Derivation for Time Dependent Gas Mixture in a Perfectly Stirred Reactor

An open system with constant pressure and volume, assumptions: ignore surface reactions and heat loss

$*$ = in
$\dot{m}$ = outlet mass flow rate
$\dot{m}^*$ = inlet mass flow rate
ρ = mass density
V = reactor volume
T = gas temperature
$\tau = m/\dot{m}^*$ = residence time

Mass Conservation

$$\frac{dm}{dt} = \frac{d(\rho V)}{dt} = \dot{m}^* - \dot{m}$$

$$V\frac{d\rho}{dt} = \frac{\rho V}{\tau} - \dot{m}$$

$$\dot{m} = \frac{\rho V}{\tau} - V\frac{d\rho}{dt}$$

Species Equation

$$\frac{dm_i}{dt} = \frac{d(\rho V Y_i)}{dt} = \dot{m}^* Y_i^* - \dot{m} Y_i + \dot{\omega}_i W_i V = \rho V \frac{dY_i}{dt} + Y_i \frac{d(\rho V)}{dt}$$

$$\rho V \frac{dY_i}{dt} = \dot{m}^* Y_i^* - \dot{m} Y_i + \dot{\omega}_i W_i V - Y_i \frac{d(\rho V)}{dt}$$

Substitute continuity

$$\rho V \frac{dY_i}{dt} = \dot{m}^* Y_i^* - \left(\dot{m}^* - \frac{d(\rho V)}{dt}\right) Y_i + \dot{\omega}_i W_i V - Y_i \frac{d(\rho V)}{dt}$$

Expand terms

$$\rho V \frac{dY_i}{dt} = \dot{m}^* Y_i^* - \dot{m}^* Y_i + \frac{d(\rho V)}{dt} Y_i + \dot{\omega}_i W_i V - Y_i \frac{d(\rho V)}{dt}$$

Cancel terms $\quad \rho V \frac{dY_i}{dt} = \dot{m}^* Y_i^* - \dot{m}^* Y_i + \dot{\omega}_i W_i V$

$$\frac{dY_i}{dt} = \frac{1}{\tau}(Y_i^* - Y_i) + \frac{\dot{\omega}_i W_i}{\rho} \qquad \tau = \frac{\rho V}{\dot{m}^*}$$

Energy Equation, specific volume not constant $\quad \frac{du}{dt} = \dot{q}_{net,in} - p\frac{dv}{dt}$

$$h \equiv u + pv$$

Definition of enthalpy $\quad \frac{dh}{dt} = \frac{du}{dt} + p\frac{dv}{dt} + v\frac{dp}{dt}$

$\frac{dp}{dt} = 0$ because const pressure, substitute $\frac{du}{dt}$ into $\frac{dh}{dt}$ equation $p\frac{dv}{dt}$ terms cancel

$\frac{dh}{dt} = \dot{q}_{net,in}$ We can conserve enthalpy instead of energy, energy is still conserved but need an additional equation from ideal gas law to calculate $\frac{dv}{dt}$

$$\frac{dH}{dt} = \frac{d(\sum m_i h_i)}{dt} = \dot{H}_{in} - \dot{H}_{out} \qquad \frac{dH}{dt} = \sum m_i \frac{dh_i}{dt} + \sum h_i \frac{dm_i}{dt} \qquad \frac{dH}{dt} = \sum \rho V Y_i c_{p_i} \frac{dT}{dt} + \sum h_i \frac{d(\rho V Y_i)}{dt}$$

$$\frac{dH}{dt} = \frac{dT}{dt}\rho V c_p + \sum h_i \left(Y_i \frac{d(\rho V)}{dt} + \rho V \frac{dY_i}{dt}\right) = \dot{m}^* \sum Y_i^* h_i^* - \dot{m} \sum Y_i h_i$$

$$\frac{dT}{dt}\rho V c_p = \dot{m}^* \sum Y_i^* h_i^* - \dot{m} \sum Y_i h_i - \sum h_i \left(Y_i V \frac{d\rho}{dt} + \rho V \frac{dY_i}{dt}\right)$$

Substitute continuity $\quad \frac{dT}{dt}\rho V c_p = \dot{m}^* \sum Y_i^* h_i^* - \left(\frac{\rho V}{\tau} - V\frac{d\rho}{dt}\right) \sum Y_i h_i - \sum h_i \left(Y_i V \frac{d\rho}{dt} + \rho V \frac{dY_i}{dt}\right)$

Expand terms $\quad \frac{dT}{dt}\rho V c_p = \dot{m}^* \sum Y_i^* h_i^* - \frac{\rho V}{\tau} \sum Y_i h_i + V\frac{d\rho}{dt} \sum Y_i h_i - \frac{d\rho}{dt} V \sum h_i Y_i - \rho V \sum h_i \frac{dY_i}{dt}$

Cancel terms $\quad \frac{dT}{dt}\rho V c_p = \dot{m}^* \sum Y_i^* h_i^* - \frac{\rho V}{\tau} \sum Y_i h_i - \rho V \sum h_i \frac{dY_i}{dt}$

Substitute species equation $\quad \frac{dT}{dt}\rho V c_p = \dot{m}^* \sum Y_i^* h_i^* - \frac{\rho V}{\tau} \sum Y_i h_i - \rho V \sum h_i \left(\frac{1}{\tau}(Y_i^* - Y_i) + \frac{\dot{\omega}_i W_i}{\rho}\right)$

Expand terms $\quad \frac{dT}{dt}\rho V c_p = \dot{m}^* \sum Y_i^* h_i^* - \frac{\rho V}{\tau} \sum Y_i h_i - \frac{\rho V}{\tau} \sum h_i Y_i^* + \frac{\rho V}{\tau} \sum h_i Y_i - V \sum h_i \dot{\omega}_i W_i$

Cancel terms $\quad \frac{dT}{dt}\rho V c_p = \dot{m}^* \sum Y_i^* h_i^* - \frac{\rho V}{\tau} \sum h_i Y_i^* - V \sum h_i \dot{\omega}_i W_i$

Substitute $\dot{m}^* = \frac{\rho V}{\tau}$ $\quad \frac{dT}{dt}\rho V c_p = \frac{\rho V}{\tau} \sum Y_i^* h_i^* - \frac{\rho V}{\tau} \sum h_i Y_i^* - V \sum h_i \dot{\omega}_i W_i$

$$\frac{dT}{dt}\rho c_p = \frac{\rho}{\tau} \sum Y_i^* (h_i^* - h_i) - \sum h_i \dot{\omega}_i W_i$$

$$\frac{dT}{dt} = \frac{1}{\tau c_p} \sum Y_i^* (h_i^* - h_i) - \frac{1}{\rho c_p} \sum h_i \dot{\omega}_i W_i$$