

CHEMICAL REACTOR DESIGN FOR PROCESS PLANTS

Volume Two:
Case Studies and Design Data

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CASE STUDY 101

Styrene Polymerization

THIS STUDY is a nontrivial case of a CSTR involving the complexities of free-radical polymerization. The weakest aspect of the model is the method for estimating viscosity, which strongly affects heat transfer and is very sensitive to temperature and concentration of polymer. Experimental work with the particular polymer-styrene product mix would yield a better correlation.

Problem Statement

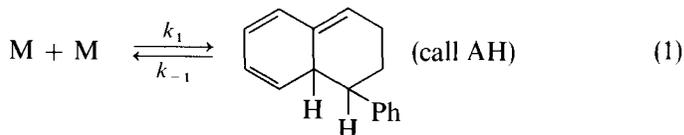
Design the first stage of a two-stage thermal polymerization system for producing 40 million lb/yr of polystyrene with an overall conversion for the system of 95%. The product from the first stage should have a number average molecular weight (\bar{M}_n) of 144,000.

Feed. 99.5 wt% styrene with 10 ppm maximum polymer and maximum weight percentages of impurities of 0.02 aldehydes as CHO, 0.01 peroxide as H_2O_2 , 0.0025 sulfur, and 0.01 chloride.

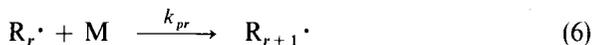
Chemistry and Kinetics

Details of the formation of a Diels–Alder adduct (AH) and its radical ($A\cdot$) from styrene monomer (M) have been described (1) and are partially illustrated as follows, together with the propagation, termination, and chain-transfer steps.

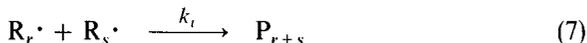
Initiation



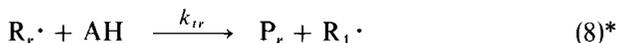
Propagation



Termination by Combination



Chain Transfer. (to AH or M)



The rate of initiation is

$$r_1 = (k_4[A\cdot] + k_5[M\cdot])[M] \quad (\text{CS-1.1})$$

By using the stationary state hypothesis, expressions for concentrations of $A\cdot$, $M\cdot$, AH, and $R_r\cdot$ can be obtained as functions of monomer concentrations so that Eq. CS-1.1 can also be written in these terms (1)

$$(r_1) = \frac{2k_1k_2[M]^3}{k_{-1} + (k_2 + k_3)[M] + k_{tr}(r_1/k_4)^{\frac{1}{2}}} \quad (\text{CS-1.2})$$

where $[M]$ is the concentration of monomer in g moles/liter. A limiting case in which k_{-1} is much greater than the remainder of the denominator appears to fit operating data.

$$(r_1) = \frac{2k_1k_2}{k_{-1}} [M]^3 = 2k_i[M]^3 \quad (\text{CS-1.3})$$

* AH represents a Diels-Alder adduct.

Other instantaneous expressions typical of free-radical polymerization with termination by combination dominating are (1).

$$r_{\text{pr}} = k_{\text{pr}}[\text{R}_r \cdot][\text{M}] = k_{\text{pr}} \left(\frac{r_1}{k_t} \right)^{\frac{1}{2}} [\text{M}] \quad (\text{CS-1.4})$$

From Eq. CS-1.3

$$r_{\text{pr}} = \left(\frac{2k_i}{k_t/k_{\text{pr}}^2} \right)^{\frac{1}{2}} [\text{M}]^{\frac{3}{2}} = A[\text{M}]^{\frac{3}{2}} \quad (\text{CS-1.5})$$

The grouping A has been found to vary with conversion.

$$A = A_0 \exp(A_1 X + A_2 X^2 + A_3 X^3) \quad (\text{CS-1.6})$$

Also

$$(\overline{DP})^{-1} = C_m + \frac{r_1}{2r_{\text{pr}}} \quad (\text{CS-1.7})$$

or

$$(\overline{DP})^{-1} = C_m + \frac{k_i[\text{M}]^{\frac{1}{2}}}{A} \quad (\text{CS-1.8})$$

$$\overline{M}_n = 104 \overline{DP} \quad (\text{CS-1.9})$$

where \overline{M}_n is the number average molecular weight. C_m , which accounts for chain transfer, also varies with conversion.

$$C_m = C_{m_0} + B_1 X \quad (\text{CS-1.10})$$

Equations for the several constants are given in Table CS-1.1.

Table CS-1.1 Kinetic Data for Thermal Polymerization of Styrene (Ref. 1)

$A_0 = 1.964 \times 10^5 \exp(-10,040/T), (1./\text{g mole})^{\frac{3}{2}} \text{sec}^{-1}$
$A_1 = 2.57 - 5.05 \times 10^{-3} T$
$A_2 = 9.56 - 1.76 \times 10^{-2} T$
$A_3 = -3.03 + 7.85 \times 10^{-3} T$
$B_1 = -1.013 \times 10^{-3} \log_{10} \left(\frac{473.12 - T}{202.5} \right)$
$k_i = 2.19 \times 10^5 \exp(-13,810/T), (1./\text{g-mole})^2 \text{sec}^{-1}$
$C_{m_0} = 2.198 \times 10^{-1} \exp(-2820/T)$
$T = ^\circ K$

Thermodynamics

The typical high exothermicity of polymerization, $\Delta H = -17,500$ cal/g mole monomer converted @ 25°C for this case (2,3), and the importance of temperature in controlling molecular weight indicates a definite need for a reactor with heat transfer. From Table 6.1, pp. 270–271¹, the adiabatic factor is moderately high, and the heat generation potential is not high.

Reactor Type

A CSTR has good heat-transfer characteristics and allows continuous operation, but it can only be used to a conversion level where heat transfer and contacting become poor because of increasing viscosity. This problem can be overcome by diluting with solvent, but then solvent handling and recovery add greatly to the cost. Alternatively, a CSTR can be specified for some low conversion range, and the remaining conversion (up to 95) can be completed in a screw-type, tubular flow unit, such as described on p. 480¹, or as shown in Fig. 10.29. We will only consider the CSTR, for the tube operates at such high viscosity that diffusion controls and modeling techniques are inadequate. Styrene polymerizes slowly relative to many other monomers and a CSTR is also advantageous for this reason.

Design Model (CSTR)

Equations CS-1.5–CS-1.10 express instantaneous values applicable to a CSTR. The following mole and heat balances apply.

Monomer Balance. (neglecting monomer used in initiation and transfer)

$$F_M X_M = \frac{-d[M]}{dt} V = r_{pr} V = A[M]^{\frac{3}{2}} V \quad (\text{CS-1.11})$$

Heat Balance

$$104F_M c_{pM}(T_e - T_0) + UA_h(T_e - T_j) = (-\Delta H_M)_{T_e}(F_M X_M) \quad (\text{CS-1.12})$$

where F_M is the molar flow rate of monomer fed, c_{pM} is the heat capacity of monomer, and T_e , T_0 , T_j are the exit, entrance, and cooling medium temperatures, respectively.

Since the heat capacities of monomer and polymer are approximately the same, the heat of reaction at 25°C can be used in Eq. CS-1.12.

Fluid Properties

$$c_{pM} = 0.353 + (0.0014)(T - 293), \text{ cal/g}^\circ\text{C} \quad (\text{CS-1.13}) \quad (2,3)$$

$$\rho_M = 924 - 0.918(T - 273.1), \text{ g/l.} \quad (\text{CS-1.14}) \quad (1)$$

$$\rho_{pr} = 1084.8 - 0.605(T - 273.1), \text{ g/l.} \quad (\text{CS-1.15}) \quad (1)$$

$$\delta_v = \left(\frac{1}{\rho_{pr}} - \frac{1}{\rho_M} \right) / \frac{1}{\rho_M} \quad (\text{CS-1.16})$$

$$[M] = \frac{\rho_M(1 - X_M)}{(104)(1 + \delta_v X_M)}, \quad \text{g moles/l.} \quad (\text{CS-1.17})$$

$$(\eta_r - 1)/w_{pr} = 109[\eta]_T \exp \{2079w_{pr}(1.09[\eta]_T + 1)/T\} \quad (\text{CS-1.18}) \quad (4)$$

where ρ_M and ρ_{pr} are the densities of monomer and polymer, respectively. η_r is the ratio of viscosity of polystyrene in styrene to that of pure styrene at the same temperature, $[\eta]_T$ is the intrinsic viscosity of polystyrene of same molecular weight and type in toluene at 30°C in dl./g, and w_{pr} is the weight fraction as mass of polymer/mass of styrene.

The viscosity is very sensitive to temperature and concentration. Equation CS-1.18 is corrected to agree with the original plot of experimental data given in the reference. Ideally the value of $[\eta]_T$ should be determined for the product in question in the laboratory. For illustrative purposes we select a value of 0.7.

Design Calculations and Decisions*Operating Temperature and Conversion*

Molecular weight in thermal polymerization is most strongly affected by operating temperature and is not sensitive to conversion. By applying Eqs. CS-1.6–CS-1.9 at various temperatures using a hand calculator, a temperature of 150°C gave $\bar{M}_n = 144,041$ @ $X = 0.4$ and $\bar{M}_n = 143,621$ @ $X = 0.45$. The corresponding solution viscosities at these two conversions are 3623 cp and 13406 cp, respectively. Styrene viscosity at 150°C is 0.22 cp (5). Thus it is seen that viscosity increases dramatically above $X_M = 0.4$, and heat-transfer rate will decline rapidly such that it will not be possible to remove the heat of polymerization. Hence for safety reasons the design will be set at $X_M = 0.4$ as a maximum, and subsequent calculation will reveal that this is operable.

Monomer Flow Rate

Basis: 95% overall conversion for 2-stages.

95% operating factor

99.5% styrene purity and no recycle

$$\frac{4 \times 10^7 \text{ lb/yr}}{(0.995)(0.95)(0.95)(365)(24)(3600)} = 1.413 \text{ lb/sec or } 641 \text{ g/sec}$$

Reactor Volume

From Eq. CS-1.11

$$V = \frac{F_M X_M}{A[M]^{\frac{1}{2}}} = \frac{(641/104)(0.4)}{(1.64243 \times 10^{-5})(4.9506)^{\frac{1}{2}}} \\ = 2752.7 \text{ liters or } 727 \text{ gal}$$

A 750 gal stainless-steel tank (60 × 60 in.) is selected from Table 8.8, $D = 60$ in., $D_1 = (1/3)60 = 20$ in. with 160 rpm for good heat transfer (838 ft/min tip speed, see Table 8.10). One 20-in. flat-blade turbine is selected initially for analysis.

Heat Balance (Eq. CS-1.12)

Basis: 150°C which is the reaction temperature

30°C inlet, 45°C average cooling water temperature.

$$(641)(0.451)(150 - 30) + U A_h (150 - 45) = (17,500)(641/104)(0.4)$$

Required $U A_h = (43144 - 34691)/105 = 80.5 \text{ cal/sec } ^\circ\text{C}$,

$$U = \frac{(80.5)(3600)}{(97)(727/750)(252)(1.8)} = 6.8 \text{ BTU/hr ft}^2$$

Estimate h and U . From Eq. 8.14

$$h = \frac{0.73 \lambda_f}{D} \left(\frac{c_p \mu}{\lambda_f} \right)^{0.33} \left(\frac{\rho N D_1^2}{\mu} \right)^{0.65} \left(\frac{\mu}{\mu_w} \right)^{0.24} \\ = \frac{0.73}{20/12} (0.055) \left[\frac{(0.451)(3623)(2.42)}{0.055} \right]^{0.33} \\ \times \left[\frac{(53.5)(160)(60)(20/12)^2}{(3623)(2.42)} \right]^{0.65} \left(\frac{\mu}{\mu_w} \right)^{0.24} = 26.4 \left(\frac{\mu}{\mu_w} \right)^{0.24}$$

$$\bar{\rho} = \frac{\rho_M/1000}{1 + \delta_r X_M} = \frac{0.786}{1 - (0.209)(0.4)} = 0.858 \text{ g/cm}^3 \text{ or } 53.5 \text{ lb/ft}^3$$

$\lambda_f = 0.055 \text{ BTU/(hr)ft}^2 \text{ } ^\circ\text{F ft}^{-1}$ @ 150°C for ethylbenzene (API Data Book)

Estimation of wall temperature ($b_w = \frac{5}{16}$ in., fouling factor, $\mathcal{R}_h = 0.001$, h_o is for water = 400 BTU/hr ft² °F.

$$h(T - T_w) = \frac{1}{(1/h_o) + (b_w/\lambda_w) + \mathcal{R}_h} (T_w - T_j)$$

$$\frac{T_w - T_j}{T - T_w} = h \left(\frac{1}{h_o} + \frac{b_w}{\lambda_w} + \mathcal{R}_h \right) = h \left(\frac{1}{400} + \frac{0.026}{30} + 0.001 \right)$$

$$= 4.367 \times 10^{-3} h$$

Assuming $h = 10$

$$\frac{T_w - 45}{150 - T_w} = 0.044 \quad \text{or} \quad T_w = 49^\circ\text{C}$$

for which μ from Eq. CS-1.18 is 52,477 cp

$$\text{corrected } h = 26.4 \left(\frac{3623}{52,477} \right)^{0.24} = 13.9$$

$$U = \left(\frac{1}{\cancel{9.98} / 13} + 4.367 \times 10^{-3} \right)^{-1} = 13.1 \text{ BTU/hr ft}^2 \text{ }^\circ\text{F}$$

Thus the design is adequate compared with required U of 6.8. It should be noted that an increase in conversion to 45% at a lower flow rate to yield the same production would produce a h equal to 6.95 or a U of 6.75, based on the viscosity correlation of Eq. CS-1.18. The required U at this new condition would be 9.9. Thus somewhere between 40% and 45% conversion the reaction will become uncontrollable by conventional jacket cooling, but the reaction is slow and corrections can be made. The vapor pressure of styrene at 150°C is 880 mm Hg (2), but at the conversion level the actual value will be less because of nonidealities attributable to the dissolved polymer. An approximate operating pressure of 2.5 psi will be assumed. This pressure or higher values at higher temperatures which could occur during upsets can be released to cause vaporizing of the monomer and rapid cooling.

Required Horsepower

Based on manufacturer's correlation Fig. 8.8 at $N_{Re} = 163$, $N_p = 5.5$

$$\text{hp} = (1.1)(3.52 \times 10^{-3})(5.5) \left(\frac{53.5}{62.4} \right) \left(\frac{160}{60} \right)^3 \left(\frac{20}{12} \right)^5 + 0.5 = 4.95 \text{ hp or}$$

specify 5 hp motor.

If one refers to Fig. 8.7, the Reynolds number is in the transition region for which the power number is 3.5 and the corresponding hp = 3.3; but the

higher hp would be selected since the reactor must be periodically washed with a low viscosity solvent which would place the operation in the turbulent region with a higher power number.

Mixing Effectiveness

Equation 8.16 can be used to estimate the effective radius of agitation.

$$R_{\text{eff}} = c \sqrt{\frac{hp}{\mu}} = c \sqrt{\frac{4.05}{3623}} = 0.033c$$

Using appropriate values of the coefficient, horizontal and vertical values are 4.2 and 1.7 ft, respectively, which is adequate in the horizontal but not the vertical direction for a 60 × 60 in. tank. Accordingly, two 18 in. impellers should be substituted. By selecting the 18 in. impellers it is possible to maintain the required power at the same value, $(18/20)^5(0.9)(2) \approx 1.0$ (see instructions in caption for Fig. 8.7, p. 348¹). The turbines should be spaced 30 in. apart.

A better decision would be to use a single curved-blade turbine (with six blades) since it provides superior axial mixing. The resulting hp will be lower, but the heat-transfer coefficient will be approximately the same (see Table 8.6). Because of the flatter power-number curve (Fig. 8.7), the power overage required for washing will not be as great. Manufacturer's representatives should be consulted for the final selection.

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