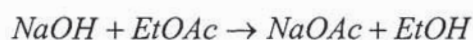# Tubular Flow Reactor

Tubular Flow Reactor

Objectives
- We wish to determine the conversion factor for different sets of conditions
- The variation of conversion with respect of residence time will be explored.
- We will also determine the reaction rate order and rate constant
- We will demonstrate the temperature dependence of the reaction and rate constant.

Introduction

The reaction we are going to use is the saponification of ethyl acetate (EtOAc) with sodium hydroxide (NaOH):

$$NaOH + EtOAc \rightarrow NaOAc + EtOH$$

Notice that the reaction is a one-to-one reaction so equimolar flow rates are going to be used in the following experiments.

The amount of excess NaOH left after the reactants have gone through the reactor can be used to determine the percent conversion and the reaction rate and order. The conversion can be calculated using the volumetric flowrates of the sodium hydroxide and the inlet and outlet concentrations:

$$X = \frac{moles\_NaOH\_in - moles\_NaOH\_out}{moles\_NaOH\_in} * 100 \tag{1}$$

$$X = \frac{F_{in}^{NaOH} * C_{initial}^{NaOH} - F_{out}^{Total} * C_{outlet}^{NaOH}}{F_{in}^{NaOH} * C_{initial}^{NaOH}} * 100 \tag{2}$$

where F denotes the flowrate and C is the concentration.

A mass balance for NaOH for the reactor gives us the equation below

$$\int_{C_{outlet}^{NaOH}}^{C_{inlet}^{NaOH}} \frac{dC_{NaOH}}{r_{NaOH}} = \frac{AL}{F_{Total}} = \tau \tag{3}$$

where r_{NaOH} is the reaction rate of NaOH, A is the cross-sectional area of the tubular flow reactor and L is the total length of the reactor. F_{Total} is the total volumetric flowrate and τ is the residence time. Assuming the reaction is second-order then the reaction rate is given by:

$$r_{NaOH} = kC_{NaOH}C_{EtOAc} \tag{4}$$

where k is the kinetic rate constant (=constant at constant temperature). Since we have equimolar flowrates and equal concentrations of NaOH and EtOAc then the rate can be given by:

$$r_{NaOH} = kC_{NaOH}^2 \qquad (5)$$

Substituting equation 5 into equation 3 and integrating gives:

$$\frac{1}{C_{outlet}^{NaOH}} - \frac{1}{C_{inlet}^{NaOH}} = k\tau \qquad (6)$$

Substituting equation 2 into equation 6 and rearranging gives:

$$k\tau C_{inlet}^{NaOH} = \frac{X}{1-X} \qquad (7)$$

Plotting X/(1-X) vs. τ should give a line with a slope of kC_{inlet}^{NaOH}. Knowledge of the inlet NaOH concentration would yield the kinetic rate constant k. The value of k is strongly dependent on temperature. It can be written as an Arrhenius relationship:

$$k = Ae^{-\frac{E}{RT}} \qquad (8)$$

where A is a constant, E is the activation energy, R is the gas constant, and T is temperature in Kelvin. Taking the log of equation 8 gives us:

$$\log k = \log A - \frac{E}{RT} \qquad (9)$$

The activation energy, E, and constant A can be calculated from a plot of log k vs. 1/T. Another way to determine reaction order and reaction rate constant is to determine the change in concentration at regular time intervals. Taking the log of equation 5 gives:

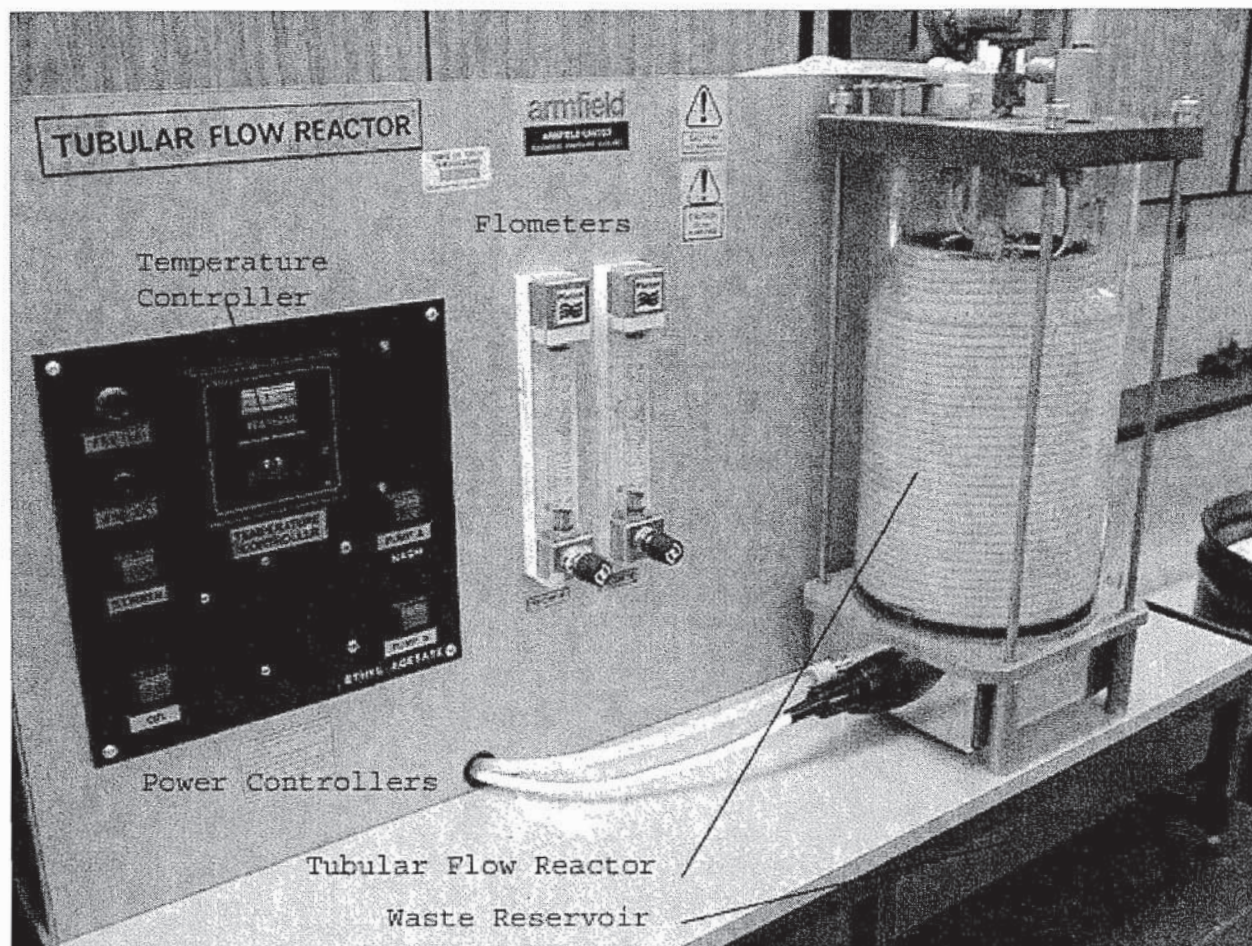$$\log \frac{dC_{NaOH}}{dt} = \log k + 2\log C_{NaOH} \qquad (10)$$

Assuming the order is unknown equation 10 becomes

$$\log \frac{dC_{NaOH}}{dt} = \log k + n\log C_{NaOH} \qquad (11)$$

where n is the reaction order. When dC/dt is plotted against C on a logarithmic plot n can be extracted from the slope of the line and k can be determined after plugging in the reaction order to equation 11.

Equipment

Procedure

Materials Preparation
- To make 0.1 M NaOH dissolve 40g NaOH into 10 L of water. This can be done in the large fresh solution containers. To prepare just one liter for titration dissolve 4g NaOH into 1 L of water.
- To make 0.1M EtOAc dissolve 99 mL EtOAc into 10 L of water.
- To make 0.1 M HCl dissolve 100 mL of 1M HCl solution into 1 L of water.

Flow Meter Calibration
1. Fill the appropriate tank with the corresponding reactant. Tank A should be filled with NaOH and tank B with EtOAc.
2. Turn on pump A and the stirrer.
3. Adjust the valve on the flow meter for pump A to 50 cm3/min.
4. At the sample outlet use a graduated cylinder (or small beaker) and a stopwatch to measure the amount of time it takes to fill a certain volume. Divide the volume by the amount of time it takes to get the actual flow rate of the reactant.
5. Repeat these steps for flow rates of 100, 150, 200, and 250 cm3/min.
6. Make plots of actual (measured) flow rate vs. marked flow rate for both pump A and pump B.

> NOTE: Make sure the stirrer stays on throughout the calibration. Make sure each flow meter is calibrated separately.

Titration
1. After taking a sample measure out 10 mL of the sample and quench it with 10 mL of 0.1 M HCl. Any unreacted NaOH that was left in the sample is now neutralized and the solution is acidic.
2. Add 2-3 drops of phenolphthalein and a stir bar.
3. Titrate using 0.1 M NaOH. The amount of unreacted NaOH is calculated by subtracting the volume of NaOH used for titration by the amount of HCl used for quenching.

Experiment A – Effect of Residence Time on Conversion
1. Refill the feed tanks if necessary.
2. Set the temperature controller to 25 C and turn on the stirrer
3. Set each flow meter to 50 cm3/min (use your calibration plots). The idea here is to have equimolar flow rates.
4. Wait about 20 minutes for steady state and take a sample from the sample outlet.
5. If you have enough time take a sample every 2 minutes after to ensure that steady state has actually occurred.
6. Record the outlet temperature (thermometer on top of reactor).
7. Titrate the sample(s) as described above to determine the amount of unreacted NaOH.

8. Repeat the above steps with flow rates of 100, 150, 200, and 250 cm3/min. Keep in mind as flow rate increases the amount of time required to reach steady state decreases so you may not need to wait a full 20 minutes for steady state.

Experiment B – Effect of Temperature on Conversion
1. Refill the feed tanks if necessary.
2. Set the temperature controller to 25 C and turn on the stirrer
3. Set each flow meter to 100 cm3/min (use your calibration plots). The idea here is to have equimolar flow rates.
4. Wait about 20 minutes for steady state and take a sample from the sample outlet.
5. If you have enough time take a sample every 2 minutes after to ensure that steady state has actually occurred.
6. Record the outlet temperature (thermometer on top of reactor).
7. Titrate the sample(s) as described above to determine the amount of unreacted NaOH.
8. Repeat the above steps with temperature settings of 35, 45, and 55 C.

Experiment C – Determination of Reaction Order and Reaction Rate Constant
1. Using a stopwatch to keep track of time fill a 500 mL beaker with 150 mL of 0.1M NaOH and 150 mL of 0.1 M EtOAc. Immediately after mixing start keeping time. Use a stir bar to thoroughly mix the reaction.
2. Take 10 mL samples every 2 min. and titrate using the procedure above.
3. Continue taking samples until the reaction has reached steady state.
4. Record the ambient air temperature.

Data Analysis

Experiment A –
- Determine the conversion for each flow rate.
- Comment on the change of conversion with respect to residence time. Use charts, tables, etc.
- Calculate the kinetic rate constant k using equation 7

Experiment B –
- Determine the conversion for each temperature.
- Comment on the change of conversion with respect to changes in temperature. Use charts, tables, etc.
- Calculate the activation energy E using equation 9

Experiment C –
- Make a plot of the $\Delta C/\Delta t$ vs. C_{avg} and extract the reaction order using equation 11.
- Calculate the kinetic rate constant k from equation 11 and compare to the value calculated in previous experiments.