Week 1: Derivation of Governing Equations and Constraints for Plug Flow with Variable Area and Surface Chemistry

Yuanjie Jiang

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1 Assumptions

- Area variation is sufficiently small and smooth

- No variation across channel, so it is a 1D problem

- Neglecting the axial diffusion compared to the convective term in flow direction (z-axis)

2 Governing Equations and Constraints

2.1 Overall mass conservation equation

The change of the mass flow rate of gas equals the generation/consumption rate by surface reaction, the equation is written as below[3]:

$$\frac{dm}{dt} = \int_{cs} \sum^{K_g} \dot{s}_k W_k dA \tag{1}$$

Based on the Reynolds transport theorem, the LHS of the above equation can be expanded. The time differential term can be canceled since only steady state (s.s.) is considered.

$$\int_{cv} \frac{\partial \rho}{\partial t} dV \overset{s.s}{\nearrow} + \int_{cs} \rho(\mathbf{v} \cdot \mathbf{n}) dA = \int_{cs} \sum^{Kg} \dot{s_k} W_k dA \tag{2}$$

Gauss theorem cannot be applied to convert the control surface integration to control volume integration since the cross-section area of the reactor is changing.Taylor expansion is applied instead.

$$-\rho u A_c + \rho u A_c + \frac{\rho u A_c}{dz} dz = \sum^{K_g} \dot{s}_k W_k \mathscr{P}' dz \tag{3}$$

$$\boxed{\frac{d(\rho u A_c)}{dz} = \mathscr{P}' \sum^{K_g} \dot{s_k} W_k} \tag{4}$$

2.2 Individual species conservation equation

Similar procedure is taken to derive the species conservation equation.

$$\frac{dm_k}{dt} = \int_{cv} \dot{\omega}_k W_k dV + \int_{cs} \dot{s}_k W_k dA \tag{5}$$

$$\int_{cv} \overbrace{\frac{\partial \rho Y_k}{\partial t}}^{s.s} dV + \int_{cs} \rho Y_k (\mathbf{v} \cdot \mathbf{n}) dA = \int_{cv} \dot{\omega}_k W_k dV + \int_{cs} \dot{s}_k W_k dA \tag{6}$$

$$-\rho Y_k u A_c + \rho Y_k u A_c + \frac{\rho Y_k u A_c}{dz} dz = \dot{\omega}_k W_k A_c dz + \dot{s}_k W_k \mathscr{P}' dz \tag{7}$$

$$\frac{d(\rho Y_k u A_c)}{dz} = \dot{\omega}_k W_k A_c + \mathscr{P}' \dot{s}_k W_k \tag{8}$$

$$\rho u A_c \frac{dY_k}{dz} + Y_k \frac{d(\rho u A_c)}{dz} = \dot{\omega}_k W_k A_c + \dot{s}_k W_k \mathscr{P}' \tag{9}$$

Incorporated with Eq.(4) into the second term of Eq. (9)

$$\boxed{\rho u A_c \frac{dY_k}{dz} + Y_k \mathscr{P}' \overbrace{\sum \dot{s}_k W_k}^{K_g} = \dot{\omega}_k W_k A_c + \dot{s}_k W_k \mathscr{P}'} \tag{10}$$

2.3 Energy balance equation

According to the first law of thermodynamics, the total stored energy change equals the sum of the heat transfer into the system and the work done by the system [3, 4].

$$\frac{dE_t}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} \tag{11}$$

$$\int_{cv} \rho \frac{\partial e_t}{\partial t} + \rho \mathbf{v} \cdot \nabla e_t dV = \int_{cv} \rho \frac{De_t}{Dt} dV = \int_{cv} \rho (\frac{De}{Dt} + \mathbf{v} \frac{D\mathbf{v}}{Dt}) dV = \frac{dQ}{dt} + \frac{dW}{dt} \tag{12}$$

$$\int_{cv} \overbrace{\rho \frac{\partial e}{\partial t}}^{s.s} + \rho \mathbf{v} \nabla e + \overbrace{\rho \mathbf{v} \frac{\partial \mathbf{v}}{\partial t}}^{s.s} + \rho \mathbf{v} \mathbf{v} \nabla \mathbf{v} dV = \frac{dQ}{dt} - \int_{cv} \overbrace{\frac{\partial p}{\partial t}}^{s.s} dV - \int_{cs} p(\mathbf{v} \cdot \mathbf{n}) dA \tag{13}$$

$$\int_{cs} (e + \frac{v^2}{2} + \frac{p}{\rho}) \rho \mathbf{v} \cdot \mathbf{n} dA = \frac{dQ}{dt} \tag{14}$$

Applied Taylor expansion on the LHS of the equation and in conjunction with $h = e + \frac{p}{\rho}$

$$-(h + \frac{u^2}{2}) \rho u A_c + (h + \frac{u^2}{2}) \rho u A_c + \frac{(h + \frac{u^2}{2}) \rho u A_c}{dz} dz = \frac{dQ}{dt} \tag{15}$$

$$\frac{d(h \rho u A_c)}{dz} + \frac{d(\frac{u^3}{2} \rho A_c)}{dz} = \frac{dQ}{dt} \tag{16}$$

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$$\rho u A_c \frac{dh}{dz} + h\frac{d(\rho u A_c)}{dz} + \rho u A_c \frac{d\frac{u^2}{2}}{dz} + \frac{u^2}{2}\frac{d(\rho u A_c)}{dz} = \frac{dQ}{dt} \tag{17}$$

$$\rho u A_c \frac{dh}{dz} + (h + \frac{u^2}{2})\mathscr{P}' \sum^{K_g} \dot{s}_k W_k + \rho u A_c \frac{d\frac{u^2}{2}}{dz} = \frac{dQ}{dt} \tag{18}$$

$$\rho u A_c \frac{d(\sum^{K_g} Y_k h_k)}{dz} + (h + \frac{u^2}{2})\mathscr{P}' \sum^{K_g} \dot{s}_k W_k + \rho u A_c \frac{d\frac{u^2}{2}}{dz} = \frac{dQ}{dt} \tag{19}$$

Incorporated with $h_k = c_{p,k}T$, Eq. (10) can be rewritten into

$$\rho u A_c c_p \frac{dT}{dz} + \rho u A_c \sum^{K_g} h_k \frac{dY_k}{dz} + \rho u^2 A_c \frac{du}{dz} + (h + \frac{u^2}{2})\mathscr{P}' \sum^{K_g} \dot{s}_k W_k = \frac{dQ}{dt} \tag{20}$$

$$\rho u A_c(c_p \frac{dT}{dz} + \sum^{K_g} h_k \frac{dY_k}{dz} + u\frac{du}{dz}) + (\sum^{K_g} h_k Y_k + \frac{u^2}{2})\mathscr{P}' \sum^{K_g} \dot{s}_k W_k = \frac{dQ}{dt} \tag{21}$$

Since kinetic energy of the flow is negligible, the above equation can be simplified.

$$\rho u A_c c_p \frac{dT}{dz} + \rho u A_c \sum^{Kg} h_k \frac{dY_k}{dz} + h\mathscr{P}' \sum^{K_g} \dot{s}_k W_k = \frac{dQ}{dt} \tag{22}$$

The second term of the above equation can be simplified incorporated with species conservation equation (Eq. 10), which can be expressed as follows.

$$\begin{aligned}
\rho u A_c \sum^{K_g} h_k \frac{dY_k}{dz} = \sum^{K_g} \rho u A_c h_k \frac{dY_k}{dz} &= \sum^{K_g} h_k[\dot{\omega}_k W_k A_c + \dot{s}_k W_k \mathscr{P}' - Y_k \mathscr{P}' \sum^{K_g} \dot{s}_k W_k] \\
&= \sum^{K_g} h_k \dot{s}_k W_k \mathscr{P}' + \sum^{K_g} h_k \dot{\omega}_k W_k A_c - \sum_{K_g} h_k Y_k \mathscr{P}' \sum^{K_g} \dot{s}_k W_k \\
&= \sum^{K_g} \cancel{h_k \dot{s}_k W_k \mathscr{P}'} + \sum^{K_g} h_k \dot{\omega}_k W_k A_c - \sum^{K_g} Y_k \sum^{K_g} \cancel{h_k \dot{s}_k W_k \mathscr{P}'}
\end{aligned} \tag{23}$$

Plug Eq. (23) into Eq. (22)

$$\rho u A_c c_p \frac{dT}{dz} + A_c \sum^{K_g} \dot{\omega}_k W_k h_k + \mathscr{P}' \sum^{K_g} h_k \dot{s}_k W_k = \frac{dQ}{dt} \tag{24}$$

The heat flow rate into the system has two expressions, one is due to the heat flux $\dot{q}_e$ from the surroundings to the outer tube wall (whose surface area per unit length is a_e) and accumulation of enthalpy in the bulk solid. The other is due to the $\dot{q}_i$ is the heat flux to the gas from the inner tube wall and accumulation of enthalpy in the surface species [2, 4]

$$\boxed{\begin{aligned}
\rho u A_c c_p \frac{dT}{dz} + A_c \sum^{K_g} \dot{\omega}_k W_k h_k + \mathscr{P}' \sum^{K_g} h_k \dot{s}_k W_k &= a_e q_e - \mathscr{P}' \sum_{bulk}^{K_b} \dot{b}_k W_k h_k \\
&= \mathscr{P}' q_i + \mathscr{P}' \sum_{gas}^{K_g} \dot{s}_k W_k h_k
\end{aligned}} \tag{25}$$

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2.4 Momentum equation

The momentum conservation in the axial direction is presented as follows, which shows the balance between pressure force, inertia, viscous drag and momentum applied to the flow due to surface reactions[3, 4].

$$\frac{d(m\mathbf{v})}{dt} = \sum F \tag{26}$$

$$\int_{cv} \rho \frac{D\mathbf{v}}{dt} dV = -\int_{cs} p dA - \int_{cs} \tau_w dA \tag{27}$$

$$\int_{cv} \rho(\overset{s.s}{\cancel{\frac{\partial \mathbf{v}}{\partial t}}} + \mathbf{v}\nabla \cdot \mathbf{v}) = \int_{cs} \rho\mathbf{v}\mathbf{v} \cdot \mathbf{n} dA = -\int_{cs} p dA - \int_{cs} \tau_w dA \tag{28}$$

$$-\rho u^2 A_c + \rho u^2 A_c + \frac{d(\rho u^2 A_c)}{dz} dz = p A_c - (p A_c + \frac{d(p A_c)}{dz} dz) - \tau_w \mathscr{P} dz \tag{29}$$

$$\frac{d(\rho u^2 A_c)}{dz} = -\frac{d(p A_c)}{dz} - \tau_w \mathscr{P} \tag{30}$$

$$\rho u A_c \frac{du}{dz} + u \frac{\rho u A_c}{dz} = -\frac{d(p A_c)}{dz} - \tau_w \mathscr{P} \tag{31}$$

$$\boxed{\rho u A_c \frac{du}{dz} + u \frac{\rho u A_c}{dz} = -\frac{d(p A_c)}{dz} - \frac{1}{2}\rho u^2 f \mathscr{P}} \tag{32}$$

where

$$f = \begin{cases} \frac{16}{Re} & laminar\, flow \\ 0.0791 Re^{-0.5} & turbulent\, flow \end{cases}$$

where $Re = \frac{uD\rho}{\mu}$, the dynamic viscosity μ is a time dependent variable, it can be roughly revised using $\mu = \mu_{in}(\frac{T}{T_{in}})^{0.5}$ without using any thermal data from input files.

2.5 Idea gas equation of state

Pressure showed above can be roughly obtained using the ideal gas equation of state:

$$pW = \rho R T \tag{33}$$

2.6 Constraints

Since we assume the system is in steady state and surface composition at tube wall is stationary. Then the net production rates of surface species by heterogeneous reaction approach 0, which is given:

$$\boxed{\dot{s_k} = 0 \quad (k = 1 \cdots K_s - 1)} \tag{34}$$

All $\dot{s}_k$ are not independent, the following constraint can be used to replace Eq. (34) for the largest site fraction species.

$$\sum_{k=1}^{K_s} Z_k = 1 \quad (k = K_s) \tag{35}$$

Every points along the tube surface should satisfy these two constraints. For solving differential - algebraic equation, some software (e.g. DASSL) need all algebraic equations satisfy at the initial point. In order to obtain the initial value of Z_k at steady state,the transient differential equation for the site fraction Z_k of surface species k can be derived as follows[1]

$$[X_k] = \frac{Z_k(n)\Gamma_n}{\sigma_k(n)} \tag{36}$$

$$\frac{d[X_k]}{dt} = \dot{s}_k \tag{37}$$

$$\frac{d(\frac{Z_k(n)\Gamma_n}{\sigma_k(n)})}{dt} = \dot{s}_k \tag{38}$$

$$\frac{\Gamma_n}{\sigma_k(n)}\frac{dZ_k(n)}{dt} + \frac{Z_k(n)}{\sigma_k(n)}\frac{d\Gamma_n}{dt} = \dot{s}_k \tag{39}$$

Assuming total surface site density (Γ_n) is constant. Then a simpler equation for $dZ_k(n)$ can be obtained.

$$\frac{dZ_k}{dt} = \frac{\dot{s}_k \sigma_k}{\Gamma} \tag{40}$$

Eq. (40) is conjunction with Eq. (35) until the steady state is reached.

2.7 Different boundary conditions

- If the reactor is isothermal or the axial temperature profile is specified, the energy balance equation will not use

- Reactor is adiabatic ($q_e = 0$) or $q_e(x)$ is specified.

- $q_i(x)$ can be expressed in terms of function of ambient temperature T_∞ and overall heat transfer coefficient U, which is given as

$$q_i = U(T_\infty - T)$$

- The heat transfer from the reactor wall is given in terms of the convection heat coefficient $\hat{h}$ and tube wall temperature T_w, which is given as $dQ/dt = \hat{h}(\mathscr{P}dz)(Tw - T)$, then the energy equation can be further simplified based on Eq. (24)

References

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[2] Michael E Coltrin, Robert J Kee, and FM Rupley. *Surface CHEMKIN (Version 4. 0): A Fortran package for analyzing heterogeneous chemical kinetics at a solid-surface—gas-phase interface.* Tech. rep. Sandia National Labs., Livermore, CA (United States), 1991.

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