Unsteady State Operation of Stirred Reactors

Startup of CSTRs
Semi-batch reactors

Two very common cases

FIRST

We want to determine the time necessary to reach steady-state operation for CSTRs

Predict concentration and conversion as a function of time

Analytical Solutions for zero and first order reactions

Must use ODE solver for n >1
Semi-batch reactors

a) Startup of CSTRs

b) Reactant B is slowly fed into reactor already containing reactant A. Used when highly exothermic, or unwanted side reactions occur at high concentrations of B.

  Gas fed (B) and bubbled thru reactant A
  e.g. chlorination and hydrolysis

• Reactive distillation: Both charged simultaneously and then one of the products vaporized and withdrawn continuously which increases the conversion!

  Also concentration increases of reactant and increases the rate of reaction, resulting in decreased processing time.

  e.g. acetylation and esterification (water removal)
Startup of CSTRs

Startup at isothermal conditions is rare but occasionally happens

Begin with the mole balance

\[ F_{A0} - F_A + r_A V = \frac{dN_A}{dt} \]

Why can’t we use conversion?

At startup we cannot separate moles reacted from moles accumulated!

This is why we **MUST** use concentration as our variable!

\[ C_i = \frac{F_i}{V} \quad V = V_0 \quad \text{and} \quad v = v_0 \]

\[ \tau = \frac{V_0}{v_0} \]

\[ C_{A0} - C_A + r_A \tau = \frac{\tau dC_A}{dt} \]
Rate of reaction – Consider 1st order

\[- r_A = kC_A \]

\[ \frac{C_{A0}}{\tau} = \frac{dC_A}{dt} \frac{C_A}{\tau} + kC_A \]

\[ C_A @ t = 0 = 0 \]

Let \( t_s \) be the time necessary to reach 99% of SS concentration, \( C_{AS} \)

\[ C_{AS} = \frac{C_{A0}}{1 + \tau k} \]

\[ C_A = 0.99C_{AS} \]

\[ t_s = 4.6 \left( \frac{\tau}{1 + \tau k} \right) \]

For most first-order systems, steady state is achieved in 3-4 space times.
Semi-Batch Reactors

Why would we want to use?

Enhance selectivity in liquid phase reactions.

\[ A + B \xrightarrow{k_D} D \quad \text{with} \quad -r_D = kC_A^2C_B \]

\[ A + B \xrightarrow{k_U} U \quad \text{with} \quad -r_U = kC_A^2C_B \]

Instantaneous Selectivity, \( S_{D/U} \): ratio of the relative rates

Guides us on how to produce the most of the desired product

\[ S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^2 C_B}{k_U C_A C_B^2} = \frac{k_D C_A}{k_U C_B} \]
B slowly added to vat containing reactant A

**Mole Balance on Species A**

\[ [\text{Rate in}] - [\text{Rate out}] + [\text{Rate of Gen}] = [\text{Rate of Acc}] \]

\[ 0 - 0 + r_A V(t) = \frac{dN_A}{dt} \]

We are going to write the semi-batch equations in terms of concentration and conversion.

\[ r_A V(t) = \frac{d(VC_A)}{dt} \]

\[ r_A V(t) = \frac{VdC_A}{dt} + \frac{C_A dV}{dt} \]
Since we are filling the reactor, the volume is changing with time.

**How do we find the reactor volume as a function of time?**

\[ [\text{Rate in}] - [\text{Rate out}] + [\text{Rate of Gen}] = [\text{Rate of Acc}] \]

\[ \rho_0 v_0 - 0 + 0 = \frac{d(\rho V)}{dt} \]

Constant density \( \rho_0 = \rho \)

Constant volumetric flow rate \( \frac{dV}{dt} = v_0 \)

Apply initial conditions, \( t=0, V=V_0 \) and integrate

\[ \int_{V_0}^{V} dV = v_0 \int_{0}^{t} dt \]

\[ V = V_0 + v_0 t \]

Semi-batch reactor volume as function of time
Substitute \[ \frac{dV}{dt} = v_0 \] into \[ r_A V(t) = \frac{VdC_A}{dt} + \frac{C_A dV}{dt} \]

\[-v_0C_A + r_A V(t) = \frac{VdC_A}{dt} \]

Divide by \( V \) \[ \frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A \]

Now we need to do the same thing for species B

\([\text{Rate in}-\text{[Rate out]}+ \text{[Rate of Gen]}=\text{[Rate of Acc]}\]

\[ F_{B0} - 0 + r_B V = \frac{dN_B}{dt} \]

\[ \frac{dN_B}{dt} = F_{B0} + r_B V \quad \rightarrow \quad \frac{d(VC_B)}{dt} = \frac{VdC_B}{dt} + \frac{C_B dV}{dt} = F_{B0} + r_B V \]
\[ \frac{V \, dC_B}{dt} + \frac{C_B \, dV}{dt} = F_{B0} + r_B V \]

Substitute

\[ V = V_0 + v_0 t \]

\[ \frac{dC_B}{dt} = r_B + v_0 \left( \frac{C_{B0} - C_B}{V} \right) \]

Now we can solve analytically for \( n = 0 \) or \( 1 \)

Or use ODE solver for \( n > 1 \)
Class exercise:

The production of ethylene glycol from ethylene chlorohydrin and sodium bicarbonate

\[ CH_2OHCH_2Cl + NaHCO_3 \rightarrow (CH_2OH)_2 + NaCl + CO_2 \]

is carried out in a *semibatch* reactor. A 1.5 M solution of ethylene chlorohydrin is fed at a rate of 0.1 mole/minute to 1500 dm³ of a 0.75 M solution of sodium bicarbonate. The reaction is elementary and carried out isothermally at 30 °C where the specific reaction rate is 5.1 dm³ /mol hr. Higher temperatures produce unwanted side reactions. The reactor can hold a maximum of 2500 dm³ of liquid. Assume constant density.
Class exercise 2:

The following reaction is to be carried out in the liquid phase

\[ \text{NaOH} + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{COO}^- \text{Na}^+ + \text{C}_2\text{H}_5\text{OH} \]

The initial concentrations are 0.2 M in NaOH and 0.25 M in CH\(_3\)COOC\(_2\)H\(_5\) with \(k=5.2 \times 10^{-5} \text{ m}^3/\text{mol s}\) at 20 °C with \(E = 42,810 \text{ J/mol}\). Design a set of operating conditions to produce 200 mol/day of ethanol in a *semibatch* reactor and not operate above 35° C and below a concentration of NaOH of 0.02 M. The semibatch reactor you have available is 1.5 m in diameter and 2.5 m tall.