



Lecture (11)

Comparison of Chemical Reactors

The mathematical models proposed for ideal plug-flow and continuous stirred-tank reactors do not include the effects of the flow pattern on conversion. In a plug-flow reactor the velocity profile is assumed to be flat and the dispersion of reactants and products by turbulence and diffusion is neglected. In the CSTR all reactants and products are presumed to be perfectly mixed with the reactor contents as soon as they enter the vessel. These requirements for the idealized models are usually not met in practice.

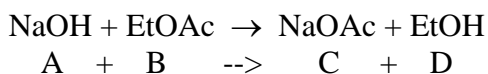
The backmixing created by turbulence and diffusion in a tubular reactor produces a conversion which is lower than predicted by the plug-flow model. Since backmixing is not as extensive as in a stirred tank, conversion in a tubular reactor is often higher than conversion in a CSTR.

The deviation of an actual tubular reactor from the plug-flow model is a function of the bulk velocity. In a laminar flow, where velocity profile is parabolic, the deviation is largest. Under conditions of fully developed turbulence ($Re \approx 10,000$) the velocity profile is more flat and the plug-flow model is more closely approximated.

In this experiment, the deviation of experimental reactors from idealized models will be illustrated. The use of a batch reactor to generate data for the determination of kinetic parameters will also be considered.

Theory

The reaction studied in this is the saponification of ethyl acetate. This reaction is elementary and second-order. The reaction equation is



(A) Batch Reactor

For a constant volume isothermal batch reactor, the design equation is:

$$\frac{dC_A}{dt} = r_A$$

For a bimolecular second order reaction, the rate equation is:



$$-r_A = k C_A C_B$$

In the case where equal amounts of A and B are charged to the reactor, the stoichiometry table looks like this:

<u>SPECIES</u>	<u>INITIAL</u>	<u>CHANGE</u>	<u>FINAL</u>
A	N_{Ao}	$-XN_{Ao}$	$N_{Ao}(1-X)$
B	$N_{Bo} = N_{Ao}$	$-XN_{Ao}$	$N_{Ao}(1-X)$
C	$N_{Co} = 0$	$+XN_{Ao}$	$N_{Ao}X$
D	$N_{Do} = 0$	$+XN_{Ao}$	$N_{Ao}X$
	<hr/> N_{To}	<hr/> 0	<hr/> $N_{To} = N_T$

where X = fractional conversion of A

* Please note, this year (2001) the initial concentrations are NOT the same and you will have to adjust the equations and your analyses accordingly.

The design and rate equations are written in terms of concentrations. Thus, we need to use the relations:

$$C_A = C_{Ao} (1 - X)$$

$$C_B = C_{Bo} (1 - X)$$

If we combine the above equations, we see that

$$\frac{dC_A}{dt} = r_A = -kC_{Ao}^2 (1 - X)^2$$

But

$$\frac{dC_A}{dt} = -C_{Ao} \frac{dX}{dt}$$

Therefore

$$\frac{dX}{dt} = kC_{Ao} (1 - X)^2$$

If we integrate both sides

$$\int_0^X \frac{dX}{(1 - X)^2} = kC_{Ao} \int_0^t dt$$

we see that

$$\frac{X}{1 - X} = kC_{Ao} t$$

(1)



Conductivity Measurements

The conductivity probe produces a voltage which is related to the concentration of ions in the solution.

$$V_t = K \sum_i C_i \ell_i$$

where: V_t = voltage at time t

C_i = concentration of species i , gmol/l

ℓ_i = conductance of species i , mho*cm²/gmol

K = proportionality constant

There are three ions present in this system: OH^- , CH_3COO^- , and Na^+ .

$$C_{\text{OH}^-} = C_B = C_{A_0} (1 - X)$$

$$C_{\text{CH}_3\text{COO}^-} + C_C = C_{A_0} X$$

$$C_{\text{Na}^+} = C_B + C_C = C_{A_0}$$

Therefore, the total voltage read by the probe is

$$V_t = K \left[C_{A_0} (1 - X) \ell_{\text{OH}^-} + C_{A_0} X \ell_{\text{CH}_3\text{COO}^-} + C_{A_0} \ell_{\text{Na}^+} \right]$$

$$V_t = K C_{A_0} \left[(1 - X) \ell_{\text{OH}^-} + X \ell_{\text{CH}_3\text{COO}^-} + \ell_{\text{Na}^+} \right]$$

At the start of the experiment, $X = 0$ and let $V_t = V_o$.

$$V_o = K C_{A_0} \left[\ell_{\text{OH}^-} + \ell_{\text{Na}^+} \right]$$

At the point where conversion is complete, $X = 1$, and let $V_t = V_c$.

$$V_c = K C_{A_0} \left[\ell_{\text{CH}_3\text{COO}^-} + \ell_{\text{Na}^+} \right]$$

Thus, at any time

$$V_o - V_t = K C_{A_0} \left[X \ell_{\text{OH}^-} - X \ell_{\text{CH}_3\text{COO}^-} \right] = K C_{A_0} X \left[\ell_{\text{OH}^-} - \ell_{\text{CH}_3\text{COO}^-} \right]$$



In addition

$$V_o - V_c = KC_{Ao} \left[\ell_{OH^-} - \ell_{CH_3COO^-} \right]$$

Therefore, at any time t:

$$\frac{V_o - V_t}{V_o - V_c} = X = \frac{C_{Ao} - C_A}{C_{Ao}}$$

(2)

If we substitute Equation (2) into Equation (1), we get

$$\frac{V_o - V_t}{V_t - V_c} = C_{Ao}kt$$

and

$$V_t = (V_o - V_c) \frac{1}{C_{Ao}kt} + V_c$$

(3)

Therefore, a plot of V_t against $(V_o - V_t)/t$ will give a straight line with a slope of $1/kC_{Ao}$. From this slope a value can be determined for the reaction rate constant.

Experimental Procedure

(A) **Batch Reactor** (Do this experiment last, but keep enough feed solution in pails.)

In this section the conversion in a batch reactor is to be determined as a function of time. A suggested procedure is outlined below.

- 1) Drain about 1.5 to 2 gallons of each reagent from the tanks and store in plastic pails provided. Weigh out equal volumes of solution so that volume ratios are preserved.
- 2) Connect the dip-type conductivity cell to the meter.
- 3) Pour the sodium hydroxide solution into the reactor.
- 4) **Start stirrer**



- 5) Pour ethyl acetate solution into the reactor and start stop watch.
- 6) Insert dip cell.
- 7) Record output (voltage) of the meter at 15-second intervals during the first few minutes and at longer time intervals during the next half hour or so. Record the final value of the voltage the following morning. At this time the reaction should be complete.
- 8) Drain the reactor contents and clean the vessel.

(B) CSTR's

In this experiment the conversion in a CSTR system is compared to the conversion in a batch reactor. Two 180-liter tanks of prepared solution should be ready for you in the laboratory. The concentration of NaOH is approximately 0.08N while ethylacetate is approximately at 0.072N. The reagents are to be reacted at equal volumetric flows.

Procedure

- 1) Start Pumps, set rotameter reading at 70 and record the conductivity as a function of time in the 2nd CSTR. When steady state is reached, record the conductivity in each of the CSTR's.
- 2) Change the flow rate from 70 to 50 on the rotameter, record the change in conductivity as a function of time in the 2nd CSTR and determine steady-state conductivities in the two reactors. Observe volume changes in the reactors.
- 3) Repeat procedure 2) for the flow rate of 10 on the rotameters.
- 4) Record temperature of the solution before and after the reaction is completed.

(C) Tubular Reactor

Two 180-litre tanks of prepared solution should be ready for you in the laboratory. The approximate concentration of NaOH is 0.08N while ethyl acetate is 0.072N. The reagents are to be reacted at equal volumetric flows.

Experimental Procedure

- 1) Open valves at the base of the supply tanks.
- 2) Turn on the pumps and adjust the flow rate so that the floats of both rotameters are at 50.



- 3) After 2-3 residence times record flow rate, conductivity and temperature. Calibration curves for rotameters are available in the lab.
- 4) Repeat Step 3 for a few other rotameter readings. Do not wait too long between runs or you may run out of reagent.
- 5) Record temperature of the solution at the outlet of the reactor.
- 6) When tanks are empty, shut off pumps, close valves at the base of the tanks and fill both tanks with tap water.

(D) Observation of Flow Pattern in a Tubular Reactor

- 1) Open valves at the base of the tanks and start pumps. Set flow rates at rotameter reading of 50.
- 2) Inject about 10 mL of concentrated KMnO_4 solution at the entrance 'T' of the reactor. Estimate the length of the colored region at the entrance, middle, and exit of the reactor.
- 3) Repeat step (2) for rotameter readings 10 and 100 and qualitatively compare the lengths of the colored region to the length in step (2).

Report

- 1) The report should include a comparison of the conversion in a batch reactor with the conversion in the CSTR's (or tubular reactor) for the same reaction time.
- 2) Determine the rate constants from results for the batch reactor and check to see if this rate constant predicts the steady state conversion in the CSTR's or tubular reactor.
- 3) Formulate a model for the system of two CSTR's (or tubular reactor) which should describe the change in concentration due to changes in inlet flow rate.
- 4) Compare the experimental transient response with model prediction. Discuss the discrepancy, if any.
- 5) Comment on the differences in flow pattern that exist at various flowrates within the tubular reactor. Discuss how these various flow patterns could affect the assumption made about a PFR.

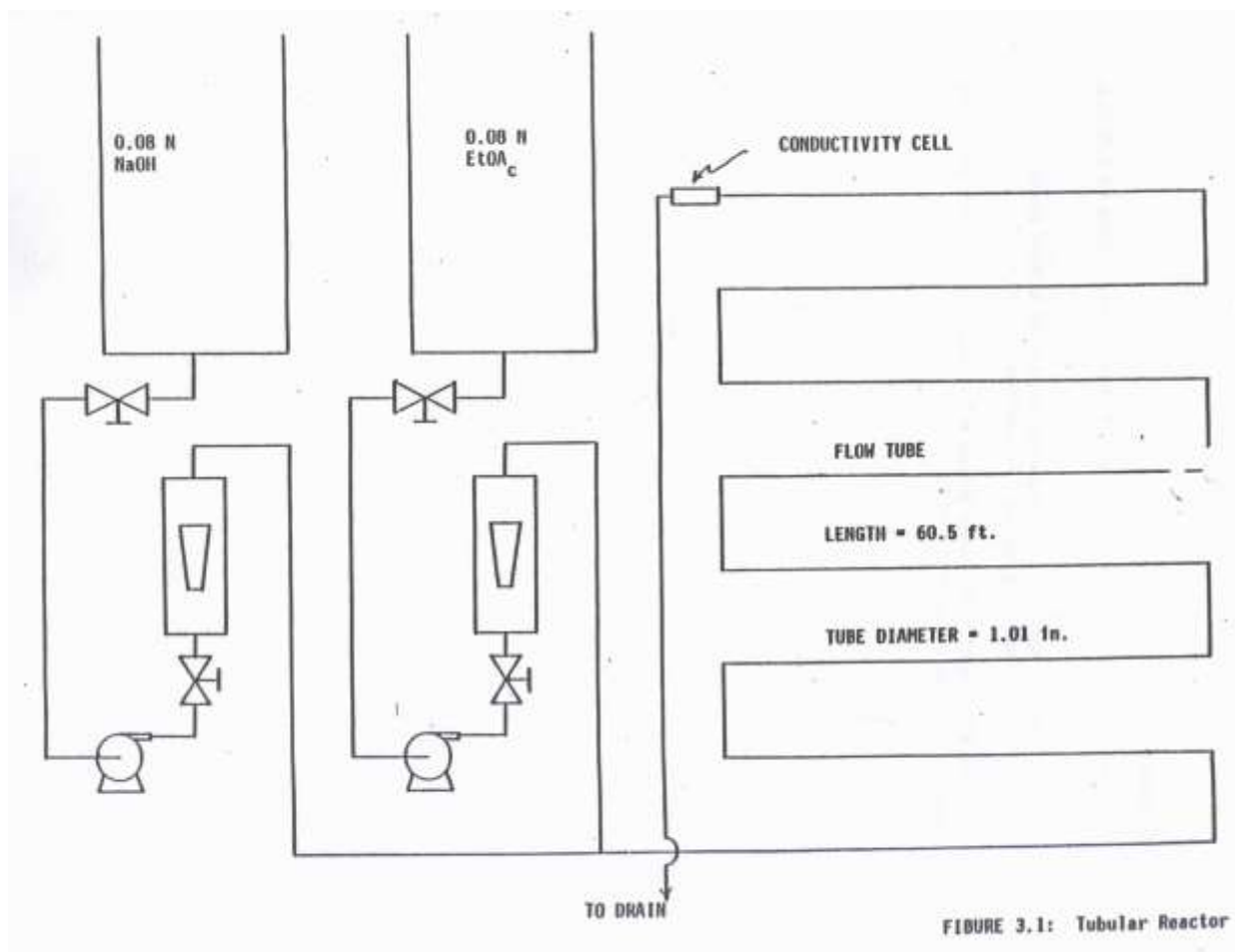


FIGURE 3.1: Tubular Reactor