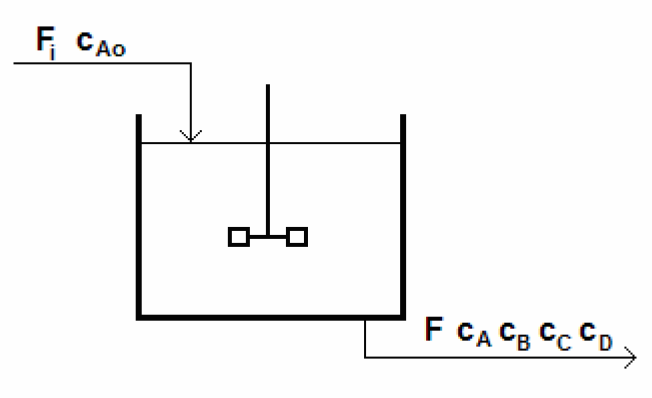
Problem 1



Overall Material Balance:

$$\frac{dn}{dt}=\frac{d(\rho V)}{dt}=\rho_i F_i-\rho F \quad \Rightarrow \quad \rho\frac{dV}{dt}+V\frac{d\rho}{dt}=\rho_i F_i-\rho F \tag{S1.1}$$

Assuming constant density and reactor volume, equation (S1.1) yields:

$$\rho\left(F_i-F\right)=0 \quad \Rightarrow \quad F_i-F=0 \tag{S1.2}$$

Therefore, the input and output flow rates are equal at each point in time.

Component A Material Balance:

$$\frac{d(Vc_A)}{dt}=F_i c_{Af}-Fc_A-k_1c_AV-k_3c_A^2V \tag{S1.3}$$

Taking into account equation (S1.1) and the fact that the reaction volume is constant, equation (S1.3) can be rewritten as:

$$\frac{dc_A}{dt}=\frac{F}{V}\left(c_{Af}-c_A\right)-k_1c_A-k_3c_A^2 \tag{S1.4}$$

Component B Material Balance:

$$\frac{d(Vc_B)}{dt}=-Fc_B+k_1c_AV-k_2c_BV \tag{S1.5}$$

Since the reaction volume is constant, equation (S1.5) becomes:

$$\frac{dc_B}{dt}=-\frac{F}{V}c_B+k_1c_A-k_2c_B \tag{S1.6}$$

Component C Material Balance:

$$\frac{d(Vc_C)}{dt}=-Fc_C+k_2c_BV \tag{S1.7}$$

As the reaction volume is constant, equation (S1.7) is rewritten as follows:

$$\frac{dc_C}{dt} = -\frac{F}{V}c_C + k_2 c_B \tag{S1.8}$$

Component D Material Balance:

$$\frac{d(Vc_D)}{dt} = -Fc_D + \frac{1}{2}k_3 c_A^2 V \tag{S1.9}$$

As the reaction volume is constant, equation (S1.9) yields:

$$\frac{dc_D}{dt} = -\frac{F}{V}c_D + \frac{1}{2}k_3 c_A^2 \tag{S1.10}$$

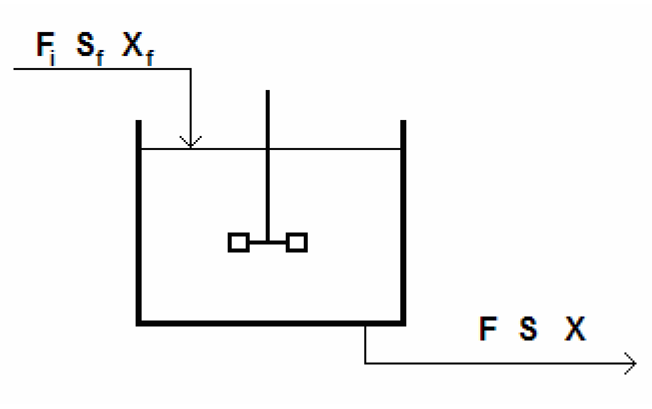
In equations (S1.4) and (S1.10), the reaction rate is defined with respect to the number of moles of A that are consumed due to reaction (1.3). Therefore, the factor 1/2 appearing in equation (S1.10) accounts for the fact that for each mole of A consumed, half mole of D is produced.

Thus,

a) The model is given by equations (S1.4), (S1.6), (S1.8) and (S1.10)

b) State variables: c_A, c_B, c_C, c_D
Input: F_i, c_{Ao}
Output: F, c_A, c_B, c_C, c_D
Parameters: ρ, V, k_1, k_2, k_3

Problem 2



Overall Material Balance:
As in problem 1, assuming constant density and reactor volume yields:

$$F_i - F = 0 \tag{S2.1}$$

Therefore, the input and output flow rates are equal at each point in time.

Biomass Material Balance:

$$\frac{d(Vx)}{dt} = -Fx + \mu x V \tag{S2.2}$$

Taking into account equation (S2.1) and the fact that the reaction volume is constant, equation (S2.2) can be rewritten as:

$$\frac{dx}{dt} = \left(\frac{\mu_{max} s}{K_s + s} - \frac{F}{V} \right) x \tag{S2.3}$$

Substrate Material Balance:

$$\frac{d(Vs)}{dt} = F_i s_f - Fs - \frac{\mu x V}{Y} \tag{S2.4}$$

Considering equation (S2.1) and the fact that the reaction volume is constant, equation (S2.4) can be rewritten as:

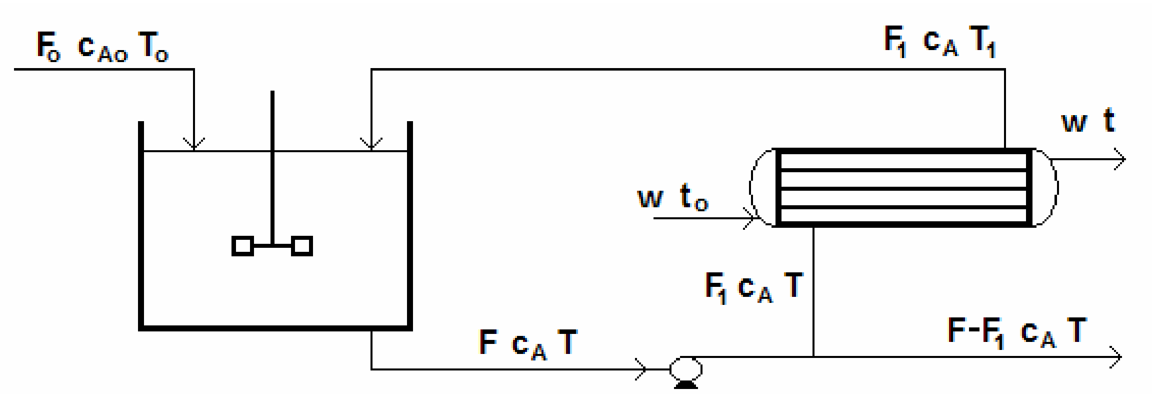
$$\frac{ds}{dt} = \frac{F}{V}\left(s_f - s\right) - \frac{1}{Y}\frac{\mu_{max} s}{K_s + s} x \tag{S2.5}$$

Hence,

a) The model is given by equations (S2.3) and (S2.5)

b) State variables: s, x
Input: F_i, s_f
Output: F, s, x
Parameters: ρ, V, K_s μ_{max}, Y

Problem 3



Overall Material Balance:

$$\frac{dn}{dt} = \frac{d(\rho V)}{dt} = \rho_i F_o + \rho F_1 - \rho F \quad \Rightarrow \quad \rho \frac{dV}{dt} + V \frac{d\rho}{dt} = \rho_i F_o + \rho F_1 - \rho F \tag{S3.1}$$

Assuming constant density and reactor volume, equation (S3.1) yields:

$$\rho\left(F_o + F_1 - F\right) = 0 \quad \Rightarrow \quad F_o = F - F_1 \tag{S3.2}$$

Therefore, the input flow rate is equal, at each point in time, to the fraction of the output flow rate that is not recycled to the reactor.

Component A Material Balance:

$$\frac{d(Vc_A)}{dt} = F_o c_{Ao} + F_1 c_A - F c_A - k c_A V \tag{S3.3}$$

Taking into account equation (S3.1), considering that the reaction volume is constant and substituting equation (3.2), equation (S3.3) can be rewritten as:

$$\frac{dc_A}{dt} = \frac{F_o}{V} c_{Ao} - \left[\frac{F_o}{V} + k_o \exp\left(\frac{-E}{RT} \right) \right] c_A \tag{S3.4}$$

Component B Material Balance:

$$\frac{d(Vc_B)}{dt} = F_1 c_B - F c_B + k c_A V \tag{S3.5}$$

Taking into account equation (S3.1), considering that the reaction volume is constant and substituting equation (3.2), equation (S3.5) becomes:

$$\frac{dc_B}{dt} = -\frac{F_o}{V} c_B + k_o \exp\left(\frac{-E}{RT} \right) c_A \tag{S3.6}$$

Overall Energy Balance:

$$\frac{dU}{dt} = F_o \rho_o u_o + F_1 \rho u - F \rho u + W - Q \tag{S3.7}$$

In equation (S3.7), U is the internal energy of the fluid (kcal), u_o and u are the molar internal energies that the system exchanges with the surrounding environment (kcal/moles). Moreover, W is the rate at which heat is generated during the reaction (kcal/h), while Q denotes the rate at which heat is removed from the stream that, leaving the heat exchanger, is recycled to the reactor (kcal/h). Letting p represent the reactor pressure and H the fluid enthalpy, one can write:

$$U = H - pV \tag{S3.8}$$

Differentiating (S3.8) yields:

$$\frac{dU}{dt} = \frac{dH}{dt} - p\frac{dV}{dt} - V\frac{dp}{dt} \tag{S3.9}$$

Assuming constant pressure p and volume V, (S3.9) becomes

$$\frac{dU}{dt} = \frac{dH}{dt} \tag{S3.10}$$

Equation (S3.10) states that the rate of enthalpy accumulation in a system is equal to the rate at which the internal energy of the same system changes in time at constant pressure and volume. Since the heat capacity is defined as the variation of the molar enthalpy due to a change in the system temperature (i.e. c_P=dh/dT), then (S3.10) can be rewritten as follows:

$$\frac{dU}{dt} = \frac{dH}{dt} = \rho V \frac{dh}{dt} = \rho V c_P \frac{dT}{dt} \tag{S3.11}$$

For liquid systems, the internal energy can be generally approximated with the enthalpy of the system at the same conditions (see Sandler (1999) for a more detail explanation). Therefore, it follows:

$$u \simeq h = c_P (T - T_{ref}) \tag{S3.12}$$

$$u_o \simeq h_o = c_P (T_o - T_{ref}) \tag{S3.13}$$

where T an T_o respectively represent the output and input temperatures whereas t_{ref} denotes a reference temperature. Choosing as reference temperature the one of the feed stream, equations (S3.12) and (S3.13) yield:

$$u \simeq c_P (T - T_o) \tag{S3.14}$$

$$u_o \simeq 0 \tag{S3.15}$$

The rate of heat produced during the reaction can be expressed as the product of the number of moles of A consumed times the heat released per mole consumed, as follows:

$$W = k_o \exp\left(\frac{-E}{RT}\right) c_A V(-\Delta H) \tag{S3.16}$$

Finally, the rate of heat removed from the fraction of fluid that is recycled to the reactor can be expressed as the product of the mass flow rate times the heat capacity times the variation between the input and output temperatures of the water, as follows:

$$Q = w c_{p,w} (t - t_o) \tag{S3.17}$$

Therefore, equation (S3.7) becomes:

$$\rho V c_P \frac{dT}{dt} = -F_o \rho c_P (T - T_o) + k_o \exp\left(\frac{-E}{RT}\right) c_A V(-\Delta H) - w c_{P,w} (t - t_o) \tag{S3.18}$$

Thus,

c) The model is given by equations (S3.4), (S3.6) and (S3.18)

d) State variables: c_A, c_B, T
   Input: F_o, c_{Ao}, T_o
   Output: F, F_1, c_A, c_B, T
   Parameters: ρ, V, k_o, c_P, $c_{P,w}$, E, R, (-ΔH), w, t, t_o

Sandler, S.I. (1999) *Chemical and Engineering Thermodynamics.* John Wiley & Son, New York.