

04.04. 2017

## **CHEM-E2145 Polymerization Reaction Engineering**

1. Heat balance of a polymerization reactor?
2. Effects of viscosity increase in polymerization reactors?
3. How to measure and calculate heat transfer coefficient by using a polymerization reaction calorimeter?
4. Main polypropylene grades and their polymerization types?
5. Calculation, next page

04.04.2017

Ethylene is polymerized at 90 °C in n-heptane with a homogeneous metallocene catalyst at steady state. The polymerization is performed in a CSTR reactor shown in figure 1. A dispersion of HDPE is formed during the polymerization ( $-\Delta H_R = 101,5 \text{ kJ/mol}$ ). The capacity of the reactor is 30 kton/a. The heat transfer coefficient of the reactor is 1500 W/(m<sup>2</sup>K). What is the surface temperature inside the CSTR reactor?

What is the surface temperature when this reaction is performed in a loop reactor (shown in figure 2) of equal volume?

A heat flow of 1 MW is transferred with the product stream from both reactors.

The area/volume of the torus in the loop reactor can be excluded.

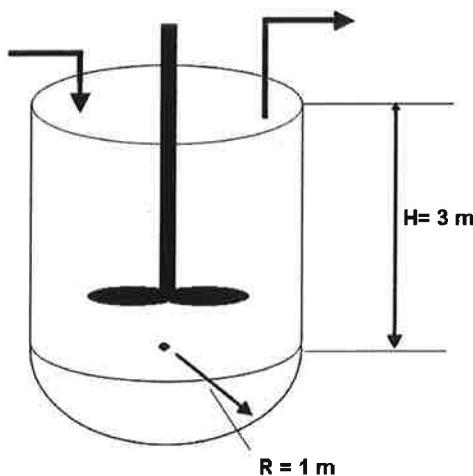


Figure 1. CSTR reactor.

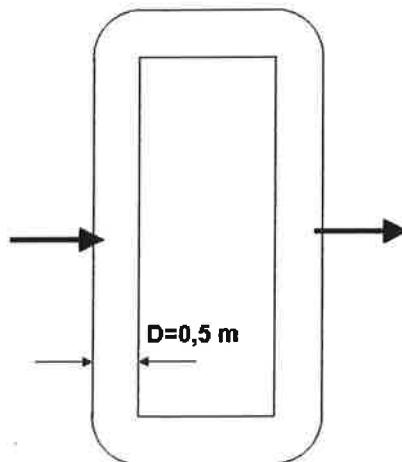


Figure 2. Loop reactor.

## Equation collection

$$n = \frac{m}{M} \quad c = \frac{n}{V} \quad \rho = \frac{m}{V} \quad V_m = \frac{n}{V} \quad pV = nRT \quad k = Ae^{-\frac{E}{RT}}$$

$$\bar{M}_n = M_0 \times \bar{X}_n \quad p = 1 - \frac{[M]}{[M]_0} \quad R_p = -\frac{d[M]}{dt}$$

**Step polymerization:**

$$\bar{X}_n = \frac{[M]_0}{[M]} \quad \bar{X}_n = \frac{1+r}{1+r-2rp} \quad r = \frac{N_{A,0}}{N_{B,0}}, r < 1 \quad r = \frac{N_A}{N_B + 2N_B} \quad p_c = \frac{2}{f_{avg}} \quad f_{avg} = \frac{\sum N_i f_i}{\sum N_i}$$

**Chain polymerization:**

$$R_i = -\frac{d[I]}{dt} = k_i [M] \times [R \cdot] = 2f \times k_d [I] \quad R_t = 2k_t [M \cdot]^2 \quad [I] = [I]_0 e^{-k_d t}$$

$$R_p = -\frac{d[M]}{dt} = k_p [M] \times [M \cdot] \quad [M \cdot] = \sqrt{\frac{R_i}{2k_t}} \quad \tau = \frac{[M \cdot]}{R_i}$$

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad \bar{X}_n = 2\nu \text{ (combination)} \quad \bar{X}_n = \nu \text{ (disproportionation)}$$

$$\bar{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,M} + R_{tr,S}} \quad \frac{1}{\bar{X}_n} = \frac{R_i}{2R_p} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]}$$

$$X_M = 1 - \exp\left(-2 \frac{K_0}{k_d} \left(1 - \exp\left(\frac{-k_d}{2} t\right)\right)\right) \quad , \quad K_0 = k_p \sqrt{\frac{fk_d [I]_0}{k_t}}$$

**ATRP:**

$$R_p = -\frac{d[M]}{dt} = \frac{k_p K [M][I][Cu^+]}{[Cu^{2+}]} \quad \bar{X}_n = \frac{p[M]_0}{[I]_0} \quad \frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{1}{\bar{X}_n}$$

**Emulsion polymerization:**

$$R_p = k_p [M][P \cdot] \quad [P \cdot] = \frac{10^3 N \bar{n}}{N_A} \quad r_p = k_p [M] \quad r_i = \frac{R_i}{N} \quad \bar{X}_n = \frac{r_p}{r_i}$$

**Ion polymerization:**

$$R_p = -\frac{d[M]}{dt} = k_p [M^-] \times [M] \quad \bar{X}_n = \frac{[M]}{[I]} \quad \frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{1}{\bar{X}_n}$$

**Copolymerization:**

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)]$$

$$\text{Finemann\&Ross: } \frac{f_1(1-2F_1)}{F_1(1-f_1)} = \frac{f_1^2(F_1-1)}{F_1(1-f_1)^2} \times r_1 + r_2$$

$$\text{Eilers: } \bar{\eta}_{rel} = \left( 1 + 1,25 * \frac{\Phi_d}{1 - \frac{\Phi_d}{\Phi_{d,max}}} \right)^2$$

### Reaction engineering:

$$P = 2\pi mn \quad P = N_p n^3 d^5 \rho \text{ (Turbulent regime)} \quad Re = \frac{nd^2 \rho}{\eta}$$

### Constants:

$$R = 8,3145 \text{ J/(K mol)} \quad N_A = 6,022 \times 10^{23} \text{ mol}^{-1} \quad g = 9,80665 \text{ m/s}^2$$

$$0^\circ\text{C} = 273,15 \text{ K} \quad 1 \text{ bar} = 10^5 \text{ Pa}$$

### Atomic weights (g/mol):

H	1,008	C	12,011	N	14,007	O	15,999
Al	26,982	Cl	35,453	Ti	47,867	Zr	91,224