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A Unit Operations Lab Project that Combines the Concepts of Reactor Design and Transport Phenomena

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Introduction

A laboratory course on Unit Operations is a critical component in the chemical engineering undergraduate curriculum, because it provides hands-on experience on the application of theoretical concepts learned in core classes such as chemical kinetics and reactor design, transport phenomena, and mass transfer operations. Typically, students carryout a number of experiments related to each concept. This modular approach, emphasizing the concepts, lacks interconnectivity and integration of novel computational tools such as simulation packages, statistical analysis tools and technical writing skills. Unit Operations Laboratory (UOL) is an ideal course to integrate all chemical engineering curriculum skills as well as the technical tools that are routinely used in the industrial environment.

At Oklahoma State University, one goal in chemical engineering education is to encourage students to connect concepts developed in multiple courses, and generate comprehensive solutions to engineering problems. Students are required to complete two 2-sch UOL courses in our undergraduate curriculum. One course is offered in the spring of the junior year and another in the fall of the senior year. In the first semester students work on fluid flow, heat transfer units. In the second course, they use reaction and mass transfer units.

Project Based Experiments

In each UOL course, randomly assigned three or four person teams work on three separate experimental projects, each lasting 5 weeks. Project objectives are to use the equipment (as though it were a pilot-scale representation of a commercial unit) to generate data upon which they can make an enterprise-relevant decision. For example, students are asked to decide if the company should replace the production trays with those of the test-unit design rather than asking them to measure distillation column tray efficiency. The broader question requires them to consider the costs of replacement, turn-up/turn-down performance range, the impact of operation pressure on efficiency, and other issues that would impact a business decision (which instructors raise in the course of the experiments).

In the first week, students work to understand the challenge and the equipment, and develop a

written plan describing the theory behind the operation, data that needs to be gathered, and operating procedures for safe and sufficient data collection. They are encouraged to develop their plans in consultation with an instructor. The second, third, and fourth week are spent in operating the equipment and data collection in a single 6-hour weekly sessions. During this time, instructors rotate between teams, and actively coach for experimental technique, comprehensiveness of scope, validity of analysis and safety issues. A written progress report is due during the third week of the project i.e., prior to their second experimentation session. This provides an opportunity to the instructors to reveal auxiliary issues and additional complexity and guide the students in further experimentation. On the fourth week of the project, students are engaged in a semi-formal oral discussion with the instructors. In the fifth week, students give an oral presentation to instructors and classmates, focusing on the business action. Students use the comments and suggestions generated during these presentations in writing their final report, which is due on the first week of the next project.

An Example Project Combining Reactor Design with Transport Phenomena

One of the UOL assignments was designing an industrial scale reactor for the catalytic hydrolysis of ethyl acetate into ethanol and acetic acid. Prior to this course, "Transport Phenomena" is introduced in the fall semester of the junior year, then "Chemical Reaction Engineering" is taught in the spring of the junior year. In the "Chemical Reaction Engineering" course, students are introduced to the concepts of non-ideal flow conditions in the reactor and the analysis of non-ideal reactors via zero order models i.e., segregation and maximum mixedness models [1]. Further, a computational fluid dynamic modeling (CFX® AEA Technologies, Pittsburgh, PA) is first introduced in the Transport Phenomena course, and they are trained to analyze RTD in the Chemical Reaction Design Course. The project stages were:

a) *determine the rate law and the rate kinetic parameters*: To minimize the time spent on determining the exact reaction mechanism, they were suggested to use a Hougan-Watson (H-W) kinetic model if the elementary reaction assumption is determined to be invalid [2]. Since the rate constant has a strong dependency on temperature, they use the Arrhenius law.

b) *determine the volume of a reactor for a required conversion assuming ideal plug flow reactor*: Using the rate law, they were asked to determine the volume of a reactor to convert 95% (by wt) of the 7 % (by volume) ethyl acetate feedstock at 500 bbl/day.

c) *determine the realizable conversion in the designed reactor using segregation model*: Using the lab-scale reactor and an easily detectable tracer, they were asked to determine the residence time distribution (RTD). Using the RTD function, they were asked to determine the conversion using the segregation model. Further, they were also told to conduct experiments at different flow rates to see the effect of flow on the RTD and the conversion.

d) *validate the experimental RTD with a simulation based RTD*: Using CFX in a PFR configured to the lab-scale, they were asked to simulate an RTD and then compare those values with the experimental results.

Experimental Setup

The experiment was performed on a lab-scale isothermal packed bed reactor filled with strong acid cationic exchange resin as the catalyst. Details of the apparatus are as shown in **Figure 1**. The reaction is operated isothermally using a shell and tube exchanger to preheat the feed and a water jacket to maintain the reactor temperature. Students prepared a 7 Vol% solution of ethyl

acetate in water as the feed. The mixture flowed upward in the packed bed at varying temperatures from 22°C to 60°C at increments of 5°C and at feed flowrates between 1.0 mL/s and 3.5 mL/s. At steady state, about 100mL of the effluent was collected in a graduated cylinder for each run and the solution was titrated with Sodium Hydroxide to determine the outlet concentration of acetic acid, from which stoichiometry provided the concentration of ethyl acetate. To determine the RTD, about 15 liters of deionized water was poured into the feed tank and was run through the reactor. For a specified feed stream flowrate, the hydrochloric acid was injected into the feed stream, and effluent samples were titrated using 0.1 M Sodium Hydroxide to determine the hydrochloric acid concentration at each time point. The concentration and time data was then used to determined the residence time distribution.

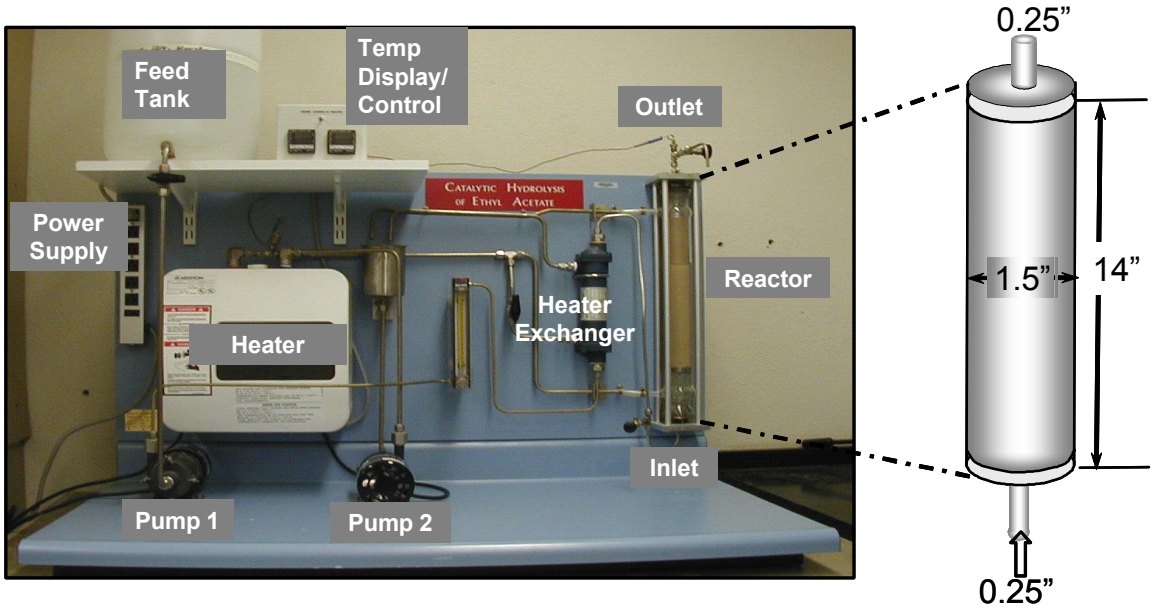

Figure 1. Components of the labscale reactor. Feed of ethyl acetate/water solution is placed in the feed tank and pumped through centrifugal pump 1 to the reactor. The centrifugal pump 2 pumps water stream through the heat exchanger where temperature is altered to the requirement using the temperature display/controller. For RTD measurement the tracer was injected valve-controlled bypass site indicated by the arrow in the bottom of the reactor. The dimensions of the packed-bed reactor are shown in the schematic.

Analysis of Results

Assuming an elementary homogenous reaction with water and the design equation for a PFR can be integrated and linearized (Equation 1).

$$\ln\left(\left(\frac{v_0}{V_R}\right)\ln\left(\frac{C_{EtAc0}}{C_{EtAc}}\right)\right) = \ln k_0 - \frac{E}{RT} \qquad (1)$$

$Ln((V_0/VR)(ln(C_{EthAC0}/C_{EthAC}))$ versus 1/T was plotted as shown in **Figure 1A**. Using the linerar regression analysis function in Excel®, slope (= –E/R) and the y-intercept (=$ln(k_0)$) were determined from which of k_0 and E were calculated to be 3.62×10^9 s^{-1} and 81700 J/mol respectively. However, a low regression coefficient (r2=0.72), prompted the students to a closure inspection of the data which showed an unusual grouping of higher flow rate data on the upper boundary of the data envelop. To understand the validity of the assumed model, data was segregated based on the flow rate, the $ln((V_0/VR)(ln(C_{EthAC0}/C_{EthAC}))$ versus 1/T plotted to obtain

E. Obtained E values were plotted as a function of flow rate (**Figure 1B**), which suggested that E was dependent on the flow rate. Since E is a property of the reactants, this dependence was an indication that the assumed first-order kinetic is not valid. Then students used the H-W kinetic model to obtain the rate law, which was substituted into the design equation. Integrating over the length of the reactor after separating variables, and rearranged to obtain Equation 2.

$$\frac{v_0}{\pi r^2 k'_0 e^{\frac{-E}{RT}}} \ln\left(\frac{C_{EtAc}}{C_{EtAc0}}\right) + \frac{v_0 K_2}{\pi r^2 k'_0 e^{\frac{-E}{RT}}}\left(C_{EtAc0} - C_{EtAc}\right) + L = 0 \qquad (2)$$

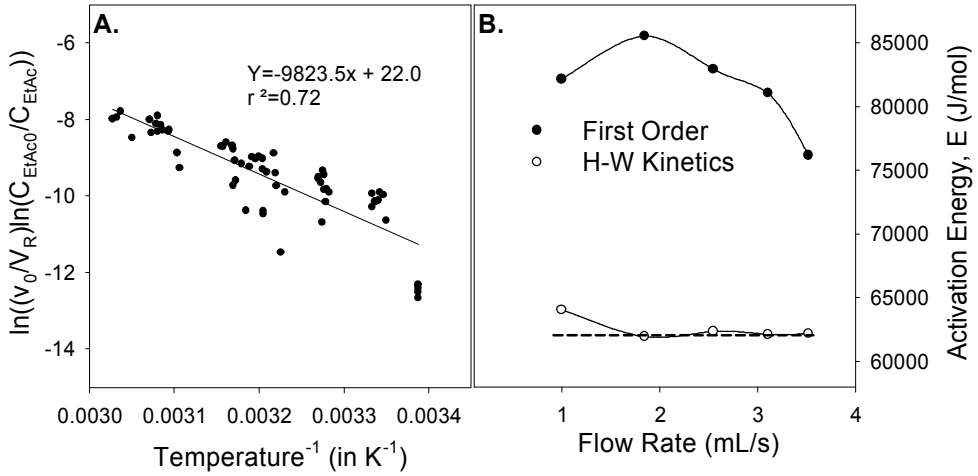

Figure 2. **Analysis of rate kinetic parameters**. **Panel A**. Kinetic Data For the Catalytic Hydrolysis of Ethyl Acetate. **Panel B**. Dependence of E on flow rate, for first order kinetics and H-W Kinetic Model.

Obtaining the value of the constants requires non-linear regression i.e., values of k'_0, K_2, and E are those that minimize the sum of the LHS squared at all data points. Based on this approach, the average k'_0, K_2, and E were found to be 3.62×10^9 s^{-1}, 2440 L/mol and 62300 J/mol respectively. To confirm the validity of the assumed reaction mechanism, obtained E values were plotted for different flow rates (also on **Figure 1B**). This suggested that E was independent of the flow rate and therefore it is preferable to use the surface catalyzed rate law (Equation 3).

$$r_{EtAC} = \frac{3.62 * 10^9 e^{\frac{-7490}{T}} C_{EtAC}}{1 + 2440 C_{EtAC}} \qquad (3)$$

Then, integrating numerically, for 95% conversion, at 30ºC and 1.8 mL/s, the volume of a PFR was found to be 23000 L and it decreased to 4860 L at 50ºC and 1.8 mL/s.

Incorporating the non-ideal reactor design component

To obtain the RTD of the lab-scale reactor, a pulse input of hydrochloric acid, a non-reactive tracer, was run through the reactor. The effluent concentration was measured at sequential time intervals by titration with a base. A concentration versus time plot was then generated and used to calculate the RTD function, E(t) [3]. E(t) was plotted against time to see the divergence from ideal plug flow (**Figure 2**). Students were able to recognize that as the flow rate increased, distribution gap narrowed and showed a trend towards ideal plug flow.

CFX simulation was carried out for the labscale reactor by following the method described in

references [1] and [4]. These results showed RTD function similar to experimental values. In future, similar project-based experiments will use CFX to simulate RTD for scaled-up reactors, validate the applicability of the labscale RTD which will be included in the design.

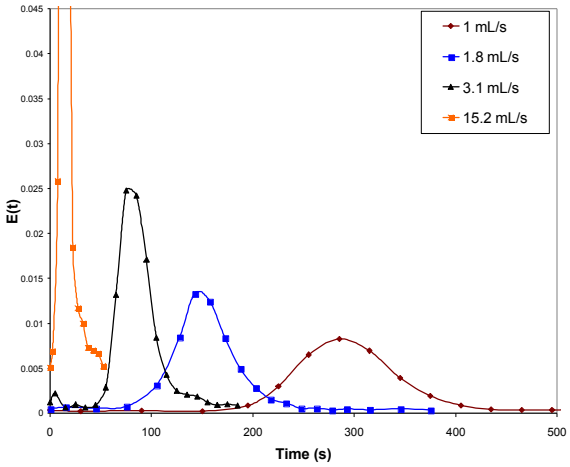

Figure 3. RTD Function. Increased flow rate showed a trend towards ideal plug flow response, despite the fact that a tracer with different physical property was used.

Conversion calculation using the segregation model

Having quantified RTD, the segregation model was used to find the conversion of the commercial scale reactor [3]. After applying the segregation model to a reactor sized as an ideal PFR, the actual conversion was found to be 92% using the 3.1 mL/s RTD and 90% using the 1.8 mL/s RTD suggesting the importance of RTD. As the flow rate increased, the conversion approached 95% i.e., approaching plug flow, reemphasizing the importance of transport phenomena in reactor design. This method shows that there is a dependence of conversion on RTD, indicating two new aspects that need to be considered.

1. The RTD should have been included in the model from which kinetic parameter values are obtained.
2. In any scale-up that is not dimensionally similar to the lab reactor, an RTD for that design needs to be included in sizing calculations.

With this information, the subsequent groups included RTD with the reactor model in their valuation of kinetic model parameters.

Conclusion

Through an experiment of this type, undergraduates can integrate non-ideal reaction systems and get a feel for the variety of aspects of reactor design including transport processes and non-ideal conditions. The chief disadvantage of this method is the time requirement; this experiment will require five weeks. The long timeframe minimizes the number of experiments that may be performed. The project oriented style will require a greater commitment from faculty members and less dependence on teaching assistants in the laboratory. However, short experiments tend to become modular and lack integration of comprehensive concepts. The advantage of this method is that it integrates concepts such as fluid flow, transport issues, reaction kinetics, reactor design, statistical analysis, differential equations and numerical methods. This experiment also trains students to work on projects that are typical industrial problems. While the lab experience includes instruction on propagation of uncertainty, safety, data presentation, and experimental

plans; predominantly this course uses a coaching, not a lecturing, instructional approach.

Undoubtedly, active coaching requires greater faculty involvement; but, when students leave, they leave having experienced their ability to analyze an overwhelmingly complicated problem, their ability to design an experiment to generate necessary but sufficient data, their ability to see theory within nonideal process units, their ability to relate process data to the enterprise objectives, and their ability to credibly defend the validity of their analysis. Student achievement is inspirational to the professors, and sustains commitment. Students rank the course workload as very high, but also rate it as one of the best courses in the curriculum for revealing the essence of chemical engineering and developing professional confidence.

In conclusion, this experiment demonstrated the integration of non-ideal reaction systems in UOL. Importantly, it provides students an opportunity to gain hands-on experience that complements the classroom instruction and analyze the non-ideal conditions. Projects like these will enable students to be more prepared to enter today's workforce and solve the difficult problems.

REFERENCES

1. Lawrence B, Beene J, Madihally SV, Lewis RS. A novel strategy to introduce non-ideal reactors to undergraduate curriculum. (submitted)

2. HAYES, R.E. Introduction to Chemical Reactor Analysis, Gordon and Breach Science Publishers, 2001

3. FOGLER, H. SCOTT, Elements of Chemical Reaction Engineering. Third Edition, Prentice Hall, Upper Saddle River, N.J. 1999

4. Lewis RS, Madihally SV, Incorporating computational fluid dynamics in the chemical reactor design course. 2003 American Society for Engineering Education (ASEE) Annual Conference. Nashville, TN (Session 3213)