

Reactor Models in Heterogeneous Catalysis and Numerical Methods

Bharat Medasani

January 2019

1 Continuous Stirred Reactor

CSTR's are defined by a perfectly mixed gaseous mixture inside the reactor with constant mass flow rate, \dot{m} . The inlet gas has a composition and temperature of Y'_k and T' , and the outlet gas is defined by Y_k and T .

1.1 Governing Equations

1.1.1 Species Conservation Equation

For species k , the change of mass in CSTR is given by

$$\frac{dm_k}{dt} = \int_V (\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}) W_k dV \quad (1)$$

Using Reynolds transport theorem and after some manipulations

$$\frac{dY_k}{dt} = \frac{\dot{m}}{\rho V} (Y'_k - Y_k) + \frac{(\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}) W_k}{\rho} \quad (2)$$

1.2 Energy balance

First law of thermodynamics gives energy balance of the system as

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} \quad (3)$$

Using Reynold's transport theorem again, we get

$$\frac{de}{dt} = \frac{\dot{m}}{\rho V} (h' - h) + \frac{\dot{Q}}{\rho V} \quad (4)$$

After some manipulations, the resulting energy balance equation is

$$c_p \frac{dT}{dt} = \frac{\dot{m}}{\rho V} \sum_{k=1}^K Y'_k (h'_k - h_k) - \sum_{k=1}^K \frac{h_k \dot{\omega}_k W_k}{\rho} + \frac{\dot{Q}}{\rho V} \quad (5)$$

No heat is transferred to the reactor, hence $\dot{Q} = 0$. Further the enthalpy is given as

$$h = \sum_{k=1}^K Y_k h_k = \sum_{k=1}^K Y_k c_{p,k} T \quad (6)$$

Plugging Eqn. 6 into Eqn. 5, we get

$$c_p \frac{dT}{dt} = \frac{\dot{m}}{\rho V} \sum_{k=1}^K Y'_k [c_{p,k}(T')T' - c_{p,k}(T)T] - \sum_{k=1}^K \frac{c_{p,k}(T)T[\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}]}{\rho} W_k \quad (7)$$

At steady state, $dT/dt = 0$, and $dY_k/dt = 0, \forall k \in \{1, \dots, K\}$. Applying these results back to Eqn 2 and 7, we get

$$\cancel{\frac{dY_k}{dt}} \xrightarrow{SS} = \frac{\dot{m}}{\rho V} (Y'_k - Y_k) + \frac{(\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}) W_k}{\rho} \quad (8)$$

$$Y_k = Y'_k + \frac{(\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}) W_k V}{\dot{m}}, \quad (9)$$

and

$$\cancel{c_p \frac{dT}{dt}} \xrightarrow{SS} = \frac{\dot{m}}{\rho V} \sum_{k=1}^K Y'_k [c_{p,k}(T')T' - c_{p,k}(T)T] - \sum_{k=1}^K \frac{c_{p,k}(T)T[\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}]}{\rho} W_k \quad (10)$$

$$0 = \frac{\dot{m}}{\rho V} \sum_{k=1}^K Y'_k [c_{p,k}(T')T' - c_{p,k}(T)T] - \sum_{k=1}^K \frac{c_{p,k}(T)T[\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}]}{\rho} W_k \quad (11)$$

$$\sum_{k=1}^K Y'_k [c_{p,k}(T')T' - c_{p,k}(T)T] = \frac{V}{\dot{m}} \sum_{k=1}^K c_{p,k}(T)T[\dot{\omega}_k + \dot{s}_k \frac{A_{surf}}{V}] W_k \quad (12)$$

2 Plug Flow Reactor

Plug flow reactor (PFR) can be characterized as a cylindrical tube in which the reactions are taking place at steady state. Gas at a constant mass flow rate, \dot{m} passes through the reactor. Further it is assumed that no gradients in either temperature or density or composition exist lateral to the gas flow. Another assumption is that tube diameter is constant through-out.

The mass flow rate, \dot{m} , is given as

$$\dot{m} = \rho A_c u, \quad (13)$$

where ρ is the density, u is the axial velocity and A_c is the reactor cross section. For a constant sized cross-section area, ρu is constant.

2.1 Mass Balance

Species in gas phase adsorb/desorb from the gas phase onto the catalyst surface. Assuming there is no net flow from inlets and outlets, the change in the mass of gas phase over time is given by

$$\frac{dm}{dt} = \int_{SA} \sum_k \dot{s}_k W_k dA + \int_{CV} \sum_k \dot{\omega}_k W_k dV, \quad (14)$$

where \dot{s}_k and $\dot{\omega}_k$ are the rates of production of kth species on catalyst surface (mol cm^{-2}) and in gas phase (mol cm^{-3}), W_k is the weight of the kth species, and SA is the surface area of the catalyst. \dot{s}_k is positive if species k is desorbed from the surface and negative if species k is adsorbed onto the surface. For a differential volume of PFR, using Reynold's theorem, we get

$$\frac{d(\rho u)}{dz} = \sum_k (\dot{\omega}_k + \dot{s}_k \frac{A}{V}) W_k \quad (15)$$

For individual species, we get

$$\rho u \frac{dY_k}{dz} + Y_k \frac{d(\rho u)}{dz} = [\dot{\omega}_k + \dot{s}_k \frac{A}{V}] W_k, \quad (16)$$

where A/V is the catalyst area specified in terms of per reactor volume. Based on Eqn. 13 and Eqn. 15, Eqn. 16 can be rewritten as

$$\frac{\dot{m}}{A_c} \frac{dY_k}{dz} + Y_k \sum_k (\dot{\omega}_k + \dot{s}_k \frac{A}{V}) W_k = \left(\dot{\omega}_k + \dot{s}_k \frac{A}{V} \right) W_k. \quad (17)$$