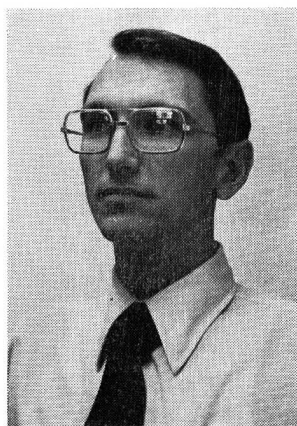
The responding departments indicated that their most popular experiments utilized single phase systems in batch, CSTR, and tubular reactors. Almost as popular was the heterogeneous catalytic type of reaction conducted in a differential tubular reactor with analysis by gas chromatography. From this it may be deduced that the demonstration of reactor behavior with simple (single phase) systems is generally of highest priority and that to illustrate more complex (heterogeneous) systems the differential reactor is being used, presumably due to its simplicity, ease of analysis, adaptability and compatibility with gas chromatography.

The objectives selected for our laboratory are:

- To complement the theory course with practical experience.
- To provide a variety of experience in reactor types, types of reacting systems, methods of data collection, methods of data analysis.
- To provide a laboratory environment in which some degree of success is assured.

The specific experience areas from the theory course which were desirable for the laboratory were:

1. Reactor types.
 - A. Batch. Homogeneous (isothermal, adiabatic). heterogeneous slurry.
 - B. Continuous stirred tank.
 - C. Continuous integral tubular.
 - D. Continuous differential tubular.
2. Reacting Systems Types.
 - A. Homogeneous.
 - B. Heterogeneous catalytic.
 - C. Heterogeneous noncatalytic.
3. Data Collection Methods.
 - A. Direct rate monitoring. Titration. Gas chromatography. Optical measurement.
 - B. Indirect rate monitoring. Temperature measurement. Pressure measurement.
4. Data Analysis Methods.
 - A. Integral method.
 - B. Differential method.



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The experiments which have been run using homogeneous systems are listed below. Each of these four experiments is run by all the student groups and collectively they occupy about one-half to two-thirds of the course:

1. Batch kinetics determination by direct sampling.
2. Prediction and experimental verification of single and multiple CSTR performance.
3. Prediction and experimental verification of packed and unpacked tubular behavior.
4. Batch kinetics by an indirect method—the adiabatic reactor.

The heterogeneous experiments which have been implemented are given below. Each student group will take one of these experiments as an independent project for the time remaining at the end of the semester.

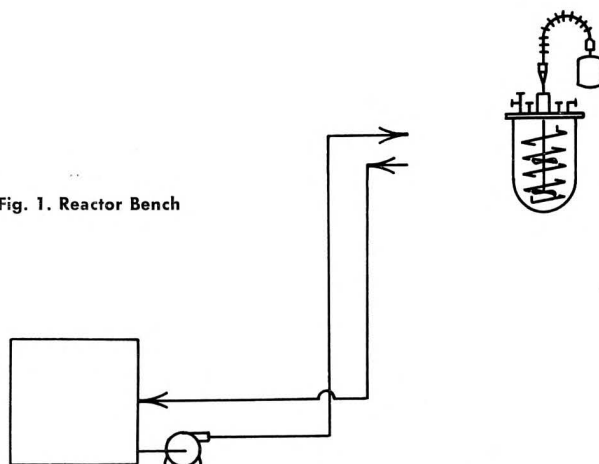
1. Hydrogenation of nitrobenzene on Pd—charcoal in a slurry reactor, with indirect pressure measurement.
2. Dehydrogenation and dehydration of IPA on Pt—charcoal in a continuous microreactor, analysis by gas chromatograph.
3. Noncatalytic TCC catalyst regeneration.

Each of the experiments will now be briefly discussed giving its advantages to the lab.

EXPERIMENTS—HOMOGENEOUS

The first experiment involves the verification of a postulated reaction order and determination of rate constant temperature dependence for a homogeneous reaction in a batch reactor. To date we have used the ethyl acetate saponification reaction. Figure 1 is a schematic of the experimental apparatus which consists of a constant

Fig. 1. Reactor Bench



temperature bath and a three liter glass-stainless steel reactor. Data is typically collected by direct sampling and titration. The methods of excess and/or half-lives may be used but in any case an integral method is used for data analysis. Our experience indicates that many students lack sufficient lab technique to get good results with this experiment. In accord with our objective of providing an environment to insure some success and especially in light of time limitations we are considering changing this experiment (and the two to follow) to automate the analytical technique.

The second experiment has been the experimental study of the transient startup of a CSTR sequence. Figure 2 illustrates our reactor bench in more detail. Reactants are contained in two pressurized 5-gallon polyethylene carboys and are passed through coils in the constant temperature bath before being metered into the continuous reactor being studied. The experimental results may be checked against theory by using the reaction rate expression developed in Experiment 1. Degrees of non-ideality may be controlled by changing mixing RPM, reactor baffling and nearness of inlet and outlet ports.

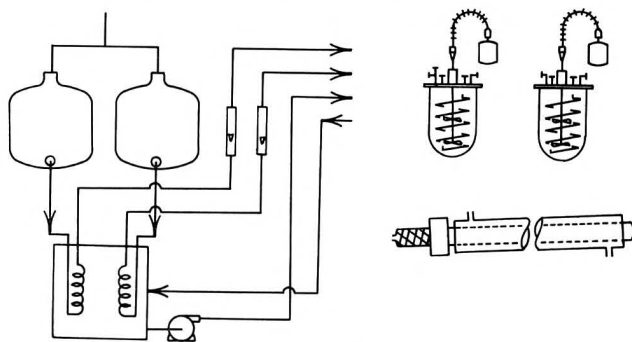


Fig. 2. Reactor Bench Detail

The third experiment uses the same feed system as Experiment 1 but in conjunction with a jacketed glass tubular reactor. In this experiment steady state conversion is obtained as a function of mean residence time for both an open tube and with the tube packed with 1/4" glass Raschig rings. These first three experiments all conducted on the same reactor bench serve to give the student a better understanding of how mixing in a chemical reactor determines reactor behavior. Other experiments which could be run on this very adaptable apparatus include residence time distribution determinations and demonstration of steady state multiplicity. These experiments are currently being prepared for future use.

The last homogeneous experiment run was chosen for several reasons. It demonstrates the operation of an adiabatic batch reactor with an exothermic reaction. Unlike the isothermal experiments which precede it, this experiment requires that an energy balance be made for data analysis. Further, since the coupled material and energy balances are nonlinear the integral method of analysis will not work. Fortunately, the differential method comes to the rescue and is fairly accurate since the continuous temperature-time trace may be easily differentiated. The reaction used is that between hydrogen peroxide and sodium thiosulfate and unlike the ethyl acetate saponification reaction it has a nonobvious stoichiometry which may be experimentally determined. Figure 3 is a schematic of the experimental arrangement.

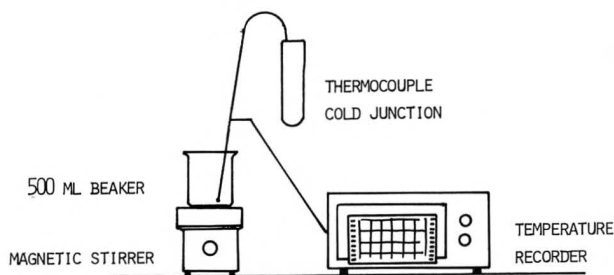


Fig. 3. Apparatus for the Adiabatic Reactor.

In a typical experiment the reactants are mixed together and the sigmoidal temperature increase with time is recorded. The temperature rise will depend on the volume of the reaction mixture and the amount of limiting reactant present. If the volume is held constant (at 400 cc for example) and the initial reactant ratio is

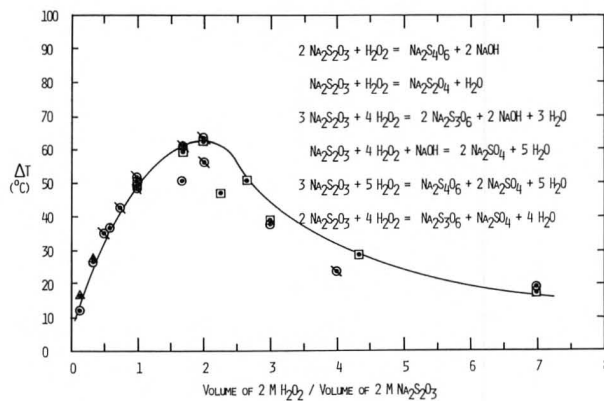


Fig. 4. Temperature Rise as a Function of Initial Reactant Ratio.

varied then the temperature rise will go through a maximum when the initial reactant ratio is equal to the stoichiometric ratio. This is shown in Figure 4 with student data from last year. The different symbols correspond to different student groups. From this graph it appears that of the possible stoichiometries listed, the appropriate one is the last equation listed. Theoretically, it can be shown that if the rate of temperature change divided by the approach to the final temperature squared is plotted against reciprocal temperature an Arrhenius plot results (Figure 5). The experimental activation energy found using student data compares very well with that

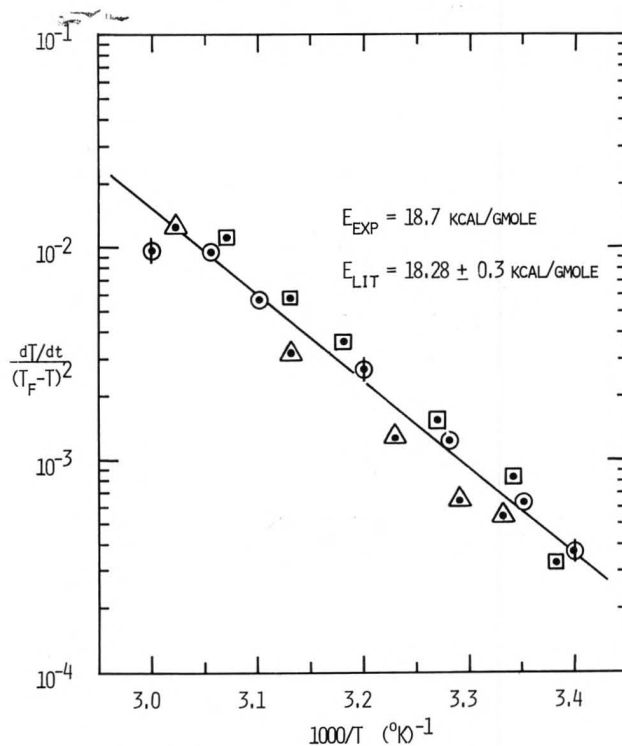


Fig. 5 Arrhenius Plot for $\text{Na}_2\text{S}_2\text{O}_3\text{-H}_2\text{O}_2$ Reaction

reported in the literature as shown. Table 1 gives a more complete list of experimental values obtained from student data compared with literature values. The agreement is quite good.

TABLE 1 COMPARISON OF STUDENT AND LITERATURE VALUES

	v_A/v_B	$-\Delta H_R$ kcal/mole $\text{Na}_2\text{S}_2\text{O}_3$	E kcal/mole	k_0 liters/mole- sec
Student	2	142 ± 7	18.7	7.33×10^{11}
Literature	2	142.5	$18.28 \pm .3$	6.85×10^{11}

EXPERIMENTS—HETEROGENEOUS

The remainder of the experiments utilize heterogeneous systems and each student group will work with just one of these for the rest of the semester.

An apparatus used to study the catalytic decomposition of isopropyl alcohol (IPA) is shown in Figure 6. Helium carrier gas is bubbled through

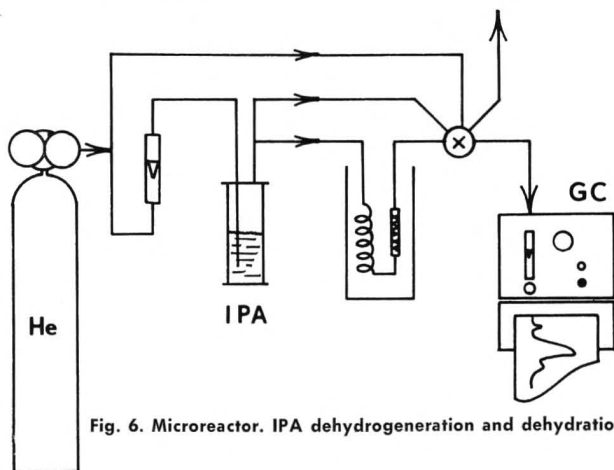


Fig. 6. Microreactor. IPA dehydrogenation and dehydration.

the IPA and then passes through a microreactor containing Pt-charcoal catalyst. The reactor effluent may be sampled and analyzed by gas chromatograph. IPA will decompose to give either propylene and water or acetone and hydrogen, depending on reactor conditions, particularly temperature. The temperature of the reactor is maintained by a sandbath and sampling is accomplished with a multiport sampling valve. This is an easy experiment to run and demonstrates well the reaction selectivity dependence on temperature, the use of a differential reactor for obtaining initial rate data, and the use of a gas chromatograph for analysis. The apparatus is very flexible in that various different reactions and catalysts may be used.

Another good example of a heterogeneous system is the hydrogenation of nitrobenzene over

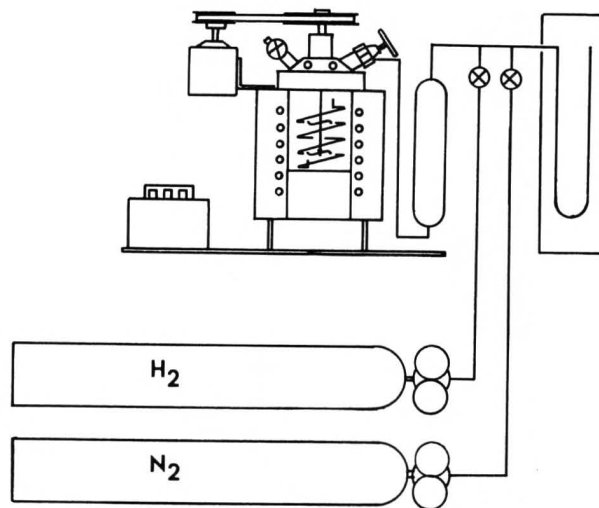


Fig. 7. Slurry Reactor. Hydrogenation of Nitrobenzene.

Pd-charcoal catalyst in a slurry reactor such as depicted in Figure 7. We use a one liter Parr autoclave with a gas storage volume and mercury manometer though the experiment can be just as well studied in glass as reaction pressures are not high. Nitrobenzene and catalyst are charged to the reactor before assembly. The air space over the nitrobenzene is flushed with nitrogen and then with hydrogen before pressurizing the system with hydrogen by reference to the manometer. To initiate the reaction, agitation is begun, dispersing the hydrogen and catalyst into the nitrobenzene. Hydrogen pressure is recorded as a function of time from which reaction rate may

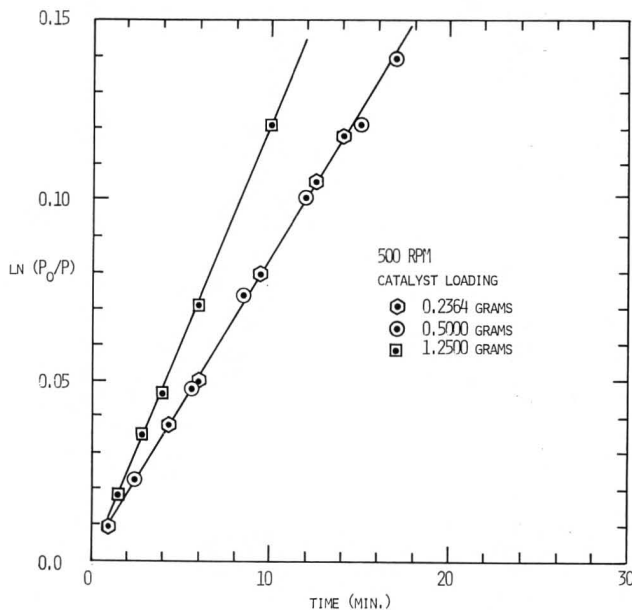


Fig. 8. Pressure ratio versus time and catalyst loading for nitrobenzene¹⁸ hydrogenation.

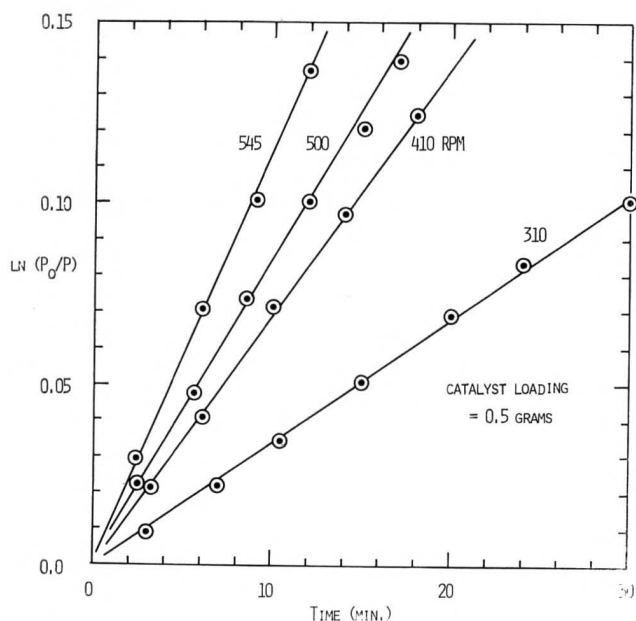


Fig. 9. Pressure ratio versus time and mixing rate for nitrobenzene hydrogenation.

be calculated. Theoretically the expected behavior is first order with the effective reaction rate constant being dependent on temperature, agitation rate, and catalyst loading. Figures 8 and 9 illustrate the type of data which is obtained. The first order behavior is verified and rate constant dependence on catalyst loading and agitation rate is shown. Figure 10 summarized the results of Figure 9, giving the reaction rate constant as a function of mixer RPM. The high RPM asymptote corresponds to chemical reaction rate control and the low RPM asymptote results from a diffusion controlled regime. Data at temperatures other than room temperature would allow for the determination of the activation energy and pre-exponential factor of the chemical reaction rate constant. Empirical correlations for catalyst load-

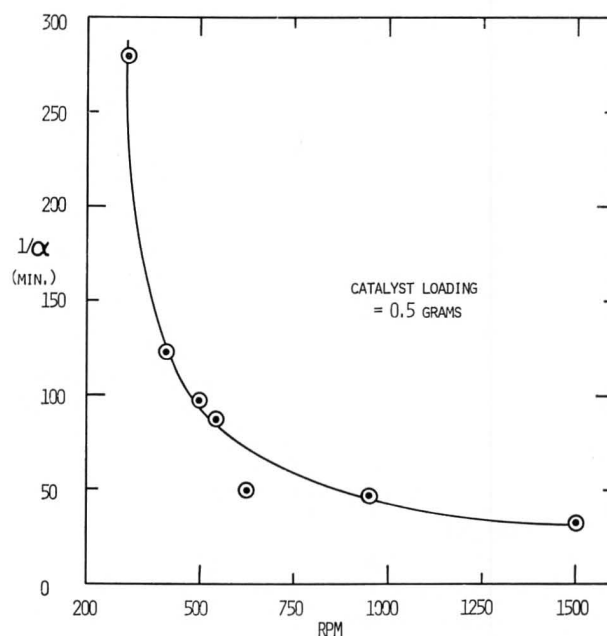


Fig. 1. Effective rate constant versus mixing rate for nitrobenzene hydrogenation.

ing and RPM (or mixing power input) are also possible alternatives.

Other heterogeneous experiments which are currently under development include the high temperature, noncatalytic regeneration of coked Thermoform catalytic cracking catalyst and the leach recovery of metals (e.g., copper) from their ores.

ACKNOWLEDGMENT

In developing such a laboratory one should be alert for experiments which others have developed which have proven to be successful and which complement the laboratory objective. In this regard, I must acknowledge the use of ideas of Drs. James B. Anderson at Yale and Gordon B. Youngquist of Clarkson They have been especially helpful in suggesting experiments which we have used successfully.

FREDENSLUND: (From page 143)

The stated course objectives appear to have been met satisfactorily, although improvements in the course are still being—and will continue to be—made. Before starting the design of a course of this type, the purpose of the course must be very clear, since the equipment design may vary a great deal with the objectives. These objectives are likely to differ somewhat from department to department.

ACKNOWLEDGEMENTS

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