"DESIGN OF A SIMPLE APPARATUS FOR REACTION KINETICS AND REACTOR DESIGN EXPERIMENTS"

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ABSTRACT

Tubular reactor experiments are an integral part of an undergraduate course in reaction kinetics and reactor design. However, the successful design of such experiments necessitates meeting a set of criteria regarding safety, simplicity of design and anlytical needs, acceptable cost, and instuctional value. The design of a tubular reactor experiment satisfying the above criteria is presented here. It is hoped that this design can serve as the basis for assembling the necessary experimental apparatus from existing equipment and contribute an additional experiment for the Reaction Laboratory of the Chemical Engineering Department of Qatar University.

1. INTRODUCTION

An undergraduate laboratory tubular reactor experiment was developed by Anderson [1] at Princeton for the reaction of acetic anhydride-water. Due to the nature of the reaction involved, elaborate safety precautions are necessary. Moreover, since the reaction is exothermic, rather expensive temperature control equipment is required. Samples taken at the reactor inlet and outlet are analyzed by the aniline-water method which is lengthy and subject to errors.

Hudgins and Cayrol [2] utilized the basic design of Anderson in developing a

simple and interesting experiment. They utilized the classical reaction system of crystal violet dye neutralization with sodium dydroxide, i.e.,

$$Dye \quad + \quad OH^- \quad \rightarrow \quad colorless\ product$$
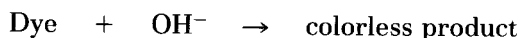
This system was studied earlier by other investigators, mainly in a batch reactor [3]. The two novel aspects of the Hudgins-Cayrol experiment compared with that of Anderson are (i) using color as a measure of concentration and (ii) running the reaction at room temperature removing the need for expensive temperature control. Also, from the safety standpoint, a dilute sodium hydroxide solution (0.02 N) is used.

However, the experimental design given by Hudgins and Cayrol can be significantly improved. The design improvements suggested in this article should make the experiment easier to run and control, significantly improve the reproducibility of results, and expedite the process of data collection within the time constraints of an undergraduate laboratory.

2. THEORY

As was established by Corsaro [3], the reaction between crystal violet dye and sodium hydroxide is of the first order in the concentration of each of the reactants, i.e. the reaction is second order overall. However, the rate expression can be made pseudo-first order, if sodium is used in great excess with respect to crystal violet dye. In other words

$$-r_{dye} \quad = \quad k\ [dye] \tag{1}$$

For this experiment, 0.02 N sodium hydroxide solution is used with a 6.86×10^{-4} M dye solution. Thus the sodium hydroxide concentration would be about 280 times that of the dye, if equal volumes of reactants are used.

Experimental conversions are calculated as described later and compared with theoretical conversions predicted from the plug flow (PFRM) and the laminar flow (LFRM) reactor models.

For a first order reaction in a plug flow reactor, the following equation applies assuming a constant reaction mixture density :

$$\tau = \frac{V}{V_o} = -\frac{1}{k} \ln (1 - x) \tag{2}$$

or

$$\tau = \frac{V}{V_o} = -\frac{1}{k} \ln \frac{C_A}{C_{AO}} \tag{3}$$

If C_A is taken as $[dye]_e$, i.e. the dye concentration at reactor exit, and C_{AO} as $[dye]_i$, i.e. the dye concentration at reactor inlet, Equation (3) can be rewritten as follows :

$$\tau = \frac{V}{V_o} = \frac{1}{k} \ln \frac{[dye]_i}{[dye]_e} \tag{4}$$

For a first order reaction in a laminar flow reactor, the following equation applies assuming no changes in volume by reaction as well as no mixing in both the radial and axial directions [4] :

$$x = 1 - \left[\frac{N_R}{2}\right]^2 E \left[\frac{N_R}{2}\right] + \left[\frac{N_R}{2} - 1\right] \exp (-N_R/2) \tag{5}$$

where

$$N_R = k \tau$$

$$\tau = \frac{V}{V_o} = \frac{L\pi r^2}{V_o}$$

The function E(y), defined by

$$E(y) = \int_{y}^{\infty} \frac{\exp(-\Phi)}{\Phi} \, d\Phi$$

is tabulated in standard mathematical handbooks as $-E_1(-X)$.

3. PROCEDURE

The flowrates of sodium hydroxide and the dye solution are set to a ratio of 9:1. (For a detailed description of the experimental apparatus see the appendix). Starting at the highest possible flowrate to expel all air bubbles from the reactor is recommended.

Waiting for slightly longer than the residence time corresponding to each experimental flowrate is also recommended in order to reach steady state. The reaction mixture is then allowed to flow through the Spectronic 20 flow-through cuvettes and the readings are recorded. Duplicate readings at two-minute intervals should be taken. Experience has shown that the Spectronic 20 readings are highly reproducible. Other flowrates of NaOH and dye solution are chosen, keeping the flowrate ratio 9:1 as before, and the Spectronic 20 reading are recorded. The experiment is expected to last one hour, provided that the solutions are prepared prior to the laboratory period.

The value of the rate constant, k, is needed for this experiment. This can be determined form a batch experiment at the same temperature as the flow experiment. Either a graphical method, i.e. collecting conversion versus reaction time data and plotting -ln(1 - x) versus reaction time, or an anlytical approach using the reaction half life can be employed. Both methods can be found in all standard texts of reaction kinetics (e.g Holland and Anthony [4]). Students should also prepare their own calibration curve of dye concentration versus absorbance. This can be easily done by preparing samples of known dye concentration, measuring their respective absorbance using the spectrophotometer, and plotting concentration versus absorbance.

4. RESULTS AND DISCUSSION

Table 1 shows the residence time, the conversion calculated from the plug flow and laminar flow reator model equations, and the experimental conversions. Figure 1 depicts these conversions against the residence time. The data reported in Table 1 and Figure 1 were obtained from an experiment conducted by one of the authors on a similar experimetal apparatus available in Windsor University, Canada.

Table 1 : Conversion versus Holding Time Data

Holding Time min.	Reynolds Number	PFRM Conv.	LFRM Conv.	Exp. Conv. x
6.42	791	.717	.633	.715
4.3	1181	.571	.503	.533
3.23	1651	.471	.416	.445
2.54	2000	.394	.3496	.369
2.13	2385	.343	.307	.3385

It is clear from Figure 1 that, as expected, the experimental conversions fall between the conversions obtained from the two theoretical models, viz. the PFRM and the LFRM.

It is worthwhile to note that the data reported by Hudgins and Cayrol indicate that the experimental conversion curve crosses the LFRM curve at short holding times, i.e., experimental conversions are lower than those predicted by the LFRM model. However, as it is known from tubular reactor theory [4], the LFRM and PFRM models represent, respectively, the lower and upper conversion limits possible. This is a consequence of the basic assumptions of no mixing occuring either in the radial or axial direction in the case of the LFRM and perfect mixing in the PFRM model. Because in real tubular reactors some mixing in both the radial and axial directions is expected, their conversions must fall within the
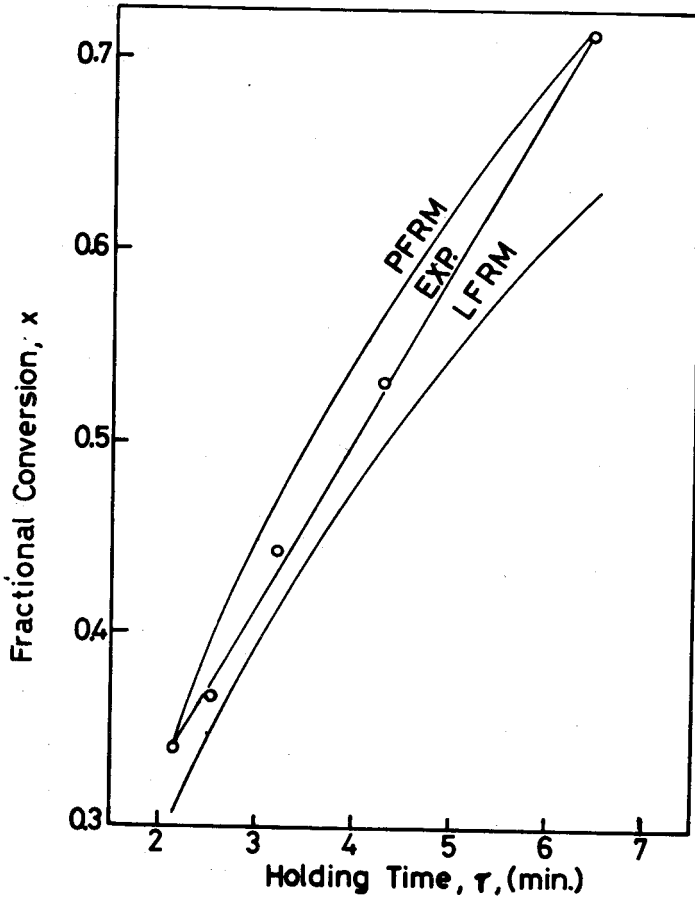
Figure 1 : Comparison between Experimental and Theoretically Predicted Conversions.

limiting values predicted by the LFRM and PFRM models. As mentioned earlier, this behavior was the case with the tubular reactor employed in this study. At the same time, the experimental data of Hudgins and Cayrol [3] indicating conversions lower than those predicted by LFRM model represent a physical impossibility. Such results can be only attributed to design and measurement flaws of the apparatus reported by these authors. These flaws include the lack of constant head tanks and determination of a single value of the rate constant k at one "ambient" temperature for use in all subsequent experiments.

The change of color of the reaction mixture between the inlet and outlet of the reactor is the result of conversion along the reactor. Such a visual effect helps the students integrate the laboratory experiment with knowledge from the lecture part of the course regarding coversion in tubular reactors.

REFERENCES

1. **Anderson, J.B.**, "A Chemical Reactor Laboratory for Undergraduate Instructons", Princeton University, 1968.

2. **Hudgins, R.R.** and **B. Cayrol**, "A Simple Tubular Reactor Experiment", CEE, XV, 1, 26, 181.

3. **Corsaro, G.**, Chem. Educ., 41, 48, 1964.

4. **Holland, C.D.** and **R.G. Anthony**, Fundamentals of Chemical Reaction Engineering, Prentice-Hall, Englewood Cliffs, N.J., 1979.

NOTATION

C_A	:	concentration of component A (mole/L)
k	:	pseudo-first order rate constant (min^{-1})
L	:	length of tubular reactor (m)
N_R	:	reaction number for a first order reaction
r	:	inside radius of tubular reactor (m)
(-r)	:	reaction rate (mol/L.min)
v_o	:	volumetric flowrate (L/min)
V	:	reactor volume (m^3)
x	:	conversion
τ	:	space time (min)

Subscripts

e	:	reactor exit
i	:	reactor inlet
o	:	initial

APPENDIX

Experimental Setup

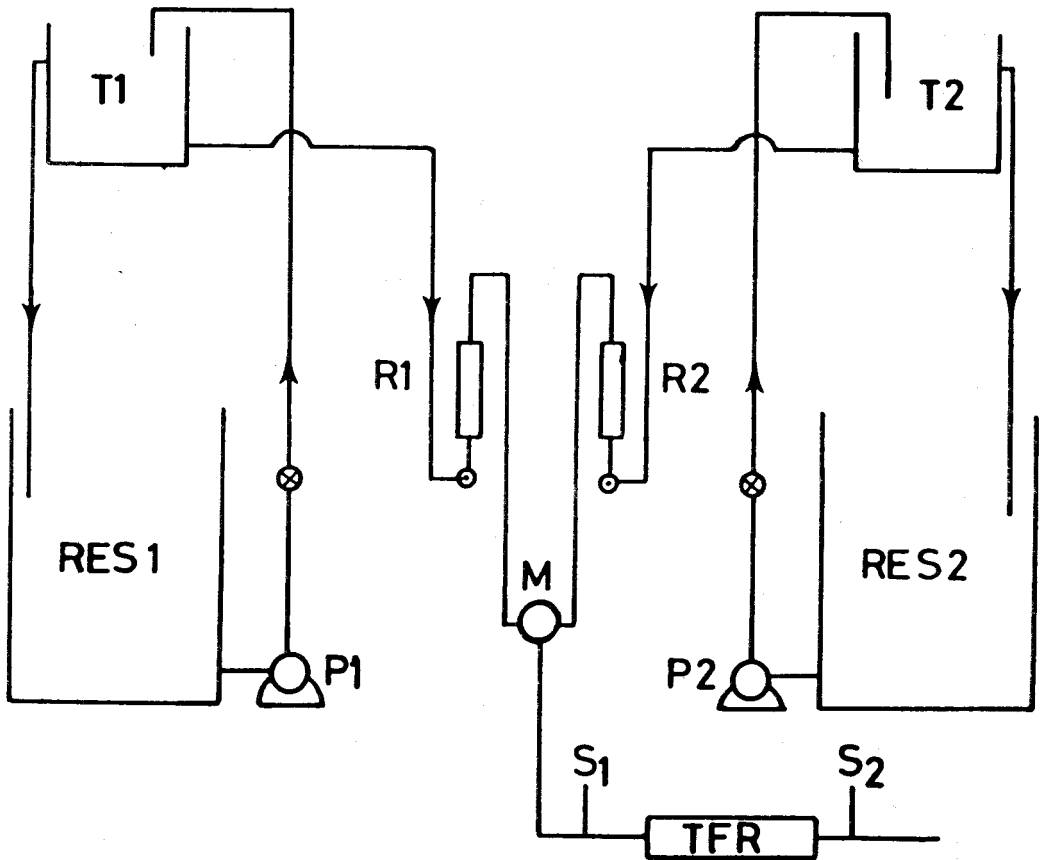A schematic diagram of the proposed experimental apparatus is given in Figure 2.

Figure 2 : Schematic Diagram of the Experimental Apparatus.
M : mixer, P : pump, R : rotameter, RES : reservoir, S : sampling point,
T : constant head tank, TFR : tubular flow reactor.

The components included are as follows:

Reservoirs	:	(RES 1) 200-L polyethylene tank for the sodium hydroxide solution.
		(RES 2) 20-L polyethylene tank for the dye solution.
Constant Head Tanks	:	(T1) 20-L polyethylene tank for the sodium hydroxide solution.
		(T2) 4-L polyethylene tank for the dye solution.
Pumps	:	(P1) Magnet drive gear pump, model P/N 81152, manufactured by Micropump Corp., Conford, California. Available from Cole-Parmer.
		(P2) Centrifugal pump. Cole-Parmer catalog No. K-7004-30.
Mixer	:	(M) Little Giant pump. Model 2E-38NT. Available from Cole-Parmer.
Rotameters	:	(R1) Size R-6-15-A rotameter. Max flow 450 ml/min with SS-float. Available from Cole-Parmer.
		(R2) Size R-6-15-B rotameter. Max flow 1300 ml/min with SS-float. Available from Cole-Parmer.
Reactor	:	40 meters of 3/8 in I.D. Tygon tubing wound on a 28 cm diameter and 55 cm long spool.
Valves	:	Needle valves.
Spectrometers	:	Spectronic 20 (Bausch and Lomb) modified, as described later, to provide continuous measurements. Available from Cole-Parmer.

Two polyethylene tanks (RES 1 and RES 2) of capacity 20 and 200 liters, respectively, serve as reservoirs for the crystal violet dye and sodium hydroxide solutions. Two pumps (P1 and P2) are employed to pump the reactants to two constant head tanks (T1 and T2). The overflows from the constant head tanks

are returned to their respective reservoirs. The underflows go via rotameters (R1 and R2) to a small pump that acts as a mixer (M). The constant head tanks (T1 and T2) are placed about 3 meters above the level of the rotameters. In this manner, a maximum flowrate of 1300 ml/min of NaOH can be obtained. The maximum flowrate of the dye is set at about 135ml/min. The reactant streams are mixed in the mixer, M, and are pumped through the reactor. The tubular reactor is in the form of a helical coil wound on a support. Connections are provided at the inlet and outlet of the reactor to the flow-through cuvettes of the spectrometers.

The main advantages of the proposed experimental apparatus over that suggested by Hudgins and Cayrol are as follows:

(i) Reservoirs and constant head tanks are used. This arrangement provides more stable rotameter operation, especially at low flowrates.

(ii) A flow-through accessory which is simpler in design and operation than that suggested by Hudgins and Cayrol is used. The flow-through accessory shown in Figure 3 allows use of the Spectronic 20 instrument for continuous measurement.
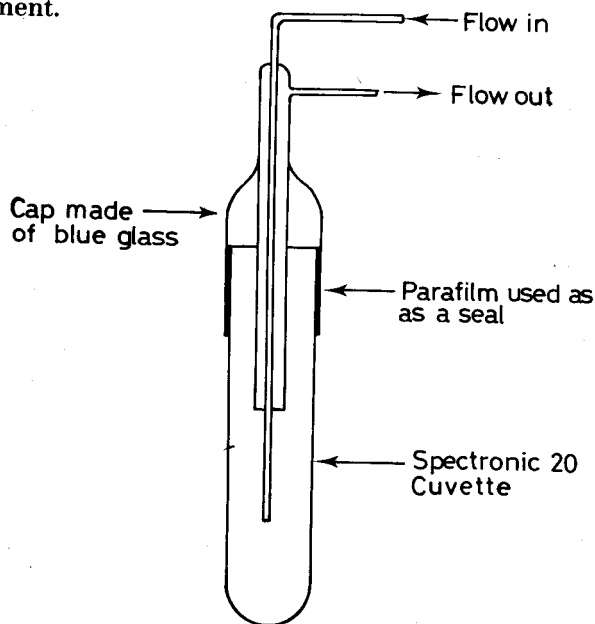

Figure 3 : Flow-through Cuvette for the Spectronic 20 Spectrophotometer.