CONTINUOUS FLOW REACTORS

Introduction

A very important chemical engineering problem is the carrying out of chemical reactions under controlled conditions. Continuous processes may take place in continuous flow stirred tank (CSTR), where reactants are fed in at a controlled rate and reacted product is drawn off continuously. Or the reactants may be fed into a long tube (tubular reactor) and discharge product at the end.

If flow in the tubular reactor is very turbulent (however the turbulence may be induced) then there will be thorough mixing in the radial direction and all material leaving the tube will have had the same residence time. Which is to say that all portions of the effluent will have reacted to the same extent. This is called a plug flow reactor (PFR). However, if flow in the tubular reactor is laminar (and the reacting liquid is Newtonian in viscosity) then the liquid in the center of the stream will have had only half the average residence time, while material close to the wall will have had a very, very long residence time.

Thus it is seen that the degree of completion of a continuous reaction depends greatly on the physical circumstances under which the reaction takes place. The subject is complex, with many ramifications. The texts by Levenspiel (1972, 1989) and Aris (1962) are excellent sources of information. Also see journal articles by Havorka and Kendall (1960) and Leitman and Ziegler (1972).

In spite of the complexity, it is possible to study a simple reaction in the laboratory under each of the above three conditions. This experiment studies the reaction kinetics of the saponification of ethyl acetate in a CSTR, in a PFR, and in a laminar flow reactor.

The saponification reaction of ethyl acetate with sodium hydroxide can be represented by the following stoichiometric equation:

\[
\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_4\text{OH}
\]

A + B \rightarrow C + D

The reaction is found to be second order and practically irreversible. The rate expression is:

\[
r = k C_A C_B \text{ kmol}/(m^3\cdot s)
\]

(2a)

where

\[
k = k_e (\frac{E}{RT})
\]

(Arrhenius law expression)  

(3)

\[
k_e = 18.6 \times 10^6 \text{ m}^3/(\text{kmol} \cdot \text{s})
\]

(4)

\[
E = 4.688 \times 10^4 \text{ J/mol}
\]

(5)

If the reactants are used in stoichiometric ratio then we have the special case \( C_A = C_B \).

For this case the design equation predicts:
A question for the student: What form do expressions (6) and (7) take when A and B are not used in stoichiometric ratio but rather \( \frac{C_{B}}{C_{A}} = M \neq 1 \)?

The equation for Newtonian laminar flow in a tubular reactor is given by Levenspiel (1989) as:

For CSTR:

\[
\frac{r}{kC_{A}^{2}} = \frac{C_{A}/v}{(1-x_{A})^{2}}
\]

For a PFR:

\[
\frac{C_{A}/v}{(1-x_{A})}
\]

For an LFR:

\[
\frac{C_{A}}{C_{A_{o}}} = \left[ \frac{kC_{A_{o}}}{V} \ln \left( \frac{2}{1+\frac{kC_{A_{o}}}{kC_{A_{o}}/v}} \right) \right] \]

where \( C_{A}, C_{A_{o}} \): molar feed conc. reactants A and B, kmol/m³

\( k \): reaction rate constant, m³/kmol.s

\( V \): reactor volume, m³

\( \eta \): total volumetric flow rate @ reactor entrance, m³/s

\( x_{A} \): fractional conversion of reactant A, dimensionless
**Theoretical Background**

- **Continuous Flow Reactors (Levenspiel's OmniBook, 1989)**

  \[-r_A = -\frac{1}{V} \frac{dNA}{dt} = \frac{\text{(amount of } A \text{ disappearing)}}{\text{(volume)(time)}} \left( \frac{\text{mol}}{m^3 \cdot s} \right)\]

  \[-r_A = f \left[ \frac{\text{temperature}}{\text{dependent terms}}, \frac{\text{concentration}}{\text{dependent terms}} \right] = \frac{k}{\text{rate constant}} \frac{C_A^a}{\text{(mol)}}^{\text{s}^{-1}} \]

  \[k = \frac{k_o e^{-E/RT}}{k \text{ is temperature dependent term}}\]

  where \( a \) is the reaction order

- **How does the temperature affect the rate?**

  This dependency is often well fitted by an Arrhenius law expression

  \[k = k_o e^{-E/RT}\]

  \[-E = \text{activation energy} \left( \frac{J}{\text{mol}} \right)\]

  \[R : \text{Gas Constant} = 8.314 \left( \frac{J}{\text{mol.k}} \right) = 8.314 \left( \frac{\text{Pa.m}^3}{\text{mol.k}} \right) = 1.987 \left( \frac{\text{cal}}{\text{mol.k}} \right) \ldots \text{etc.}\]
- Steady State Plug Flow Reactor

\[
\begin{align*}
C_{A_0} & \quad \rightarrow \quad F_{A_0} \\
F_{A_0} & \quad X_{A_0} = 0 \\
v_o & \\
F_{A_v} &= \frac{\text{moles } A \text{ fed}}{\text{hr}} \\
v_o &= \frac{m^3 \text{ fluid entering}}{\text{hr}} \\
C_{A_v} &= \text{concentration of } A \\
&\quad \text{in feed stream}
\end{align*}
\]

**Plug flow:**
- Fluid passes through the reactor with no mixing of earlier and later entering fluid
- Composition changes progressively through the reactor
- Fluid flows with a flat velocity profile, in single file, with no overtaking

\[
\begin{align*}
&v_o \cdot C_{A_v} \\
\ln \quad - \quad \text{out} = Accumulation + Disappearance by reaction
\end{align*}
\]

\[
\begin{align*}
&\uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
&F_{A_{in}} \quad F_{A_{out}} \quad 0 \text{ for steady state} \quad (-r_A)dV
\end{align*}
\]

\[
F_{A_v}(1-x_A)
\]

Thus at any point in the reactor

for any \( \varepsilon_A \) value \( F_{A_v} \cdot dx_a = (-r_A)dV \)

for any \( \varepsilon_A = 0 \) \( -dC_A = (-r_A)d\tau \)

\( \varepsilon_a \) is the fraction of the volume that changes with conversion.

\( \varepsilon_a=0 \) means the volume of the reacted elements does not change with conversion

\( \varepsilon_a \neq 0 \) \( \varepsilon_a = (V_{A_{\text{reacted}}}-V_{\text{no reaction}})/V_{\text{no reaction}} \)
\[
\frac{V}{F_{A_0}} = \int_{0}^{x_{A_f}} \frac{dx_A}{-r_A}
\]

\[
\varepsilon_A = 0
\]

\[
\tau = \frac{C_A v}{F_{A_0} v_o} = \frac{1}{-r_A} \int_{0}^{x_{A_f}} \frac{dC_A}{-r_A}
\]

\[
F_A = F_{A_0} (1 - x_A), \quad F_{A_0} = v_o C_A
\]

\[
x_A = 1 - \frac{C_A}{C_{A_0}}
\]

\[
\frac{C_A}{C_{A_0}} = 1 - x_A
\]

\[
\tau = \text{time needed to treat, one reactor volume of feed stream}
\]

\[
\text{the space time, the capacity measure for the reactor}
\]

\[
\frac{V}{v_o} = \frac{C_A v}{F_{A_0}} = \tau, \quad (hr)
\]

\[
\frac{1}{\tau} = s \left( hr^{-1} \right) \text{space velocity}
\]

\[
\text{number of reactor volumes of feed at specified conditions which can be treated in unit time}
\]

\[
\bar{t} = \text{mean residence time of fluid in the reactor} \quad (hr)
\]

\[
\text{for constant density systems (all liquids and some gases) } \bar{t} = \tau = \frac{V}{v_o}
\]

\[
\text{for changing density systems } \bar{t} \neq \tau, \bar{t} \neq V/v_o, \text{ and it is difficult to find how these two times are related (i.e. Space time } \left( \frac{V}{v_o} \right) \text{ relies on the entrance flow rate } (v_o),
\]
while residence time $(\bar{t})$ relies on the actual flow rate inside the reactor. If this changes compared to the entrance flowrate then $\bar{t} \neq \tau$, otherwise $\bar{t} = \tau$.

**Plug Flow:**

\[
\begin{align*}
F_A &= (F_A + dF_A) + (-r_A)dV \\
dF_A &= d(F_{A_0}(1-x_A)) = -F_{A_0}dx_A \\
o &= -F_{A_0}dx_A + (-r_A)dV \\
F_{A_0}dx_A &= (-r_A)dV \\
\int dV &= \int_x^{-x_A} dx_A \\
F_{A_0} &= \int_o^{-r_A} dx_A \\
V &= x_A \left( \frac{dx_A}{F_{A_0}} \right) \\
F_A &= C_{A_0}v_o \\
v_o &= \frac{F_{A_0}}{CA_0} \\
V &= x_A \left( \frac{dx_A}{C_{A_0}v_o} \right) \\
\tau &= C_{A_0} \int_o^{-r_A} dx_A \\
Zero order reaction & \quad -r_A = k \\
k\tau &= k \frac{V}{V_o} k \left( \frac{C_{A_0}V}{F_{A_0}} \right) = C_{A_0}x_A \\
1st order reaction & \quad -r_A = kC_A \\
k\tau &= ln \left( \frac{1}{1-x_A} \right) = ln \left( \frac{C_{A_0}}{C_A} \right) \\
2nd order reaction & \quad 2A \rightarrow .... -r_A = kC_A^2
\end{align*}
\]
For $\varepsilon_A = 0$

Zero order reaction \[ A \rightarrow ... - r_A = k \]

\[ k \tau = C_{A_0} - C_A \]

\[ k \tau = \frac{C_{A_0} - C_A}{C_{A_0}} = x_A \]

1st order reaction \[ A \rightarrow ... - r_A = kC_A \]

\[ k \tau = \frac{x_A}{1 - x_A} \]

\[ k \tau = \frac{C_{A_0} - C_A}{C_A} \Rightarrow \frac{C_A}{C_{A_0}} = \frac{1}{1 + k \tau} \]

2nd order reaction \[ A + B \rightarrow ... - r_A = kC_A C_B, C_{A_0} = C_{B_0} \text{ or } - r_A = kC_A^2 \]

\[ k \tau \frac{C_{A_0}}{C_A} = \frac{x_A}{(1 - x_A)^2}, \tau = \frac{V}{v_o} \]

\[ k \tau = \frac{C_{A_0} - C_A}{v_o} = \left( \frac{x_A}{(1 - x_A)^2} \right)^2 \]

\[ k \tau = \frac{C_{A_0} - C_A}{C_A^2} \Rightarrow k \tau C_{A_0} = \left( \frac{C_{A_0}}{C_A} \right)^2 - \frac{C_{A_0}}{C_A} \]

\[ \frac{C_{A_0}}{C_A} \]

\[ \text{slope} = k \]
Comments:

For more information, see attached papers in the reading materials section (Levenspiel's OmniBook, 1989).

- **Newtonian Laminar Flow in a Tubular Reactor (Levenspiel’s, OmniBook 1989)**

  When a vessel is long enough then the dispersion or tanks.in.series model well describes its flow behavior.

  - If the tube is long enough then molecular diffusion in the lateral direction will have enough time to distort the parabolic velocity profile so that the "dispersion model" applies.

  - If the tube is short enough and the flow rate is high then molecular diffusion does not have enough time to act so all we need to consider as causing a spread in residence time of fluid is the velocity profile. We are in the "pure convection" regime.

  - If the flow is so slow that the main movement of fluid is by molecular diffusion, not by bulk flow, then we enter the "pure diffusion" regime. We rarely meet this situation in real practice.

RTD Curves typical of these regimes:

\[
\theta = \frac{t}{\tau} = \frac{1}{V} \frac{1}{u},
\]

In the pure convection regime (negligible molecular diffusion) each element of fluid follows its own streamline with no intermixing with neighboring elements. In essence this gives macrofluid behavior even though you may have a microfluid.

For a macrofluid, any RTD and any kinetics, the conversion expression is then (Levenspiel, 1989, Ch. 61 and 68):

![Diagram](image-url)
\[
\frac{C_A}{C_{A_0}} = \int_0^t \left( \frac{C_A}{C_{A_0}} \right)_e \cdot E_i \, dt
\]

for zero order reaction: \(\frac{C_A}{C_{A_0}} = 1 - \frac{kt}{C_{A_0}}\) for \(t \leq \frac{C_{A_0}}{k}\)

for first order reaction: \(\frac{C_A}{C_{A_0}} = e^{-kt}\)

for second order reaction: \(\frac{C_A}{C_{A_0}} = \frac{1}{1 + kC_{A_0}t}\)

For zero order reaction of a Newtonian in a pipe integration gives:

\[
\frac{C_A}{C_{A_0}} = \left(1 - \frac{k\bar{t}}{2C_{A_0}}\right)^2
\]

For first order reaction of a Newtonian in a pipe:

\[
\frac{C_A}{C_{A_0}} = \frac{\bar{t}^2}{2} \int_{\bar{t}/2}^{\bar{t}} e^{-\tau} \, d\tau \quad \text{...this requires numerical integration}
\]

For a second order reaction of a Newtonian in a pipe:

\[
\frac{C_A}{C_{A_0}} = 1 - kC_{A_0} \bar{t} \left[1 - \frac{kC_{A_0} \bar{t}}{2} \ln \left(1 + \frac{2}{kC_{A_0} \bar{t}}\right)\right]
\]

For other kinetics, channel shapes or types of fluids insert the proper terms in the general performance expression and integrate.

For more information see Levenspiel's OmniBook (1989) - Chapters 61 and 68.

- **Criterion for Steady State**
  - For PFR and laminar tubular reactors
    - Steady State reaches after about \(\tau (\text{or } \bar{t})\). Therefore each change in flow rate, wait \(2\tau\) before start collecting samples.
  - For CSTR, Perform linearization to identify the duration required for steady state.

This will be performed by the linearized approximation of the nonlinear dynamic system expressed in terms of the deviation variable (i.e. concentration at any time - concentration at steady state, \( c' \)).
- **One Variable**

unsteady state (dynamic mode)

\[
\frac{dx}{dt} = f(x)
\]

(1)

linearize \( f(x) \) by Taylor series about \( x_s \),

\[
\frac{dx}{dt} = f(x_s) + \frac{df}{dx}igr|_{x_s} (x - x_s)
\]

steady state mode

\[
\frac{dx_s}{dt} = 0 = f(x_s)
\]

(2)

By taking deviation from the steady state (subtract eq. 2 from 1)

\[
\frac{d(x - x_s)}{dt} = f(x_s) - f(x_s) + \frac{df}{dx}igr|_{x_s} (x - x_s)
\]

\[
\frac{d(x - x_s)}{dt} = \frac{df}{dx}igr|_{x_s} (x - x_s)
\]

By considering \( x - x_s = x' \)

\[
\frac{dx'}{dt} = \frac{df}{dx}igr|_{x_s} x'
\]

\[
f'(x) = f(x) - f(x_s) - \frac{df}{dx}igr|_{x_s} x'
\]

- **Two Variables**

unsteady state (dynamic model)

\[
\frac{dx}{dt} = f(x, y)
\]

\[
\frac{dx}{dt} = f(x_s, y_s) + \frac{\partial f}{\partial x}igr|_{x_s, y_s} (x - x_s) + \frac{\partial f}{\partial y}igr|_{x_s, y_s} (y - y_s)
\]

\[
f(x, y)
\]
steady state

\[ \frac{dx}{dt} = 0 = f(x, y) \]

By subtracting eq 2 from 1

\[ \frac{d(x-x_0)}{dt} = f(x, y) - f(x_0, y_0) = \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt} \]

\[ \frac{dx}{dt} = \frac{\partial f}{\partial x} \]

\[ \frac{dy}{dt} = \frac{\partial f}{\partial y} \]
**Linearization of CSTR dynamic equation with 2nd order reaction**

The following steps should be taken to linearize CSTR and to obtain the required time for steady state:

1. **Unsteady state model (Mass Balance) for CSTR**

   \[
   \frac{dC}{dt} = \nu_o (C_o - C) - V_k C^2
   \]

   where, \( C_o \) is the inlet concentration, \( C \) is the outlet concentration and \( \nu_o \) is volumetric flow rate.

   When \( \nu_o \) changes, \( C \) changes, therefore the term \( \nu_o (C_o - C) \) is nonlinear besides \( V_k C^2 \).

2. **For term \( \nu_o (C_o - C) \) using two variables linearization expressed in variable deviation (i.e., \( \nu'_o, C' \)).**

   For example:

   \[
   \nu_o (C_o - C) = \nu_o (C_o - C)|_{\nu_o, C} + \left. \frac{\partial (\nu_o (C_o - C))}{\partial \nu_o} \right|_{\nu_o, C} \nu'_o + \left. \frac{\partial (\nu_o (C_o - C))}{\partial C} \right|_{\nu_o, C} C'
   \]

3. **For the term \( V_k C^2 \) use one variable linearization expressed in variable deviation (i.e. \( C' \)).**

   \[
   f(C) = V_k C^2 = V_k C^2|_{C} + 2 V_k C|_{C} C'
   \]

4. **Substitute equations (2) and (3) into equation (1).**
\[ V \frac{dC}{dt} = v_o (C_o - C) + (C_o - C) \cdot v_o\dot{v} - v_o | C' - V k C^2 | - 2 V k C | C' \]  \hspace{1cm} (4)

5. Write steady state model (mass balance) for CSTR.

\[ V \frac{dC}{dt} = v_o (C_o - C) - V k C^2 = 0 \] \hspace{1cm} (5)

6. Subtract equation (5) from equation (4).

\[ V \frac{dC}{dt} = (C_o - C) v_o\dot{v} - v_o | C' - 2 V k C | C' \] \hspace{1cm} (6)

\[ V \frac{dC}{dt} = C' (v_o | C_o - 2 V k C | + v_o' (C_o - C) \] \hspace{1cm} (7)

7. Take laplace transform for the equation obtained in step 6 (i.e. equation (6)).

\[ V_s C'(s) = C'(s) [v_o | C_o - 2 V k C | + v_o' (C_o - C) \] \hspace{1cm} (8)

8. Find the transfer function from step (7) \( G(s) \). Transfer function is the output \( C'(s) \) over the input \( v_o'(s) \).

\[ G(s) = \frac{C'(s)}{v_o'} = \frac{(C_o - C)}{V s + v_o | C_o + 2 V k C} \] \hspace{1cm} (9)

9. Rewrite the transfer function in the following form:

\[ G(s) = \frac{k}{\tau p \cdot s + k} \] \hspace{1cm} (9)
\[ C_{i_s} \text{ is the outlet concentration at the steady state} \]

Identify \( k \) and \( \tau_p \)

\[
k = \frac{(C_o - C_{i_s})}{v_{o_{i_s}} + 2VkC_{i_s}}
\]

\[
\tau_p = \frac{V}{v_{o_{i_s}} + 2VkC_{i_s}}
\]

10. Take inverse laplace of the output.

\[
v'_o(s) = \frac{\Delta v_o}{s} \Rightarrow \Delta v_o = \text{change in } v_o
\]

\[
C'(s) = \frac{\Delta v_o}{s} \frac{k}{\tau_p s + 1}
\]

\[
C'(t) = k\Delta v_o \left[1 - e^{-\frac{t}{\tau_p}}\right]
\]

\[
C'(t) = \Delta C(t) = k\Delta v_o \left[1 - e^{-\frac{t}{\tau_p}}\right]
\]

\[
\Delta C(t) = \frac{C_o - C_{i_s}}{v_{o_{i_s}} + 2kVC_{i_s}} \Delta v_o
\]

For a step change (i.e. changing flow rate from its steady state to a new flow rate).

\[
\Delta C(\text{att}=\infty) = \frac{C_o - C_{i_s}}{v_{o_{i_s}} + 2kVC_{i_s}} \Delta v_o
\]
11. Estimate the time required for steady state in terms of $\tau_p$. Consider the steady state is when the concentration reaches about 95% of the concentration obtained at $t = \infty$.

i.e. $\Delta C$ (at $t = \text{time required for new steady state}) = 0.95 \times \Delta C (at \ t = \infty)$

Then $t$ can be calculated to achieve this

$$0.95 \left( \frac{C_o - C|_s}{v_o|_s + 2kVC|_s} \right) \Delta v_o = \frac{C_o - C|_s}{v_o|_s + 2kVC|_s} \Delta v_o \left[1 - e^{-\frac{t}{\tau_p}} \right]$$

$$e^{-\frac{t}{\tau_p}} = 0.05$$

$$-\frac{t}{\tau_p} = -3$$

$$\therefore \quad t = 3\tau_p = \frac{V}{v_o|_s + 2kVC|_s}$$

Accordingly, you should wait $5\tau_p$ before you start taking samples to ensure the steady state to a certain extent.

**Equipment Description**

The apparatus for this experiment is schematically represented in Figure 1. The reactants are a solution of ester and a solution of sodium hydroxide. Each reactant has a tank, a small centrifugal pump to transfer it to the reaction apparatus, a flow control valve, a rotameter to indicate the flow rate and a tempering coil to bring the solution to the temperature of the system.

Flow of the reactants can be directed, by means of valves V1 and V2, either to the CSTR (Continuous Stirred Tank Reactor) or to the tubular reactors.

When flow is directed to the tubular reactors the two reactant streams come together at a tee and flow through a small static mixer where they become thoroughly mixed. (See Middleman (1973) for an explanation of the functioning of a static mixer). From there they can flow either through TBR1 or TBR2. Valve V3 controls this choice.

Both TBR1 and TBR2 are tubular reactors, and both have approximately the same contained volume. The difference is that TBR1 contains a static mixer, so that the flow through it is essentially plug flow. TBR1 may be considered a PFR (Plug Flow Reactor). TBR2 is not a PFR, it is a plain tube, and flow through it is streamline laminar. Thus the product from TBR2 is a mixture which has had a range of residence times.
Product from TBR1 can be directed by means of valve V4 either to Sample Port #1, or to the CSTR. Product from TBR2 exits through Sample Port #2, and product from the CSTR exits through Sample Port #3.

The entire apparatus, from the tempering coils to the sample ports, is immersed in a water bath with an automatic temperature controller. The operating temperature for the experiment will have been set by the laboratory technician, since it takes several hours for the apparatus to come to uniform steady state temperature.

- **Dimensions**

  - **TBR 1** contained volume = 358 cm$^3$
  - **TBR 2** contained volume = 305 cm$^3$ (TBR2 has an I.D. of 0.635 cm)
  - **CSTR** contained volume = 945 cm$^3$ (Note that the actual liquid volume is somewhat different than this. The actual liquid volume should be measured by one of the following: shutting off the inflow and outflow simultaneously, then measuring the actual volume of liquid that was present during operation). Then the liquid in the CSTR is drained.  
  The volume of the liquid in the CSTR is equal to the total volume drained (collected) minus the volume of the liquid in the pipe between the reactor and the liquid outlet. This volume can be estimated based on the pipe length and its inner diameter. Filling the reactor with water (or solution) before or after the experiment, the level of the liquid should be about the same as that during the normal operation. Then the liquid is drained to estimate its volume as above.

**Operation and Measurements**

An ester such as methyl acetate, ethyl acetate, ethyl propionate, or propyl acetate will be saponified. The material will be specified by the Teaching Assistant.

Prepare approximately 6 gallons of 0.2 molar NaOH solution by dissolving an appropriate amount of NaOH pellets in deionized water. Recirculate the flow thoroughly to mix the solution well. When you come to the lab you need to determine the exact concentration of NaOH. Use the 1.0N HCl standard and titrate the NaOH to a phenolphthalein endpoint to determine the exact concentration of the NaOH solution.

Prepare approximately 6 gallons of 0.2 molar ester (whatever is assigned by the T/A, but commonly ethyl acetate) solution by diluting the required volume of pure ester with deionized water.

Place the feed tanks under or beside the water bath and hook up the feed pumps. In order to operate the tubular reactor No. 1, turn valves V1 and V2 to the TBR mode. Turn valve
V3 to position TBR 1. Turn valve V4 to the sample position. Attach the drain hose to sample port #1 and turn on the feed pump. In a similar manner, by positioning the valves properly one can operate tubular reactor No. 2, the CSTR, or the TBR 1 + CSTR series combination.

Adjust the flow rotameters according to the calibration curves (Figures 2 and 3) to give equimolar concentrations for the total flow rate desired for the run being made. You will need to take data for five different total flow rates, for a combined flow of 0.05 liters/minute to 0.50 liters/minute, for each of the three reactors, CSTR, TBR 1, and TBR 2. For example, set both streams to a flow of 0.025 liters/minute for a total flow of 0.05 liters/minute. At some flow rates repeat the sampling procedure and conversion determination several times to determine the reproducibility of your results.

**Note:** Run with the bypass valves closed only enough to obtain the desired flow rate.

- **Analytical Procedure**

  The reaction between ester and NaOH is a homogeneous reaction. Therefore, to measure the conversion at each reactor outlet you must quench the reaction immediately. This can be done by 1.0N HCl. Hence, pipette exactly 5.0 ml of 1.0 N HCl into a 50 ml Erlenmeyer flask and weigh it. (Record the weight). Hold the flask under the sample port from the reactor being sampled and collect about 25 ml of effluent. Swirl the two solutions together to mix them. The acid quenches the saponification reaction. Weigh the combined solutions. (Record the Weight). Add two drops of phenolphthalein indicator solution and titrate immediately with NaOH solution. The NaOH feed solution you have measured its normality, is used for this titration. Prior to this step fill the buret with NaOH. With solutions this dilute you may assume that the effluent has the same density as water at that temperature. Alternatively, instead of phenolphthalein, you may use a pH meter (if one is available) and titrate to an end point of 9.0. Based on the titration results, calculate the conversion as follows.

- **Preparation Outline**

  \[
  \text{normality} = \frac{\text{eq. solute}}{\text{lit solution}} = \text{molarity} \left( \frac{\text{mole solute}}{\text{lit solution}} \right) \times n \left( \frac{\text{eq. solute}}{\text{mole solute}} \right)
  \]

  \[n = 1\] for NaOH, HCl and CH₃COOH See the reading materials

  + Preparation of 6 gallon of 0.2N NaOH or 0.2 molarity NaOH (since \(n = 1\)) this step is prepared by the lab technician before you come to lab. However, you must measure the normality of the prepared solution before you run the experiment.

  \[22.712 \text{ lit } \times \ 0.2 \ N \Rightarrow \text{mole of solute}\]
mole of solute × M_{wt} (40) = weight of solute required.
Mix the weight of solute with deionized water and stir.

- **Determination of the exact N of NaOH:**
  (This you must do before the experiment)
  - Pipette exactly 5 ml of (0.1N or 1.0N HCl) into a 50 ml Flask
  - Add drop of phenolphthalein
  - Fill the buret with the NaOH and titrate to the color change endpoint

\[
(N_1V_1)_{\text{HCl}} = (N_2V_2)_{\text{NaOH}}
\]

This gives Normality (or Molarity) of the NaOH solution prepared.

+ Preparation of 6 gallon of 0.2N of ethyl acetate (liquid, \( \rho_l = 0.894 \text{ gm/ml} \)).
  This step is prepared buy the lab technician befr you come to the lab. However, you Must measure the normality of the prepared solution before you start the experiment.

\[
22.7 \times 0.2N \rightarrow \text{moles of equivalent solute} \rightarrow \text{moles of solute}
\]

Mole of solute × MWT(88) = weight of solute required (399.73)

The volume of liquid ethyl acetate contains

\[
(399.73 \text{ gm}) = \frac{399.73}{0.894 \text{ gm/mole}} = 447.13 \text{ ml} = 0.447 \text{ lit}
\]

Add 0.447 lit of ethyl acetate liquid to 22.265 lit of deionized water to get 0.2 N of ethyl acetate.

- **Conversion Measurement Outline**

This can be achieved by measuring the NaOH concentration at the outlet. Since the reaction is homogeneous and noncatalytic, we need to stop the reaction immediately at the outlet (quench). This can be done by using highly concentrated HCl (more than one samples are preferred).

- Pipette exactly 50 ml of 1.0 N HCl standard into 50 ml flask. Weigh it.

- Collect 25 ml sample from the effluent. The exact volume of the collected sample will be measured as follows: Swirl the two solutions together to mix them. HCl will react with all NaOH left in the sample (that is not reacted in the reactor). This means that the acid quenches the saponification reaction. Weigh the combined solutions.
Weight_{(flask + HCl + sample)} - Weight_{(flask + HCl)} = Weight_{(sample)}

Volume_{(sample)} = Weight_{(sample)} \rho_{water}

- Add two drops of phenolphthalein indicator

- Titrate immediately with NaOH (0.2 N in buret). NaOH will neutralize the remaining HCl (unreacted with NaOH in the sample)

\[
\left( N_1 V_1 \right)_{HCl} = \left( N_2' V_2 \right)_{NaOH}
\]

\[
\text{mole unreacted in the sample} = \frac{\left( N_1 V_1 \right)_{HCl}}{M_{HCl}} - \left( N_2 V_2 \right)_{NaOH}
\]

\[
= 1 \times 5 \times \frac{1}{1000} - \left( N_2 V_2 \right)_{NaOH} \times \frac{1}{1000}
\]

\[
\therefore \text{mole NaOH unreacted in the sample} = 1 \times 5 \times \frac{1}{1000} - \left( N_2 V_2 \right)_{NaOH} \times \frac{1}{1000}
\]

\[
C_{NaOH} = \frac{\text{mole NaOH unreacted in the reactor}}{\text{Sample volume drawn from the effluent}}
\]

\[
x_A = \frac{C_{A_s} - C_A}{C_{A_s}} = 1 - \frac{C_A}{C_{A_s}}
\]

Where Cao is the NaOH is the total volumetric flowrate entering the reactor. Hence, both the flow rates are equal when Cain = Ca(feed tank)/2

**Note:** \( C_{A_s} \) in the feed tank of NaOH is \( \sim 0.2 \text{ M (mol/lit)} \). Since we use the same volumetric flow rate for NaOH and ethyl acetate, this means that

\[
C_{A_s} = \frac{1}{2} 0.2 \text{ M} = 0.1 \text{ mol/lit}
\]

- Set the NaOH and ethyl acetate flowrate.

Using calibration curves set NaOH and ethyl acetate solutions at the same flow rates.

**Shut-down Procedure**

Empty the feed tanks and rinse them with water. Open valve VS and drain and rinse CSTR. Empty the receiving tank and rinse with water. Fill one of the feed tanks with
\[
\text{Weight}_{(\text{flask} + HCl + \text{sample})} - \text{Weight}_{(\text{flask} + HCl)} = \text{Weight}_{(\text{sample})}
\]
\[
\text{Volume}_{(\text{sample})} = \text{Weight}_{(\text{sample})} \rho_{\text{water}}
\]

- Add two drops of phenolphthalein indicator
- Titrate immediately with NaOH (0.2N in buret). NaOH will neutralize the remaining HCl (unreacted with NaOH in the sample)

\[
\frac{(N_1 V_1)_{HCl}}{\text{mole unreacted in the sample}} = (N_2 V_2)_{NaOH}
\]

\[
\text{mole of HCl reacted in the sample} = \text{mole NaOH unreacted in the reactor (MV)}
\]
\[
= (N_1 V_1)_{HCl, initial} - (N_2 V_2)_{NaOH}
\]
\[
= 1 \times 5 \text{ ml} \times \frac{1}{1000} - (N_2 V_2)_{NaOH} \frac{1}{1000} \text{ (mole)}
\]
\[
\therefore \text{mole NaOH unreacted in } = 1 \times 5 \times \frac{1}{1000} - (N_2 V_2)_{NaOH} \text{ buret} \times \frac{1}{1000}
\]

\[
C_{NaOH}^{(A)} = \frac{\text{mole NaOH unreacted in the reactor}}{\text{Sample volume drawn from the effluent}}
\]

\[
\chi_A = \frac{C_{A_b} - C_A}{C_{A_b}} = 1 - \frac{C_A}{C_{A_b}}
\]

Where \( C_a \) is the NaOH is the total volumetric flowrate entering the reactor. Hence, both the flow rates are equal when \( C_a = \frac{C_a}{\text{feed tank}}/2 \)

**Note:** \( C_{A_b} \) in the feed tank of NaOH is \( \sim 0.2 \text{ M (mol/lit)} \). Since we use the same volumetric flow rate for NaOH and ethyl acetate, this means that

\[
C_{A_b} = \frac{1}{2} \times 0.2 \text{ M} = 0.1 \text{ mol/lit}
\]

- Set the NaOH and ethyl acetate flow rate.

Using calibration curves set NaOH and ethyl acetate solutions at the same flow rates.

**Shut-down Procedure**

Empty the feed tanks and rinse them with water. Open valve V5 and drain and rinse CSTR. Empty the receiving tank and rinse with water. Fill one of the feed tanks with
water and pump it through all reactors and sample ports. Turn off feed tank and empty it. Clean analytical equipment. Turn off circuit breaker switch.
Assignment

For pre-lab proposal, provide a detailed flow diagram (P&ID – Process and Instrumentation Diagram) showing all the related components and instruments, correctly labeled (e.g. value types, pump types, etc.). DO NOT SIMPLY COPY THE ONES PROVIDED WHICH ARE USED IN THE MANUAL ONLY AS A GUIDELINE.

1. Estimate the time required for CSTR to reach steady state (i.e. 95% of the steady state that is reached at \( t = \infty \)).

2. Compare experimentally and theoretically the performance of CSTR, PFR and LFR. This can be done by plotting the conversion vs. space time; space time is equal to the residence time in this experiment.

   Hint:

   Experimental Comparison:

   Plot the measured conversion vs. space time for CSTR, PFR and LFR on the same graph.

   Theoretical Comparison:

   Plot the predicted conversion using the design equation and given \( k \) vs. space time for CSTR, PFR and LFR on the same graph.

3. Compare between the performance obtained experimentally and that obtained theoretically for each reactor.

   Hint:

   Plot the measured and predicted conversions vs. space time of CSTR on one graph. The same for PFR and LFR.

4. Discuss how the observed \( k^\frac{1}{2} \) vary from the \( k \) value given in the manual. Are there any differences? Why? If there are no significant differences, state why and how? Should there be any differences? Cite any references that support your discussion and claim. If you mention or discuss any theoretical trend you should refer to a proper reference.
Results and Data Analysis Outline

Present the direct and indirect results that represent the assignment in the form of equations, tables, values, and figures. Meanwhile, provide interpretations of the results (i.e. provide a thorough discussion of findings). The results should be discussed briefly and concisely in the light of uncertainties of measurements (i.e. identifying the sources and magnitude of the experimental errors, if any), statistical analysis experimental data, significance and meaningful of any calculated numbers, trend of the experimental data and models, etc. Cite any references that support your analysis and conclusion.

Data analysis may include, but is not limited to, the following discussion outline:

1. Discuss how reliable in the estimation of the time required for CSTR to reach steady state. How can you be sure experimentally that the time you set is enough to ensure steady state.

2. Discuss the differences between the performance of CSTR, PFR and LFR experimentally and theoretically. Explain why? Are the experimental results consistent with the theory. Explain.

3. Discuss the comparison between the performance obtained experimentally and theoretically for each reactor (i.e. CSTR, PFR and LFR). Report the mean relative error of the prediction of the design equation for each reactor. Are the experimental results consistent with the theory?

4. Estimate the observed $k$ (reaction rate constant) for each reactor by fitting the experimental data to the design equation. $k$ in the design equation is the fitted parameter. Compare the fitted $k_i$ with the given one used in assignments 2 and 3 above. Report the mean relative error.

Hint:
- For CSTR and PFR equations, linear regression is used
- For LFR nonlinear regression is required. This can be done as follows:
  1. Using nonlinear algorithm or subroutine from IMSL, NAG packages. Mathematica and MATLAB can also be used.
  2. The other approach can be outlined as follows:

Part 1: Solve the LFR as nonlinear equation for $k$ for each experimental data point

$$\frac{C_{A, t}}{C_{A, 0}} = 1 - k C_{A, 0} \left[ 1 - \frac{k C_{A, 0} t}{2} \ln \left( 1 + \frac{2}{k C_{A, 0} t} \right) \right]$$
Part 2:

- Take the average of $k_i$. This average value with the first guess for the second part.

- Manipulate the LFR equation as follows:

\[
\frac{C_A}{C_{A_0}} = \frac{kC_A}{C_{A_0}} \left(1 - \ln \left(1 - \frac{2}{kC_{A_0}} \right) \right)
\]

- Use the obtained average value of $k$ as first guess. Calculate $y$ and $x$, for all the experimental data points. 

- Check the slope of the best line. If it is 1 or close to 1 you find the fitted $k$. If not, choose new $k$ and repeat part 2. Do this until the slope of the fitted line between $y$ and $x$ become close to 1. This value of $k$ is the fitted one.

References


Middleman, S., "Fundamentals of Polymer Processing", New York, John Wiley and Sons (1973). Pages 327-335 have an excellent explanation of the mechanism by which the mixer is so effective.