46. Polystyrene Production in a PFR.

Styrene monomer, *M*, can be industrially polymerized to polystyrene, P_n, by homogeneous free-radical polymerization in an incompressible liquid mixture containing only monomer, initiator, and polymer

$$nM \longrightarrow P_n \qquad (1)$$

The degree of polymerization is not constant but evolves during polymerization. Also, Reaction 1 is not elementary. The elementary steps in the homogeneous polymerization mechanism are:

1. Initiation: the initiator I decomposes into two equally reactive primary radicals, with a rate constant k_d, according to

$$I \xrightarrow{k_d} 2R\cdot$$

2. Propagation: the propagation steps can be written as follows, k_p being the rate constant of propagation

$$R\cdot + M \xrightarrow{k_p} RM\cdot$$

$$RM_n^{\cdot} + M \xrightarrow{k_p} RM_{n+1}^{\cdot}$$

It is generally assumed that the rate constant for the propagation reaction remains the same regardless of the length of the chain to which the radicals attach.

3. Termination: it will be assumed in this problem that termination only involves two radicals reacting by recombination. In this case a bond is formed between growing radicals, whereby the polymer molecule is –on average- twice the size of the radicals upon termination. The termination reaction can be written as

$$M_i^{\cdot} + M_j^{\cdot} \xrightarrow{k_t} M_{i+j}\ (polymer)$$

Rate equations for the consumption of initiator, r_i, and monomer r_M are, thus, given by

$$-r_I = k_d C_I \qquad (2)$$

and

$$-r_M = k_p \left(\frac{2k_d C_I}{k_t}\right)^{\frac{1}{2}} C_M \qquad (3)$$

These expressions for polymerization kinetics can be used to design reactors, here a homogeneous, isothermal plug flow reactor (PFR) operating in turbulent flow.

The reacting liquid mixture needs to be pumped through the tubular reactor at a high enough pressure to maintain a constant flow rate. For steady operation of a PFR in turbulent flow (where the velocity profile is constant), engineering practice defines two dimensionless groups: the friction factor f and the Reynolds number, *Re*, respectively

$$f = \left(-\frac{dP}{dx}\right)\left(\frac{D}{2\rho v^2}\right) \tag{4}$$

and

$$Re = \frac{Dv\rho}{\mu} \tag{5}$$

where P is pressure, x is axial distance, D is the reactor tube diameter, and v, ρ, μ are the axial velocity, density, and viscosity of the liquid mixture, respectively. For turbulent flow of a simple liquid in a circular pipe, the friction factor obeys the Blasius relation

$$f = \frac{0.079}{Re^{\frac{1}{4}}} \tag{6}$$

Equations 4-6 allow calculation of the pressure profile in the PFR once the viscosity of the liquid mixture is known. Experimental data for viscosity of the liquid mixture is summarized by the relation

$$\ln\left(\frac{\mu}{1\ Pa.s}\right) = -13.04 + \frac{2013}{\frac{T}{1\ K}} + M_w^{0.18}\left(3.915w_p - 5.437w_p^2 + \left(0.623 + \frac{1387}{\frac{T}{1\ K}}\right)w_p^3\right) \tag{7}$$

where w_p is the weight fraction of polymer in the mixture, and M_w is the polystyrene weight-average molecular weight given by

$$M_w = M_{w,styrene}\left(2 + 3\left(\frac{k_p C_M}{2(k_t k_d C_I)^{\frac{1}{2}}}\right)\right) \tag{8}$$

You are to design a PFR to produce 1000 kg/h of polystyrene using azobisisobutyronitrile initiator (AIBN) at a 10^{-3}mol/L initial concentration. Assume that the reactor reaches 65% conversion and that the heat-transfer systems can be designed to keep the contents isothermal at 60 ^{o}C.

a) List the necessary conservation design equations to calculate the monomer conversion, initiator conversion, and reactor pressure as a function of reactor volume, $V = \pi D^2 x/4$.

b) Write a Matlab code to calculate monomer conversion, initiator conversion, and reactor pressure as a function reactor volume. You are to hand in your code.

c) Plot the conversion of AIBN and styrene versus PFR volume, and the pressure versus reactor volume. What are the volume, conversions, pressure drop across your reactor, rate of polymer production, and its degree of polymerization?

Data

Physical properties:

$\rho_{styrene} = \rho_{polystyrene} = \rho_{mixture} = 909.3$ kg m^{-3}

$Mw_{styrene} = 104.15$ g mol^{-1}

Diameter of the PFR: D = 0.1 m

Kinetic Rate Constants:

$k_d = 0.85 \times 10^{-5}$ s^{-1}

$k_p = 145$ L mol^{-1} s^{-1}

$k_t = 5.8 \times 10^7$ L mol^{-1} s^{-1}