Introduction to Monolith Reactor Modelling: Mass, Energy and Momentum Transport

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Objectives of this presentation

• To give an introductory overview to the area of monolith reactor modelling

• To highlight some of the factors that must be taken into consideration when choosing a model.
Why use computer modelling?

• Experiments are expensive and take time.

• Analysis of reactors can be difficult, especially for fast highly exothermic reactions. Non-intrusive measurement methods may not be available.

• Modelling can eliminate scenarios that do not offer promise.

• Faster design and optimisation.

Models are not intended to eliminate experiments completely.
Typical catalytic converter

- The catalytic converter uses a metal or ceramic monolith support structure.
- Typical automotive converters use 400 CPSI cell density.


Observations

- The problem involves the transport of mass, energy and momentum. It is a multi-physics problem.
- Transport occurs at different scales in space.
- The transient response of the gas phase and solid phase occurs at different time scales.
- Modelling of monolith reactors is thus an exercise in multi-scale modelling.

The monolith reactor presents a challenging modelling problem.
Heterogeneous catalytic reactions

Heterogeneous gas phase catalytic reactions typically comprise the same steps.

Fluid flow over the solid results in a boundary layer through which heat and mass diffuse to the gas/solid interface.

Reactants diffuse into the porous catalyst.

Reactants adsorb on the active sites.

The reaction occurs on the active sites, located on the walls of the tortuous pores.

Products desorb and diffuse back to the surface, and then through the boundary layer to the bulk fluid.
Model Scales

**Micro scale**: At the atomic/molecular level, the basic chemistry involves a set of adsorption/desorption and surface reaction steps. The genuine mechanism may be very complicated.

**Meso scale**: Single channel of a monolith. Includes gas phase flow, transport to the surface of the washcoat by diffusion, diffusion and reaction in the washcoat. The basic process in a heterogeneous catalytic reaction are present at the meso scale.

**Macro scale**: Entire catalytic converter, which includes transport and interaction among channels.
Model complexity: Points to note

• **How much complexity is wanted and or needed?**
  - At what level do you wish to model?
  - How much information do you want to include?
  - Do you need to include all of the scales?

• **The model should be as simple as possible, but not simpler (Albert Einstein).**

• **Models do not have to be perfect to be useful.**
Mathematical formulation

• The fundamental model is represented by a set of equations, which include key assumptions
  – Algebraic equations, linear or non-linear
  – Ordinary differential equations (IVP or BVP)
  – Partial differential equations

• Practical monolith modelling problems do not have analytical solutions; models are solved numerically.

• The model selected and the way it is represented will determine the numerical method used for its solution.
Mathematical formulation

• Reactors are fundamentally distributed parameter systems; Concentration, temperature and velocity vary with spatial coordinate.

• The dimensionality (and hence complexity) can be reduced by using average parameter values over specified model dimensions. The result is referred to as a lumped parameter model.

• Lumped parameter models are approximations.
Basic models in common use

- Single channel of monolith structure
  - 1D, 2D or 3D
  - Diffusion in the washcoat may be considered

- Whole reactor with variable channel conditions and channel interactions
  - 2D or 3D, several model options exist
  - The upstream and downstream duct work might be included
Single channel model (SCM)

- Single channel of monolith structure
- For a radially uniform monolith, the SCM is representative of the whole reactor
- There are many approaches to writing a single channel model:
  - PDE models (all 2D and 3D models, some 1D)
  - ODE models (some 1D models)
  - Algebraic equations only (some 1D models)
The 3D SCM

• The real monolith does not have axial symmetry.
• The washcoat can have a variety of possible shapes.
• 3D is required for exact channel representation
The 3D SCM

- A minimum of a one-eighth section must be considered.
- For complex shapes such as the “sinusoidal” channel, the entire cross section must be considered.
- There is no analytical solution for the velocity.
- Must solve the transport equations in three dimensions.
The 2D approximate SCM

- The 2D model approximates the channel as a right circular cylinder with a uniform annular washcoat layer, thus giving axi-symmetry.

- The flow area, washcoat area and substrate area should be the same for each system.

- The 2D model is still the most complex model that is used routinely.

- The fully developed flow field can be approximated, thus reducing the number of equations to solve.
2D and 3D SCM

- 2D and 3D SCM are both distributed parameter models.

- Temperature, concentrations and velocities vary with both axial (flow direction) and radial (transverse to flow) directions.

- The most general model requires the solution of a set of coupled non-linear partial differential equations.

- The equations are the same in each case – only the number of space dimensions changes.
The 2D SCM

- All of the physical/chemical processes present in 2D and 3D can be illustrated using a two dimensional model.
Basic solution procedure

• Each physical space (fluid, washcoat and substrate) is a computational domain governed by the conservation equations.

• Write the governing differential equations for each domain (fluid, washcoat and substrate).

• Often only the solid state energy balance equations retain the transient terms, owing to the relative magnitude of the time scales for fluid and solid.
Modelling the fluid domain

Velocity and pressure are obtained from the Navier-Stokes equation and the equation of continuity:

\[
\rho (v \cdot \nabla)v = \nabla \left[ -p I + \eta \left( \nabla v + (\nabla v)^T \right) - \left( \frac{2\eta}{3} - \kappa \right) \nabla \cdot v I \right]
\]

\[
\nabla \cdot (\rho v) = 0 \quad \text{The density depends on temperature.}
\]

The mass balance (assuming Fick’s law) is:

\[
\nabla \cdot (D_A \rho \nabla w_A) - \nu \rho \cdot \nabla (w_A) = 0
\]

The energy balance is:

\[
\nabla \cdot \left( k_f \nabla T \right) - \left( \rho C_p \right)_f \nu \cdot \nabla T = 0
\]

Species conservation should be expressed in terms of the mass fraction because mass is conserved.
Observations

• The fluid equations are very classical and can be readily solved.

• The mass and energy balances are coupled to the washcoat at the gas solid interface.

• A zero slip condition is usually imposed at the gas solid interface and a zero velocity boundary condition imposed.

• One mass balance equation needed for each species.
Modelling the washcoat domain

- The washcoat is a porous matrix containing solid and fluid fractions.
- The diffusion/reaction occurs in the fluid fraction, which is comprised of a network of tortuous pores.
- It is too complicated to model the actual diffusion in the porous network (and the structure is unknown in any case).
- Diffusion is thus assumed to occur across the entire matrix and is governed by an effective diffusion coefficient, with a Fickian type of approach.
Washcoat balance equations:

The mass balance equations are solved for the washcoat:

\[ \nabla \cdot \left( (D_{\text{eff}})_A \rho \nabla w_A \right) - (-R_A) = 0 \]

One mass balance for each species

The energy balance is:

\[ \nabla \cdot \left( k_{\text{eff}} \nabla T \right) + (-\Delta H_R) (-R_A) = \left( \rho C_p \right)_S \frac{\partial T}{\partial t} \]

Normally the momentum balance equation is not solved in the washcoat.
Diffusion in the washcoat

- Diffusion in the pore is governed by a combination of bulk diffusion (molecular collisions) and Knudsen diffusion (collisions of molecules with the wall).
- The relative importance of the two depends on the gas pressure and the pore size.
- The effective diffusion coefficient is then computed by adjusting for catalyst porosity and tortuosity.
- For a real catalyst with a given pore size distribution, the calculation of effective diffusion coefficients is not obvious.
Diffusion in the washcoat

- For binary eqi-molar counter diffusion of molecules A and B we write, for the diffusion of A:

$$D_{AB} = 0.01013 \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5} \frac{T^{1.75}}{P} \left( \left( \sum_{i} v_{i} \right)_{A}^{0.333} + \left( \sum_{i} v_{i} \right)_{B}^{0.333} \right)$$

$$\left( D_K \right)_A = 48.5 d_p \sqrt{\frac{T}{M_A}}$$

**Knudsen diffusion**

$$\left( D_{eff} \right)_A = \left( D_{pore} \right)_A \frac{\varepsilon}{\tau}$$

**Effective diffusion coefficient in the washcoat**
Modelling the substrate domain

The energy balance is:

$$\nabla \cdot (k_{\text{eff}} \nabla T) = \left( \rho C_p \right)_S \frac{\partial T}{\partial t}$$

The substrate is a porous medium and is modelled using effective properties.
Remarks: 2D and 3D models

- The basic equations are the same for 2D and 3D models.

- Solution can be done using commercial or custom software. 3D models will take much longer to solve.

- Normally, a finite element or finite volume method will be used.

- For steady state models, the substrate equations can be eliminated.
Comparing 2D and 3D models

- The channel reconfiguration can cause model differences.

Reactant concentration at two temperatures in a washcoat fillet.
Comparing 2D and 3D models

Reactant concentration in a complex shape
Comparing 2D and 3D models

• The following light-off simulations show some comparisons between 2D and 3D models.

• 2D model uses a circular washcoat and a circular substrate (circle/circle)

• 3D model 1 uses a circular washcoat in a square substrate (circle/square)

• 3D model 2 uses a square washcoat in a square substrate (square/square).

Comparing 2D and 3D models

Inlet temperature ramp rate of 30 K/min at a GHSV of 20 000 h\(^{-1}\) and 80 000 h\(^{-1}\).

Inlet temperature ramp rate of 300 K/min at a GHSV of 80 000 h\(^{-1}\).

The 1D SCM approximation

- 2D and 3D models can be time consuming to run and may not be necessary.
- The radial dimension is eliminated using radial average properties. The model is transformed into a lumped parameter model in the radial direction.
- Parameter lumping introduces a discontinuity at the gas solid interface which is handled using mass and heat transfer coefficients.
- The washcoat and substrate are collapsed into a single one dimensional equation.
Review of boundary layer flow

Flow over a flat plate with exothermic reaction at the surface:

Boundary layers develop for velocity, temperature and concentration.

The boundary layer thickness increases with length

The boundary layers have different thickness:

\[
\frac{\delta}{\delta_C} = Sc^n \quad \frac{\delta}{\delta_T} = Pr^n \quad \frac{\delta_T}{\delta_C} = \frac{Sc^n}{Pr^n}
\]
The heat transfer at the surface is:

\[ q'' = -k \frac{\partial T}{\partial y}_{|y=0} \]

The heat transfer can be defined as:

\[ q'' = h(T_S - T_\infty) \]

The heat transfer coefficient \( h \) assumes a value to make the equality true. If the temperature gradient at the surface is known, then \( h \) can be calculated.
Boundary layers in a tube

- At the entrance, boundary layers grow from the surface.
- After the entry length, the boundary layers meet.
- The fully developed region can be considered a boundary layer flow.
- For laminar flow in a tube, the velocity, temperature and concentration fields can be obtained from the solution of the governing PDE.

With reaction at the wall, the concentration boundary layer development is similar.
Heat transfer in a tube

- In a tube, the flow becomes *fully developed* after an entry length.

- There is no well defined reference temperature external to the boundary layer, and therefore the heat transfer coefficient is defined in terms of the mixing cup temperatures (average radial temperature).

- The mass transfer coefficient is defined in a similar way.
Heat and mass transfer

- Heat and mass transfer coefficients can be expressed in terms of dimensionless groups, the Nusselt and Sherwood numbers.

- For a circular tube:

\[ \frac{hD}{k} = Nu \quad \frac{k_mD}{D_A} = Sh \]

- The heat and mass transfer coefficients can be calculated by solving the 2D or 3D flow problems.
1D SCM: Model equations

- The form of the equation depends on the channel geometry and the basis for the reaction rate:

- Example is shown for a circular tube with the rate expressed in terms of washcoat volume:
1D SCM mass balances

The fluid phase mass balance expressed in terms of the mixing cup concentration and the mass transfer coefficient is:

$$\frac{\partial}{\partial z} \left( D_A \rho_f \frac{\partial w_{A,f}}{\partial z} \right) - \left( \rho_f v \right) \frac{\partial w_{A,f}}{\partial z} - k_m \rho_f \left( w_{A,f} - w_{A,S} \right) \left( \frac{4}{D_H} \right) = 0$$

The axial diffusion coefficient is now a dispersion coefficient.

The velocity is an average velocity.
1D SCM mass balances

The solid phase mass balance is:

\[
\frac{4D}{\left( D_{WC}^2 - D^2 \right)} k_m \rho_f \left( w_{A,f} - w_{A,S} \right) = \eta \left(-R_A \right)_S
\]

Washcoat diffusion is included via the effectiveness factor.

The rate here is evaluated at the surface temperature and concentration.

The rate is expressed in terms of washcoat volume.
1D SCM energy balances

The fluid phase energy balance is:

\[
\frac{d}{dz}\left(k_f \frac{dT_f}{dz}\right) - \nu_m \left(\rho C_p\right)_f \frac{dT_f}{dz} + \frac{4}{D} h \left(T_S - T_f\right) = 0
\]

The fluid thermal conductivity is an effective value that accounts for laminar flow.

The solid phase energy balance is:

\[
\frac{\partial}{\partial z}\left(k_s \frac{\partial T_S}{\partial z}\right) - \frac{4D}{(D_s^2 - D^2)} h \left(T_S - T_f\right) - \eta(\Delta H_R) \left(\frac{D_{WC}^2 - D^2}{D_s^2 - D^2}\right) (-R_A)_s = \left(\rho C_p\right)_s \frac{\partial T_S}{\partial t}
\]

The solid thermal conductivity is an average value for washcoat and substrate.
Nusselt and Sherwood numbers

• The correct values of Nu and Sh are not obvious.

• In the fully developed region, the heat and mass transfer coefficients are constant. The value depends on the wall boundary condition.

• The classical boundary conditions are constant wall temperature and constant wall flux.

• With a reaction on the surface, neither boundary condition is true.
Nusselt and Sherwood numbers

• For flow in a circular tube with constant physical properties, the classical result is:
Nusselt and Sherwood numbers

- Equations for the local Nu for Pr=0.7 with combined entry length have been proposed. They can be expressed generically as:

\[
\text{Nu} = C_1 \times \left[ 1 + C_2 \sqrt{Gz} \exp\left(-\frac{50}{Gz}\right) \right]
\]

The constants depend on channel shape and wall boundary condition.

The value with reaction is found by interpolation between the values for constant wall temperature and constant wall flux.:

\[
2\text{Nu} = \text{Nu}_H - Da \frac{\text{Nu}_H}{\text{Nu}_T} + \sqrt{\left(\text{Nu}_H - Da \frac{\text{Nu}_H}{\text{Nu}_T}\right)^2 + 4Da \text{Nu}_H}
\]
Nusselt and Sherwood numbers

• However, when the properties are not constant, the entry length can be more complicated:

Local Nusselt number obtained from entry length solutions for laminar flow in a channel with different wall temperature. No reaction.

More, MSc Thesis, University of Alberta, 2007
Nusselt and Sherwood numbers

- So, what should we choose for the correct value?
- On the bright side, for circular channels, it might not be that important:

Axial conversion for a typical monolith channel for CO oxidation.

More, MSc Thesis, University of Alberta, 2007
Nusselt and Sherwood numbers

- However, for non-circular channels, or non-uniform washcoat, the Nu and Sh can vary around the washcoat perimeter.

Sherwood number along the washcoat/channel interface for the case of a circular channel in a square substrate. Interface length shown corresponds to 1/8th of the total interface. Fully developed flow.

Comparing 1D and 2D models

- 1D models can give very close agreement to 2D models in many situations.

- Generally the most difficult region to map exactly will be the developing flow region, but that length is often not significant.

Several studies in the literature comparing 1D and 2D models, e.g. Groppi and Tronconi, Aiche Journal 1996.
Simplified 1D models

• Dispersion in the gas phase is sometimes ignored, and plug flow assumed.

• If axial conduction in the solid phase is ignored, the model can be reduced to an initial value problem.

• With these two assumptions, the channel can be modelled as a finite number of stirred tanks in series.
The effectiveness factor

Because the washcoat thickness is not explicitly modelled, the washcoat diffusion is incorporated using an effectiveness factor, defined as:

\[ \eta = \frac{\text{Average reaction rate in washcoat}}{\text{Rate evaluated at surface conditions}} \]

The effectiveness factor can be estimated from a sub-model that usually involves solving a 1D diffusion-reaction problem. Washcoat geometry effects may be included.

Models for the converter

• In reality the channels in the converter may not all have the same operating conditions.

• The substrate constrains the velocity and concentrations to each channel, but heat transfer can occur among the channels.

• A model of the entire converter may therefore be required. There are two general methods for modelling a converter:
  – Discrete models
  – Continuum models
Discrete converter models

- In a discrete model both the fluid and solid domains are solved:

End view of a quarter section of a circular monolith with imposed temperature gradient.

Heat transfer occurs through a combination of gas and solid with very different properties.

Hayes et al., Catalysis Today, 2009
Discrete converter models

- A passenger car converter has about 7 – 10 thousand channels.

- Laboratory tests often use 1-2” diameter cores with 300 – 1200 channels.

Discretizing the entire physical space result in a problem too large to solve by conventional means. Until new methods are proven typically use ….
Continuum converter models

- Classical porous media models treat the domain as a continuum containing fluid and solid phases.
- The common term for developing the resulting equations is called volume averaging – the balances are made on a representative elemental volume that contains both fluid and solid.
- Each node in the computational domain represents both a fluid and a solid – the spatial identity is lost.
- The conservation equations are then fairly classical:

Momentum balance equation

Velocity and pressure are obtained from the Volume Averaged Navier-Stokes equation and the equation of continuity:

\[
\rho (v \cdot \nabla) v = \nabla \cdot \left[ -p I + \eta \left( \nabla v + (\nabla v)^T \right) - \left( \frac{2\eta}{3} - \kappa \right) (\nabla \cdot v) I \right] + S_i
\]

\[
\nabla \cdot (\rho v) = 0
\]

The velocity is the superficial velocity.

The source term \( S \) accounts for the porous inertia.

\[
S_i = -\left( \frac{\mu}{K} v_i + C_2 \frac{1}{2} \rho_f |v| v_i \right)
\]

\( K \) is the permeability.

For laminar flow, the second term is zero.

The Brinkman equation is a classical version of the VANS.
Energy and mass balances

• There are two main classes of porous media models.
  
• Heterogeneous model:
  – The fluid and solid temperatures and concentrations are taken to be different. The two phases are coupled using heat and mass transfer coefficients.

• Pseudo-homogeneous model
  – The fluid and solid temperatures and concentrations are taken to be the same. This situation corresponds to infinitely large heat and mass transfer coefficients.

For transient simulations the heterogeneous model is recommended.
Energy balances

The fluid phase energy balance is:

\[ \phi \rho_f C_{P,f} \frac{\partial T_f}{\partial t} + \rho_f C_{P,f} \mathbf{v} \cdot \nabla T_f = \nabla \cdot \left( k_{\text{eff},f} \nabla T_f \right) - h a_v (T_f - T_S) \]

The solid phase energy balance is:

\[ (1 - \phi) \rho_S C_{P,S} \frac{\partial T_S}{\partial t} = \nabla \cdot \left( k_{\text{eff},S} \nabla T_S \right) + h a_v (T_f - T_S) + \sum_{i=1}^{m} (\Delta H_R)_i \eta(R_i) \]

The effective thermal conductivity for each phase depends on the porosity and material properties.

see Hayes et al., Catalysis Today 2009
Mass balances

The fluid phase mass balance is:

\[ \frac{\partial}{\partial t}\left( \rho_f w_{i,f} \right) + \rho_f \vec{v} \cdot \nabla w_{i,f} = \nabla \cdot \left( \phi \rho D_{i,m} \nabla w_{i,f} \right) + k_m a_v \rho_f \left( w_{i,f} - w_{i,s} \right) \]

Mass diffusion occurs only in the flow direction

The solid phase mass balance is:

\[ 0 = \eta_i R_i + k_m a_v \rho_f \left( w_{i,f} - w_{i,s} \right) \]

Washcoat diffusion is included via the effectiveness factor
Continuum model

- In effect, the continuum model solves a set of 1D single channel models with channel coupling via solid phase heat transfer.

- However, every channel is not modelled.

- Heat and mass transfer coefficients are the same as used in the 1D SCM.

- The continuum model consists of a set of coupled PDE, which are solved using the FEM or the FVM.
Example: 3D reverse flow Condor\textsuperscript{TM} converter

3D heterogeneous model. 10 litre converter for methane IC engine with reverse flow. Fluent was used, dual zone model.

Model validation

• All models must be validated for:
  - (1) Coding (errors in model implementation)
  - (2) Numerical errors
  - (3) Simplifying assumptions

• Models can be validated by
  - Comparison to experiments
  - Analytical solutions

• No model can be completely validated.
Model validation - Example

- Oxidation of methane in air
- Reactor wall temperature measured along reactor length
- Step changes in methane concentration
- Kinetics determined in separate experiments
- 2D single channel model with washcoat diffusion
Model validation - Example

Heating curve with step increase in methane concentration  
Cooling curve when methane switched off

Concluding remarks

• An appropriately chosen model can provide a useful design aid.

• Models can be used as a tool to investigate the phenomena occurring in the reactor.

• Recognize the limitations imposed by the simplifying assumptions.

• Good values for the physical properties are essential.
R.E. Hayes and S.T. Kolaczkowski

Introduction to Catalytic Combustion

Taylor and Francis, 1997