

Chemical Reaction Engineering

Reactor models

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Computer-Aided Chemical Reaction Engineering Course

Graduate School in Chemical Engineering (GSCE)
Åbo Akademi - POKE Researchers network

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Contents

0. Perspective

1. Thermodynamic consistency

1.1 Equilibrium calculation

1.2 Software

1.3 Applications (Methane Steam Reforming)

2. Reactor models (heterogeneous catalysis)

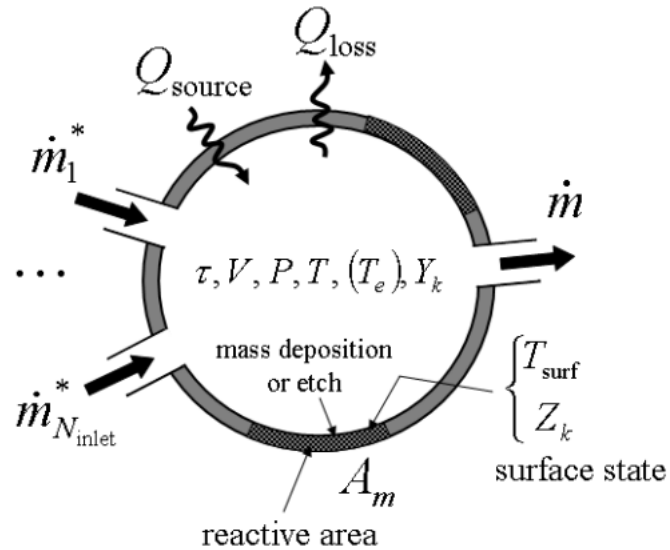
2.1 Ideal

2.2 Ideal with heat- & mass transfer

2.3 Real reactors (CFD)

Reactors

2.1 - 0D

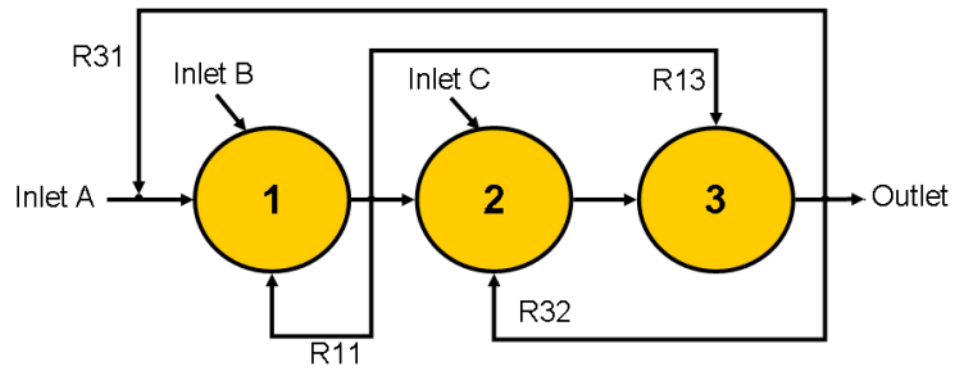


Perfect mixing assumption \rightarrow uniform concentration inside,
at any position, down to the surface proximity

Includes BR & CSTR

Reactors

2.1 - 0D reactors network



Independent inlets

Internal recirculations



Reactors

2.1 - 0D (well mixed)

Total mass balance for j -th reactor in a network

$$\frac{d}{dt}(\rho V)^{(j)} = \sum_{i=1}^{N_{\text{inlet}}^{(j)}} \dot{m}_i^{*(j)} + \sum_{r=1}^{N_{\text{PSR}}} \dot{m}^{(r)} R_{rj} - \dot{m}^{(j)} + \sum_{m=1}^M A_m^{(j)} \sum_{k=1}^{K_g} \dot{s}_{k,m}^{(j)} W_k \quad j = 1, N_{\text{PSR}}$$

IN's R-to-R OUT surf→gas

* = inlet

R_{rj} = fraction of the outflow of reactor r that is recycled into reactor j

A_m = surface of material m

s_{km} = molar production rate of species k on the m material (per unit surface)



Reactors

2.1 - 0D (well mixed)

Gas species k material balance for j -th reactor in a network (1..NG)

$$(\rho_k V)^{(j)} \frac{dY_k^{(j)}}{dt} = \underbrace{\sum_{i=1}^{N_{\text{inlet}}^{(j)}} \dot{m}_i^{*(j)} (Y_{k,i}^* - Y_k)}_{\text{IN-OUT}} + \underbrace{\sum_{r=1}^{N_{\text{PSR}}} \dot{m}_k^{(r)} R_{rj} (Y_k^{(r)} - Y_k^{(j)})}_{\text{R-to-R}} - \underbrace{Y_k^{(j)} \sum_{m=1}^M A_m^{(j)} \sum_{k=1}^{K_g} \dot{s}_{k,m}^{(j)} W_k}_{\text{mass loss to surf.}} + \underbrace{(\dot{\omega}_k V)^{(j)} W_k}_{\text{homog.}} + \underbrace{\sum_{m=1}^M A_m^{(j)} \dot{s}_{k,m}^{(j)} W_k}_{\text{heterog.}}$$

Balances reduce to ODEs (transient) or AEs (stationary)



Reactors

2.1 - 0D (well mixed)

Surface species k material balance (1..NS)

$$\frac{d}{dt}(A_m c_k W_k) = A_m W_k \dot{s}_k$$

No convection!

Surface concentration usually treated as surface coverages, Z_k

$$c_k = \frac{\rho_{n,m} Z_k}{\sigma_k} \quad 1 = \sum Z_k$$

Additional eqs. for surface site variations

Again: ODEs (transient) or AEs (stationary)



Reactors

2.1 - 0D - example

Homogenous/heterogeneous CH_4 combustion
on the Pt walls of a well-mixed vessel

illustration through modified Cantera example surfreactor.m,
by varying the T and initial CH_4/O_2 ratio



Reactors

2.1 - 0D - example

Surface Chemistry

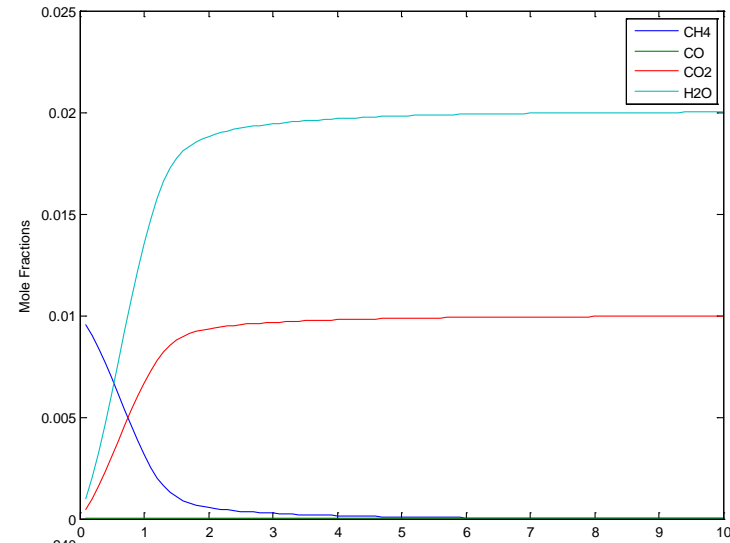
Deutschman et al., 26th Symp. (Intl.) on Combustion, 1996, pp. 1747-1754

REACTIONS		JOULES/MOLE		
H2 + 2PT(S) => 2H(S)		4.4579E+10	0.5	0
	FORD/PT(S) 1/			
2H(S) => H2 + 2PT(S)		3.70E+21	0	67400
	COV/H(S) 0 0		-6000/	
H + PT(S) => H(S)		1.00	0	0
	STICK			
O2 + 2PT(S) => 2O(S)		1.80E+21	-0.5	0
	DUPLICATE			
O2 + 2PT(S) => 2O(S)		0.23	0	0
	DUPLICATE STICK			
2O(S) => O2 + 2PT(S)		3.70E+21	0	213200
	COV/O(S) 0 0		-60000/	
O + PT(S) => O(S)		1.00	0	0
	STICK			
H2O + PT(S) => H2O(S)		0.75	0	0
	STICK			
H2O(S) => H2O + PT(S)		1.0E+13	0	40300
OH + PT(S) => OH(S)		1.00	0	0
	STICK			
OH(S) => OH + PT(S)		1.0E+13	0	192800
H(S) + O(S) = OH(S) + PT(S)		3.70E+21	0	11500
H(S) + OH(S) = H2O(S) + PT(S)		3.70E+21	0	17400
OH(S) + OH(S) = H2O(S) + O(S)		3.70E+21	0	48200
CO + PT(S) => CO(S)		1.618E+20	0.5	0
	FORD/PT(S) 2/			
CO(S) => CO + PT(S)		1.00E+13	0	125500
CO2(S) => CO2 + PT(S)		1.00E+13	0	20500
CO(S) + O(S) => CO2(S) + PT(S)		3.70E+21	0	105000
CH4 + 2PT(S) => CH3(S) + H(S)		4.6334E+20	0.5	0
	FORD/PT(S) 2.3/			
CH3(S) + PT(S) => CH2(S) + H(S)		3.70E+21	0	20000
CH2(S) + PT(S) => CH(S) + H(S)		3.70E+21	0	20000
CH(S) + PT(S) => C(S) + H(S)		3.70E+21	0	20000
C(S) + O(S) => CO(S) + PT(S)		3.70E+21	0	62800
CO(S) + PT(S) => C(S) + O(S)		1.00E+18	0	184000

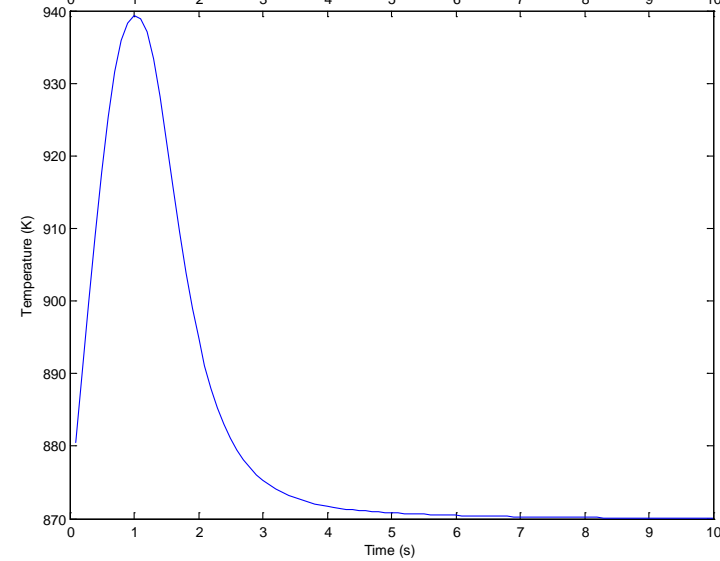
Reactors

2.1 - 0D – example

Gas phase

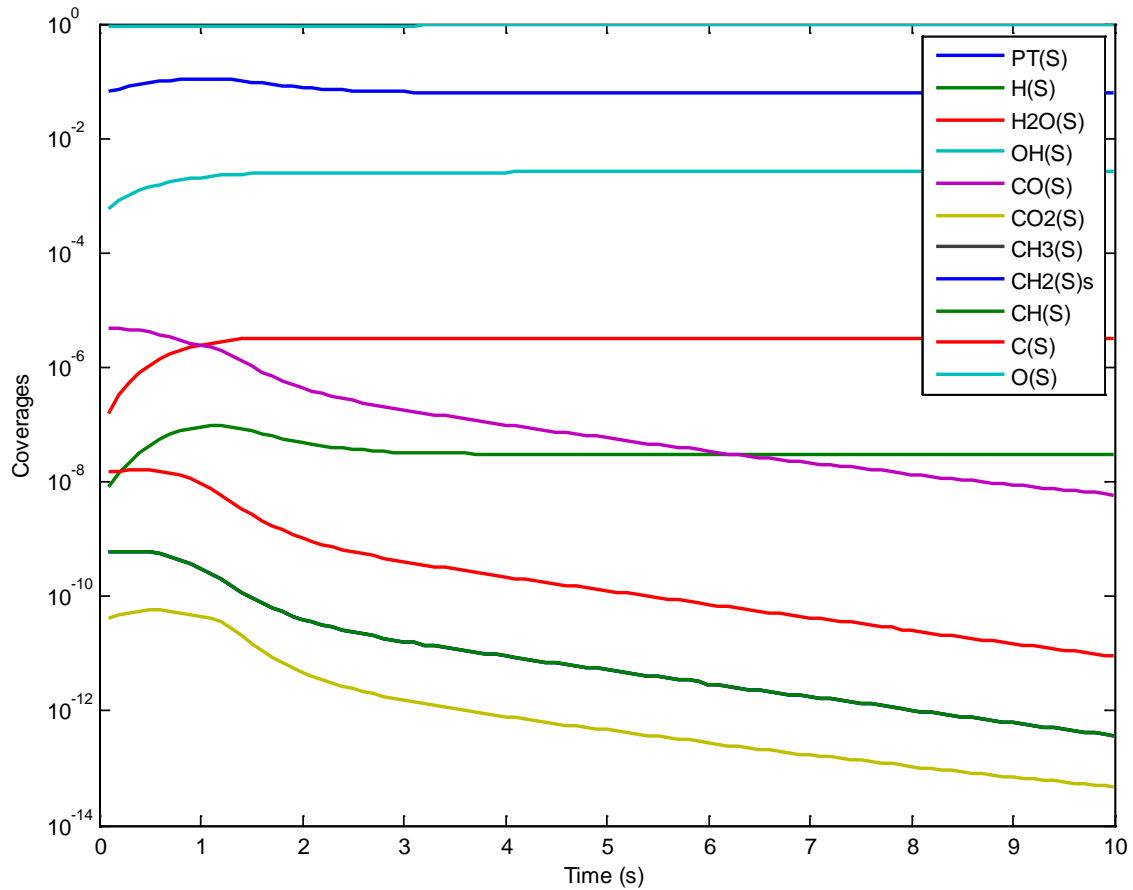


Temperature



Reactors

2.1 - 0D – example



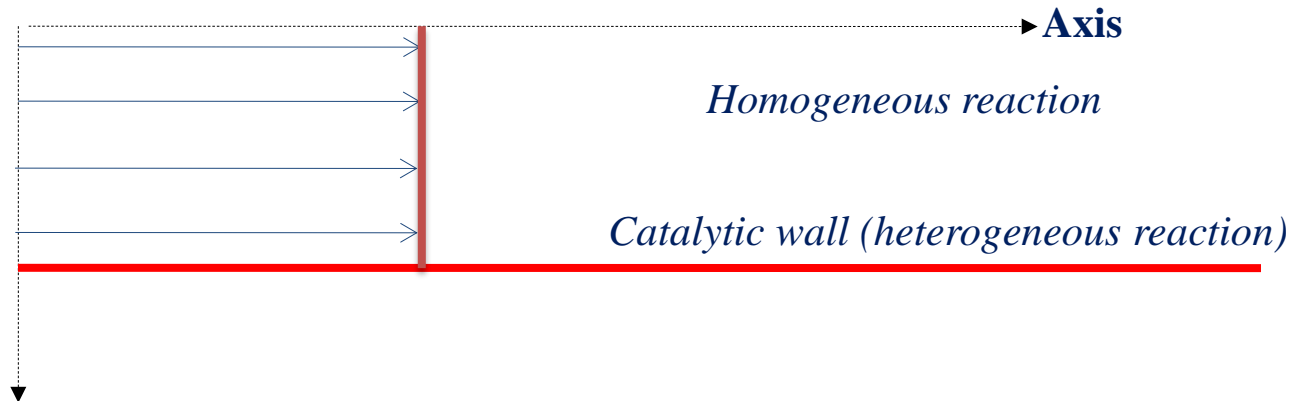
Surface species

Reactors

2.1 - 1D – Plug Flow



Species in the gas phase are uniform at given z
questionable assumption when used for catalytic walls





Reactors

2.1 - 1D – Plug Flow

Gas species k material balance (steady state!)

$$\rho u A \frac{dY_k}{dx} + Y_k \sum_{m=1}^M a_{i,m} \sum_{k=1}^{K_g} \dot{s}_{k,m} W_k = W_k \left(\sum_{m=1}^M \dot{s}_{k,m} a_{i,m} + \dot{\omega}_k A \right)$$

convection

ρ variation

surf -

homog.- production

Balances are always ODEs



Reactors

2.1 - 1D – Plug Flow

Surface species k material balances

$$\dot{s}_k = 0$$

Assumes steady state of the surface composition with respect to the gas

AEs! Coupled with gas MB becomes ADEs



Reactors

2.1 - 1D – Plug Flow

Momentum balance may be useful

$$A \frac{dP}{dx} + \rho u A \frac{du}{dx} + \frac{dF}{dx} + u \sum_{m=1}^M a_{i,m} \sum_{k=1}^{K_g} \dot{s}_{k,m} W_k = 0$$

Accounts for pressure drop



Reactors

2.1 - 1D – Plug Flow

Energy balance

$$\rho u A \left(\sum_{k=1}^{K_g} h_k \frac{dY_k}{dx} + \bar{C}_p \frac{dT}{dx} + u \frac{du}{dx} \right) + \left(\sum_{k=1}^{K_g} h_k Y_k + \frac{1}{2} u^2 \right) \sum_{m=1}^M a_{i,m} \sum_{k=1}^{K_g} \dot{s}_{k,m} W_k = a_e Q_e - \sum_{m=1}^M a_{i,m} \sum_{k=K_b^f}^{K_b} \dot{s}_{k,m} W_k h_k$$

Accounts for heat exchange at the wall

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



Reactors

2.2 - beyond ideal ones: 0D with partial mixing

Do not solve the actual fluid equation
→ Mixing degree is a parameter

Use of approximate form of the joint pdf of flow variables
as a function of displacement and time $P(T, \underline{C}, \underline{x}, t)$
(which would require a PBE)

A number of fluid 'particles' are allowed to move across the reactor, while
reacting segregated (use of RTD pdf)



Reactors

2.2 - beyond ideal ones: pseudo-2D PFR

Gas species distinguish between

- bulk
- in front of the surface

Mass balances in the bulk lose the s_k (heterogeneous) term

$$\rho u A \frac{dY_k}{dx} + Y_k \sum_{m=1}^M a_{i,m} \sum_{k=1}^{K_g} \dot{s}_{k,m} W_k = W_k \left(\sum_{m=1}^M \dot{s}_{k,m} a_{i,m} + \dot{\omega}_k A \right)$$



Reactors

2.2 - beyond ideal ones: pseudo-2D PFR

Surface species k material balances

$$\dot{s}_k = 0$$

Depend on

surface concentrations (coverages)

gas composition in front of the surface



Reactors

2.2 - pseudo-2D PFR; mass

Total mass balance $\rho \cdot v = cost$

Single species mass balances

$$\frac{dY_i}{dz} = -a \cdot hm_i \cdot (C_{b,i} - C_{s,i}) \cdot \frac{MW_i}{(\rho \cdot v)} \quad \text{in the bulk}$$

$$0 = hm_i \cdot (C_{b,i} - C_{s,i}) + r_i \quad \text{at the surface:}$$

h_m introduces large uncertainties!

It can be very detailed on the chemistry
but approximated on mass transport



Reactors

2.2 - pseudo-2D PFR; energy

Adiabatic Energy balance

$$\frac{dT_b}{dz} = \frac{-a \cdot ht \cdot (T_b - T_s)}{(\rho \cdot v \cdot Cp)} \quad \text{in the bulk}$$
$$0 = ht \cdot (T_b - T_s) - \Delta H_R \cdot R \quad \text{at the surface:}$$

h_t better known that h_m

Surface thermodynamics can be poorly available



Reactors

2.3 - Real reactors (CFD)

- *Fluent, CFX*
most of the market, together in ANSYS
- *StarCD*
strong development skills, automotive
- *Flow3D, Phidap, Phoenix*
older, still active
- *Multiphysics (formerly Femlab)*
rapidly emerging, large potential, interface to Matlab



Reactors

2.3 – CFD Conservation Equations

single fluid, pure, isothermal, compressible, newtonian

Total mass conservation (continuity)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = 0$$

Momentum conservation

$$\frac{\partial \rho \mathbf{U}}{\partial t} + \nabla \cdot (\rho \mathbf{U} \otimes \mathbf{U}) = \nabla \cdot \boldsymbol{\sigma} + \mathcal{S}_{mom}$$



Reactors

2.3 – CFD notation

Nabla $\nabla = \left[\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right]$

of a scalar

$$\nabla\phi = \frac{\partial\phi}{\partial x}\mathbf{i} + \frac{\partial\phi}{\partial y}\mathbf{j} + \frac{\partial\phi}{\partial z}\mathbf{k}$$

of a vector (divergence)

$$\nabla\bullet\mathbf{U} = \frac{\partial U_x}{\partial x} + \frac{\partial U_y}{\partial y} + \frac{\partial U_z}{\partial z}$$

tensor product

$$\mathbf{U} \otimes \mathbf{V} = \begin{bmatrix} U_x V_x & U_x V_y & U_x V_z \\ U_y V_x & U_y V_y & U_y V_z \\ U_z V_x & U_z V_y & U_z V_z \end{bmatrix}$$

Divergence of tensor

$$\delta = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\nabla\bullet(\rho\mathbf{U} \otimes \mathbf{U}) = \begin{bmatrix} \frac{\partial}{\partial x}(\rho U_x U_x) + \frac{\partial}{\partial y}(\rho U_y U_x) + \frac{\partial}{\partial z}(\rho U_z U_x) \\ \frac{\partial}{\partial x}(\rho U_x U_y) + \frac{\partial}{\partial y}(\rho U_y U_y) + \frac{\partial}{\partial z}(\rho U_z U_y) \\ \frac{\partial}{\partial x}(\rho U_x U_z) + \frac{\partial}{\partial y}(\rho U_y U_z) + \frac{\partial}{\partial z}(\rho U_z U_z) \end{bmatrix}$$



Reactors

2.3 – CFD Additional Equations

single fluid, **pure**, isothermal, compressible, newtonian

Stress tensor $\sigma = -p\delta + \mu \left[\nabla \mathbf{U} + (\nabla \mathbf{U})^T \right]$

Thermodynamics: volumetric EoS $\rho = \rho(T, p)$



Reactors

2.3 – CFD: non-isoT flow

Total mass conservation (continuity)

+

Momentum conservation

+

Energy conservation:

$$\frac{\partial \rho h_{tot}}{\partial t} + \nabla \cdot (\rho \mathbf{U} h_{tot}) = \nabla \cdot (\lambda \nabla T) + \frac{\partial p}{\partial t} + S_{en}$$

$$h_{tot} = h(T, p) + \frac{1}{2} |\mathbf{U}|^2 = \text{Total enthalpy (specific)}$$

Thermodynamics: thermal EoS

$$h = h(T, p)$$

single fluid, **pure**, isothermal, compressible, newtonian



Reactors

2.3 – CFD: non-isoT flow

When (frequently):

$$h_{tot} = h(T, p) + \frac{1}{2}|\mathbf{U}|^2 \approx h$$

Energy balance becomes

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho \mathbf{U} h) = \nabla \cdot (\lambda \nabla T) + S_{en}$$

More familiar!



Reactors

2.3 – CFD: Multicomponent fluids (single phase)

‘conservation’ of species i

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (\mathbf{U}C_i) = \nabla \cdot (D_i \nabla C_i) + S_i$$

C_i = concentration of i [mass/volume]

S_i = production rate of species i

mixing rules are required!

for thermodynamic (h, c_p, r) and transport properties (η, λ, D)



Reactors

2.3 – CFD: Comparing equations

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = 0$$

$$\frac{\partial \rho \mathbf{U}}{\partial t} + \nabla \cdot (\rho \mathbf{U} \otimes \mathbf{U}) = \nabla \cdot \left(\mu \left[\nabla \mathbf{U} + (\nabla \mathbf{U})^T \right] \right) - \nabla \cdot (p \boldsymbol{\delta}) + S_{mom}$$

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho \mathbf{U} Y_i) = \nabla \cdot (D_i \nabla \rho Y_i) + S_i$$

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho \mathbf{U} h) = \nabla \cdot (\lambda \nabla T) + S_{en}$$

Similar structure

(Transport phenomena analogies)



Reactors

2.3 – CFD Unified eq.

The general form of the transport equation for an Additional Variable (non-reacting scalar) in the presence of turbulence is:

$$\frac{\partial \Phi}{\partial t} + \nabla \cdot (U\Phi) = \nabla \cdot \left(\left(\rho D_{\Phi} + \frac{\mu_t}{Sc_t} \right) \nabla \cdot \left(\frac{\Phi}{\rho} \right) \right) + S_{\Phi}$$

where

- ρ is the mixture density, mass per unit volume.
- Φ is the conserved quantity per unit volume, or *concentration*.
- Φ/ρ is the conserved quantity per unit mass.
- S_{Φ} is a volumetric source term, with units of conserved quantity per unit volume per unit time.
- D_{Φ} is the Kinematic Diffusivity for the scalar.
- μ_t is the turbulence viscosity, with Sc_t the turbulence Schmidt number.



Reactors

2.3 – CFD Boundary conditions

A crucial piece of information

Unknown functions:

$$U(t,\mathbf{x}), \rho(t,\mathbf{x}), P(t,\mathbf{x}), T(t,\mathbf{x}), Y(t,\mathbf{x})$$

Dirichlet: Value of unknown function given

Neumann: Flux of unknown function given

Mixed: Any function!



Reactors

2.3 – CFD facts

- Chemistry poorly developed
 - Simple power laws (reduced kinetics)
 - Limitations on NC (practical, not theoretical issue)
 - Interaction with micromixing (turbulent reactive models!)
- Incompressible flow (not all codes)
- Qualified users/complex codes
- Symmetries/nD/complex geometries (CAD interface)
- Moving boundaries
stirrer, free surfaces, moving walls,...
- Multiphase (particularly dispersed phases!)
- Sub-models (turbulence!, non-newtonian, EoS,..)