Aalto University
School of Engineering

Heat and mass transfer in the condensed phase

MaCFP workshop 11. June 2017, Lund
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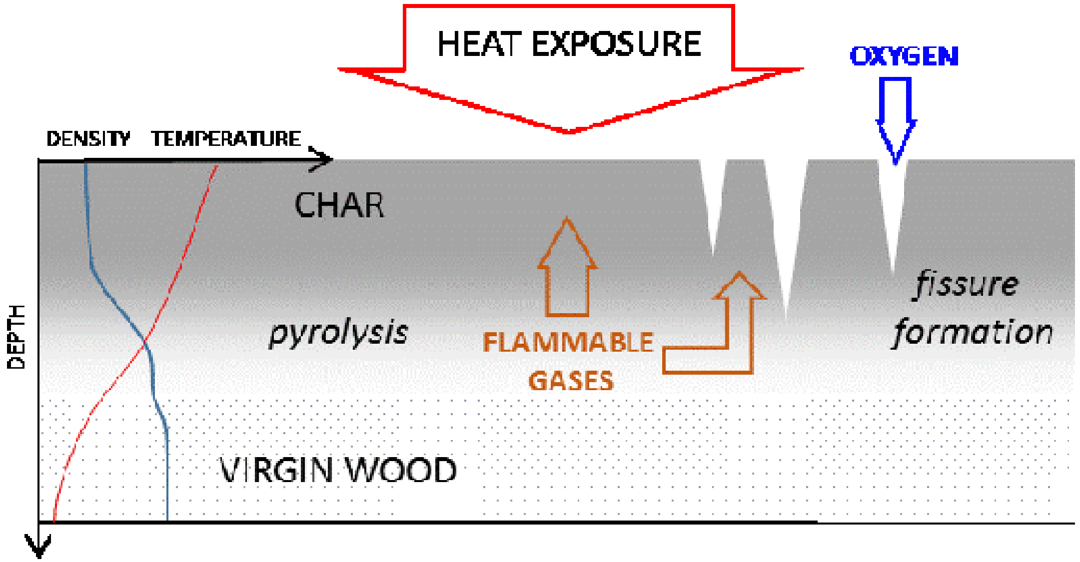
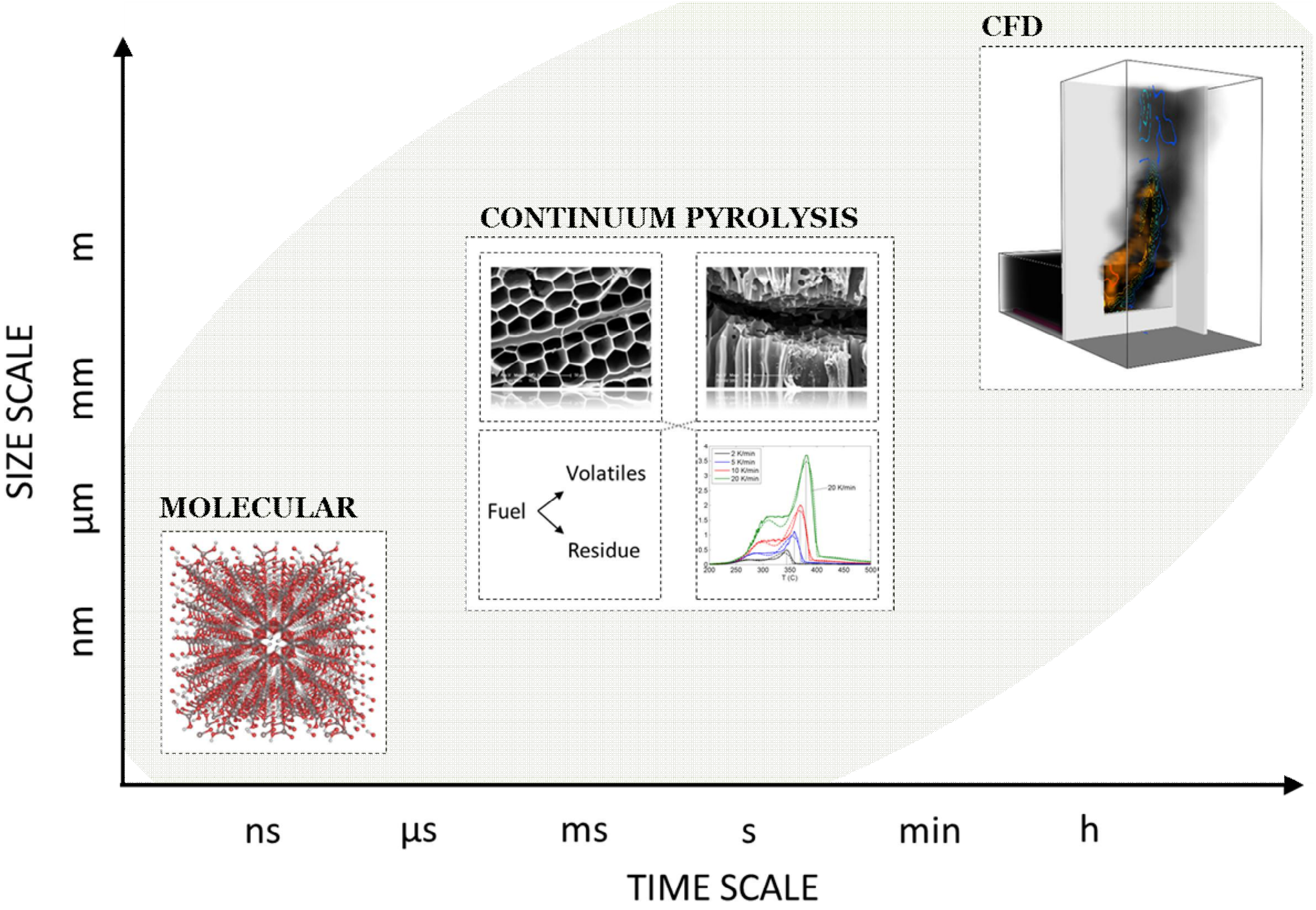
Outline

1. **Governing equations**
2. **FDS Pyrolysis model**
3. **Special topics and challenges**
4. **Possible MaCFP topics**

Classical research scenario



Scales of pyrolysis modelling



GOVERNING EQUATIONS

Condensed phase species conservation

$$\frac{\partial \rho_{s,\alpha}}{\partial t} + \nabla \cdot \left(\mathbf{u} \rho_{s,\alpha} \right) = S_{s,\alpha}$$

- Condensed phase = solid which does not move $\Rightarrow$ **u** = 0

$$\frac{\partial \rho_{s,\alpha}}{\partial t} = S_{s,\alpha}$$

- Conservation of total mass as a sum of components.

Gas species conservation

$$\frac{\partial \phi \rho_{g,i}}{\partial t} + \nabla \cdot \left(\mathbf{u}\rho_{g,i}\right) + \nabla J_i = S_{g,i}$$

- Porosity ϕ prescribed or solved
- Fickian diffusion $\Rightarrow$ $\nabla J_i = -\nabla \phi D_i \nabla \rho_{g,i}$
- No accumulation of gaseous components $\Rightarrow$

$$\nabla \cdot \left(\mathbf{u}\rho_{g,i}\right) = S_{g,i}$$

Condensed phase energy conservation

- Neglecting the kinetic and potential energy and the external work

$$\frac{\partial}{\partial t}\left(\rho_s h\right)+\nabla\cdot\mathbf{q}_c+\nabla\cdot\mathbf{q}_{rad}=\dot{Q}'''_{s-g}+\dot{Q}'''_{chem}$$

- Solve radiation from separate equation $\Rightarrow$ consider as a source/sink.
- Combine with mass conservation $\Rightarrow$

$$\rho_s c_s\frac{\partial T}{\partial t}=\nabla\left(k\nabla T\right)+\dot{Q}'''_{s-g}+\dot{Q}'''_{chem}+\dot{Q}'''_{rad}$$

Gas phase energy and momentum

Gas phase energy conservation

- Assuming unity Lewis number and transparent gas

$$\frac{\partial}{\partial t}\left(\rho_g \phi h_g\right) + \nabla \cdot \mathbf{u} h_g = \nabla \cdot \left(\rho_g \phi D \nabla h_g\right) - \dot{Q}'''_{s-g} + \dot{Q}'''_{chem}$$

Gas phase momentum conservation

- Needed for finite mass fluxes and pressure calculation
- Darcy’s law, no gravity

$$\mathbf{u} = -\frac{B}{\mu}\nabla P$$

- Pressure evolution by combining this with continuity and ideal gas law

Chemical reaction source term

- Source term consists of the heat of pyrolysis (reaction) at reference temperature and the difference between the heat capacities between original material and the products

$$\dot{Q}'''_{chem} = \sum_{\alpha=1}^{N_{species}} \sum_{\beta=1}^{N_{reac}} \dot{m}'''_{\alpha,\beta} \left[\Delta H_r + \int_{T_{ref}}^{T} c_\alpha dT - \sum_{i=1}^{N_{prod}(\beta)} \nu_{\beta,i} \int_{T_{ref}}^{T} c_{g,i} dT \right]$$

- If we assume that the reaction takes place at the temperature where heat of reaction was determined, this simplifies to

$$\dot{Q}'''_{chem} = \sum_{\alpha=1}^{N_{species}} \sum_{\beta=1}^{N_{reac}} \dot{m}'''_{\alpha,\beta} \Delta H_r$$

FDS PYROLYSIS MODEL

Approximations made in FDS

1. 1D
2. No mass accumulation
3. Instantaneous mass transfer
4. Thermal equilibrium between gases and solids
5. Chemical source term as a heat of reaction

Pyrolysis model equations for FDS

$$\rho_s c_s \frac{\partial T_s}{\partial t} = \frac{\partial}{\partial x}\left(k_s \frac{\partial T_s}{\partial x}\right) + \dot{q}_s'''$$

$$\frac{\partial}{\partial t}\left(\frac{\rho_{s,\alpha}}{\rho_s(0)}\right) = -\sum_{\beta=1}^{N_{r,\alpha}} r_{\alpha\beta} + S_\alpha$$

$$\dot{q}_s''' = \dot{q}_{s,c}''' + \dot{q}_{s,r}'''$$

$$S_\alpha = \sum_{\alpha'=1}^{N_m} \sum_{\beta=1}^{N_{r,\alpha'}} \nu_{\alpha,\alpha'\beta}\, r_{\alpha'\beta} \qquad \text{(where Residue}_{\alpha'\beta} = \text{Material}_\alpha)$$

$$r_{\alpha\beta} = \underbrace{\left(\frac{\rho_{s,\alpha}}{\rho_s(0)}\right)^{n_{s,\alpha\beta}}}_{\text{Reactant dependency}} \underbrace{A_{\alpha\beta}\, \exp\left(-\frac{E_{\alpha\beta}}{RT_s}\right)}_{\text{Arrhenius function}} \underbrace{[X_{O_2}(x)]^{n_{O_2,\alpha\beta}}}_{\text{Oxidation function}}$$

$$\dot{q}_{s,c}'''(x) = -\rho_s(0) \sum_{\alpha=1}^{N_m} \sum_{\beta=1}^{N_{r,\alpha}} r_{\alpha\beta}(x) H_{r,\alpha\beta}$$

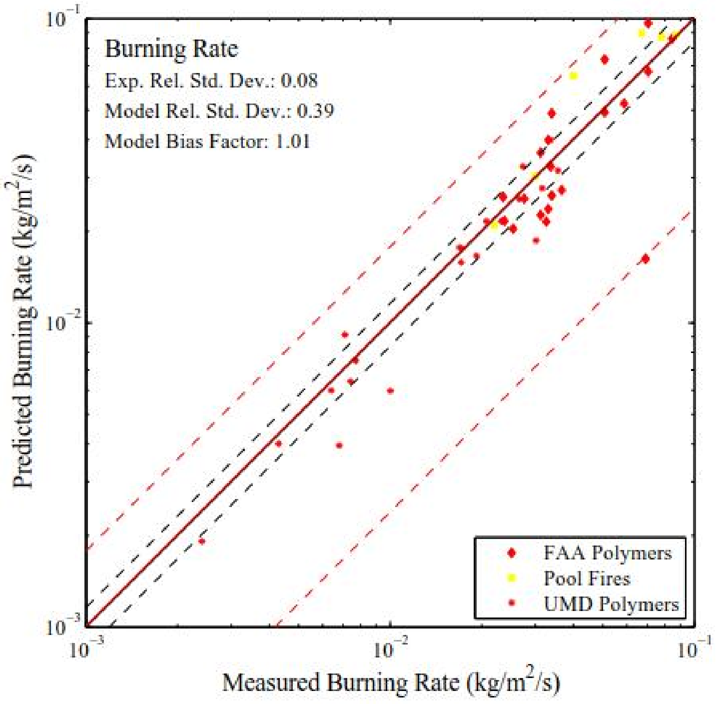
FDS V&V

Verification

- Heat conduction and radiation through a plane layer
- Mass conservation and reaction rate

Validation

- Usually HRRPUA and MLRPUA
- Almost all published studies include model calibration.
- In the FDS Validation Guide: FAA and UMD Polymers have most parameters measured.



SPECIAL TOPICS AND CHALLENGES

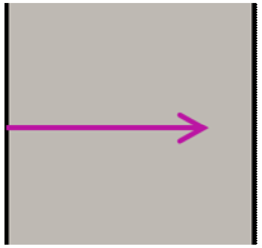
Radiation transfer – models

Effective radiant conductivity of a porous medium

$$\dot{q}_r'' = -\underbrace{\left(4Fd\sigma T^3\right)}_{k_r}\frac{\partial T}{\partial x}$$

Beer-Lambert's law augmented by emission term

$$\frac{\partial q_{in}}{\partial x} = -q_{in}a_s, \qquad \frac{\partial q_{out}}{\partial x} = f(a_s T^4)$$

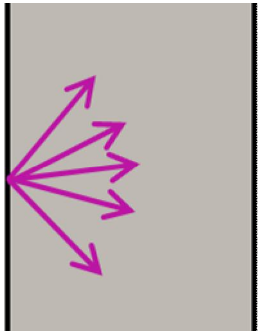


- Unidirectional (normal) boundary condition

Two-flux model

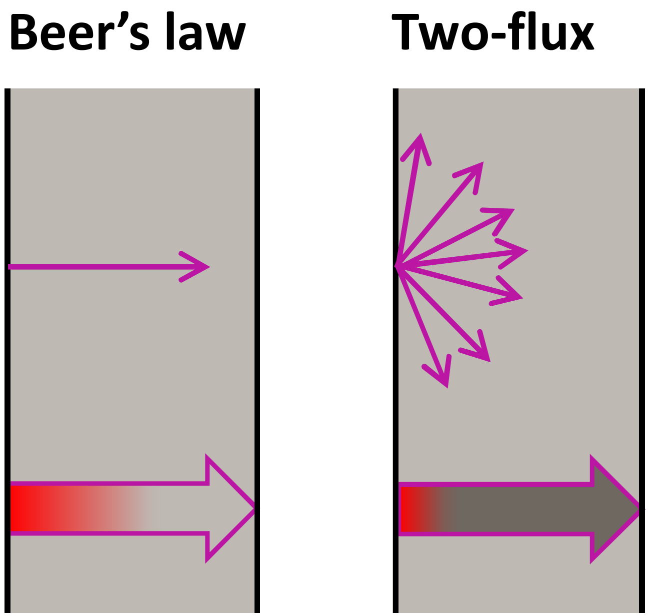
$$\frac{1}{2}\frac{\partial q_{in}}{\partial x} = -(a_s + s_{back})q_{in} \quad + s_{back}q_{out} \quad + a_s\sigma T(x)^4$$

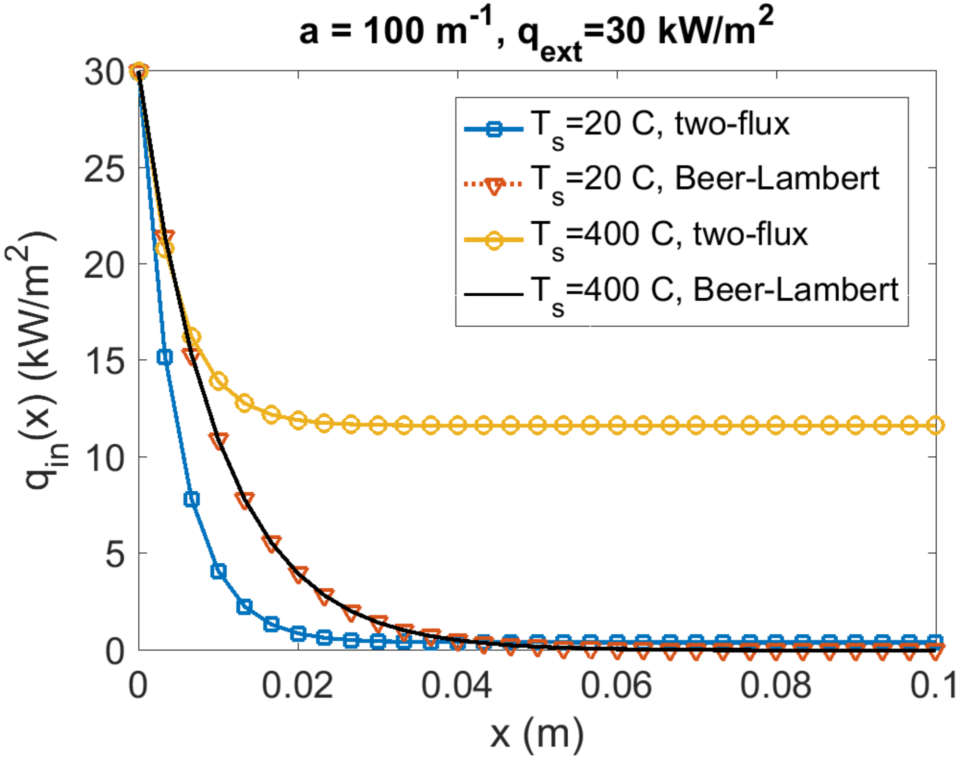
$$-\frac{1}{2}\frac{\partial q_{out}}{\partial x} = -(a_s + s_{back})q_{out} \quad + s_{back}q_{in} \quad + a_s\sigma T(x)^4$$



- Diffuse boundary condition

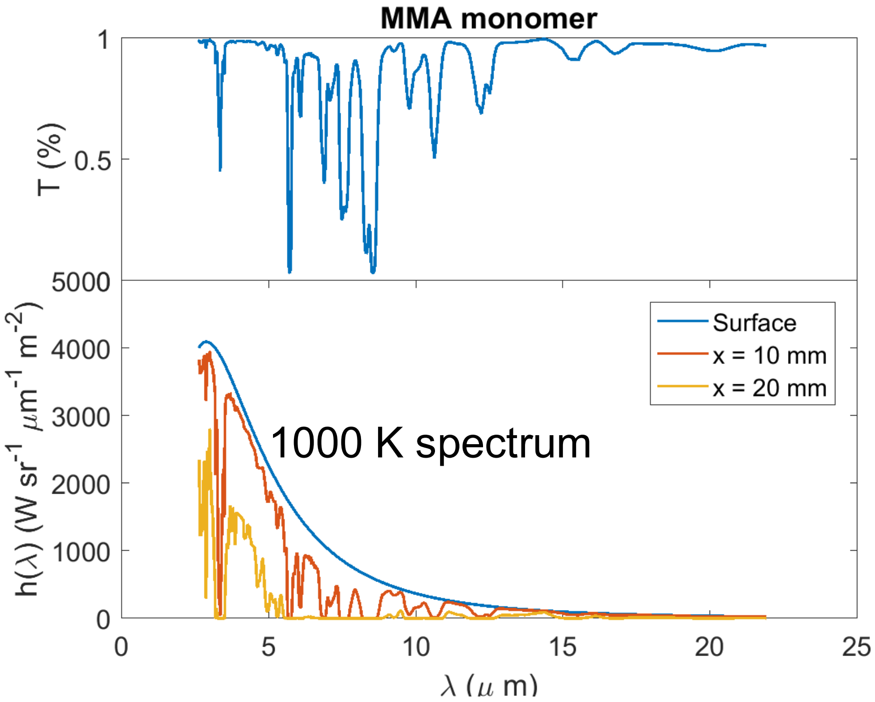
Radiation transfer – model features



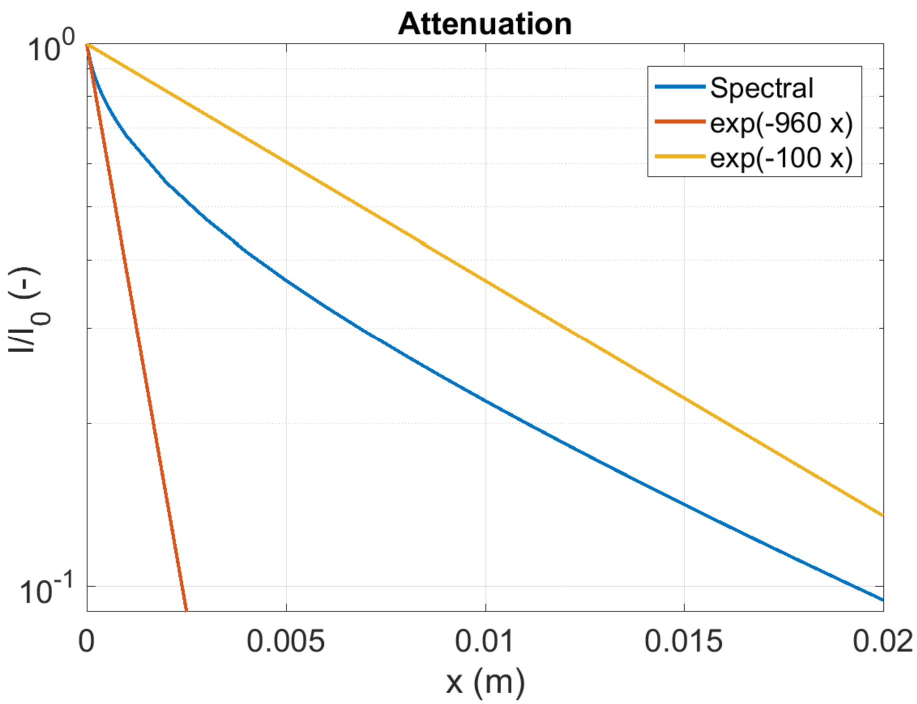


- Beer's law is good when external radiation is unidirectional and internal sources are small.
- Two flux model is good when boundaries are diffuse and internal terms are significant.

Radiation transfer – spectral properties



NIST Chemistry webbook (2017)



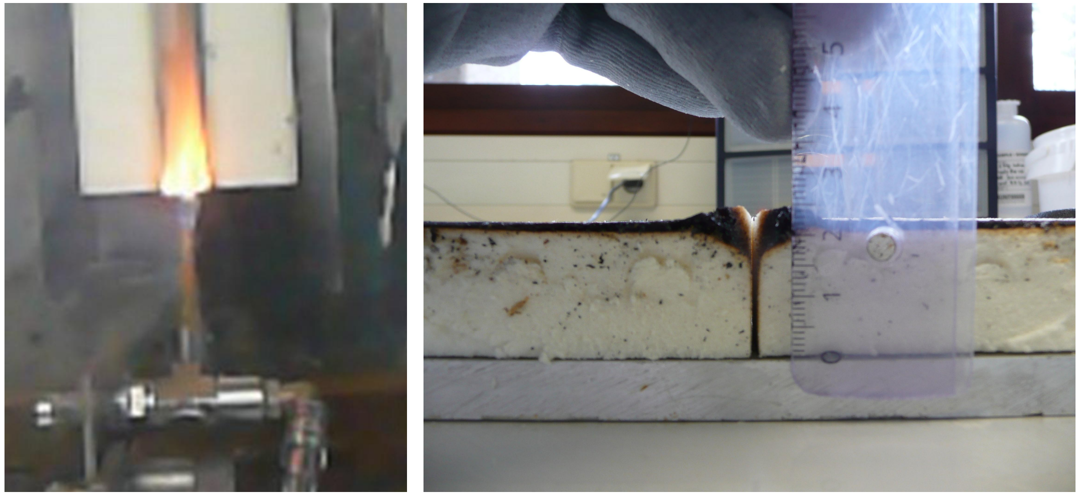
960 m^{-1} from Jiang et al., Fire Safety J 44 (2009)

Data is indicative only. Do not use!

Shrinking / swelling

- **Shrinkage due to the non-charring pyrolysis or the collapse of microstructure**
- **Intumescence has huge impact on conductance.**
    - Important for the heat barrier effect of fire / flame retardant materials.
    - Models are based on the density ratios.
    - Numerical solution schemes very different.
    - Predictive calculation in mixtures with strength-retaining matrix?

Figures: Rigid PU foams by Huntsman Polyurethanes (Europe).



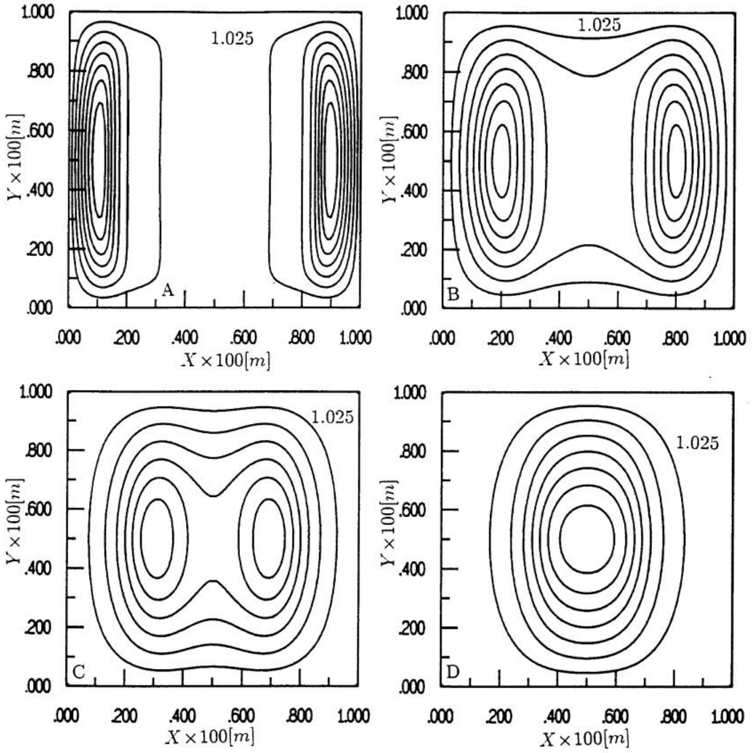
Pressure build-up

Wood

- Contribution to cracking and possibly explosive removal of char[1]
- Modelling studies[2,3] show overpressures up to $p/p_0 \sim 1.2$

Polymer composites

- Role in delamination of layered structures



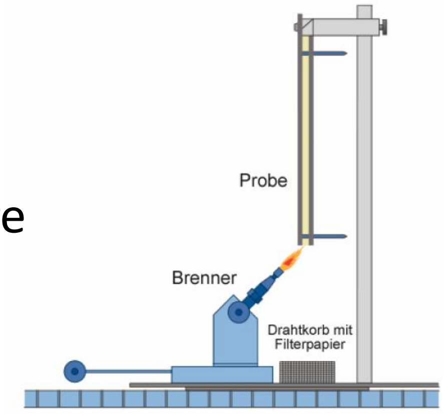
[1] Emmons, H.W. Fire Safety Sci 1 (1986)

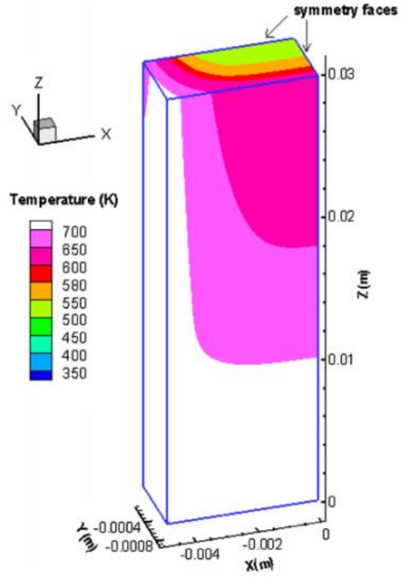
[2] Di Blasi, C. Int. J. Heat Mass Trans 41 (1998)

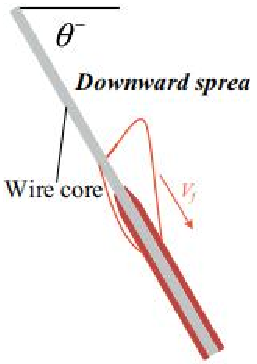
[3] Baum & Atreya, Proc. Comb Inst 31 (2007)

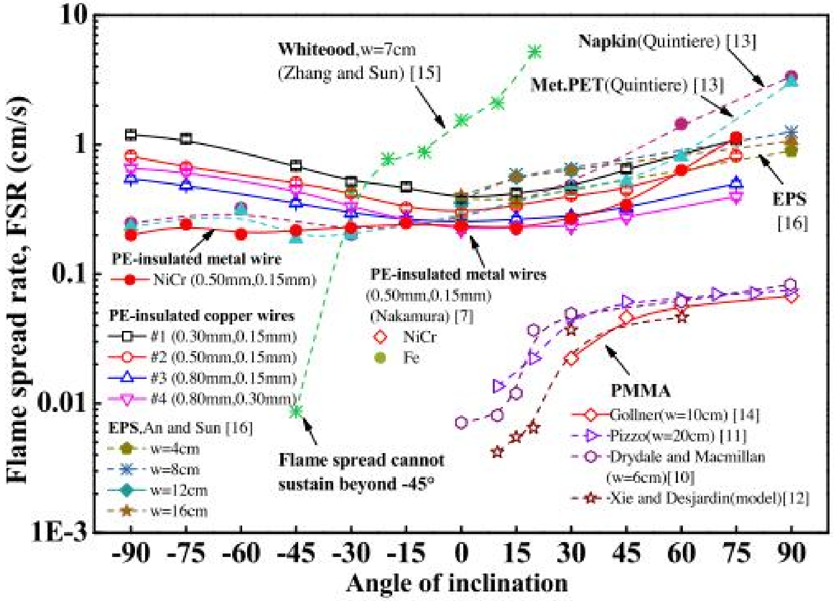
Need for 2D/3D solutions

- **2D/3D geometries**
- **Small-flame simulations**
  - Length scales of the flame exposure and conduction are similar[1].
- **Strongly anisotropic materials**
  - Wood
  - Fibre-reinforced polymer composites
  - Flame spread on electrical wires





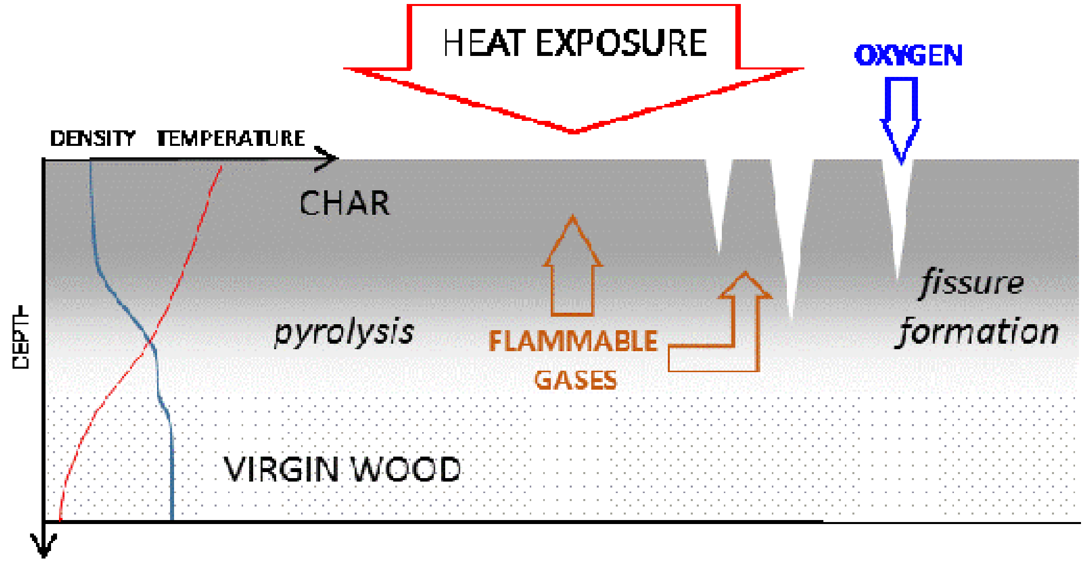




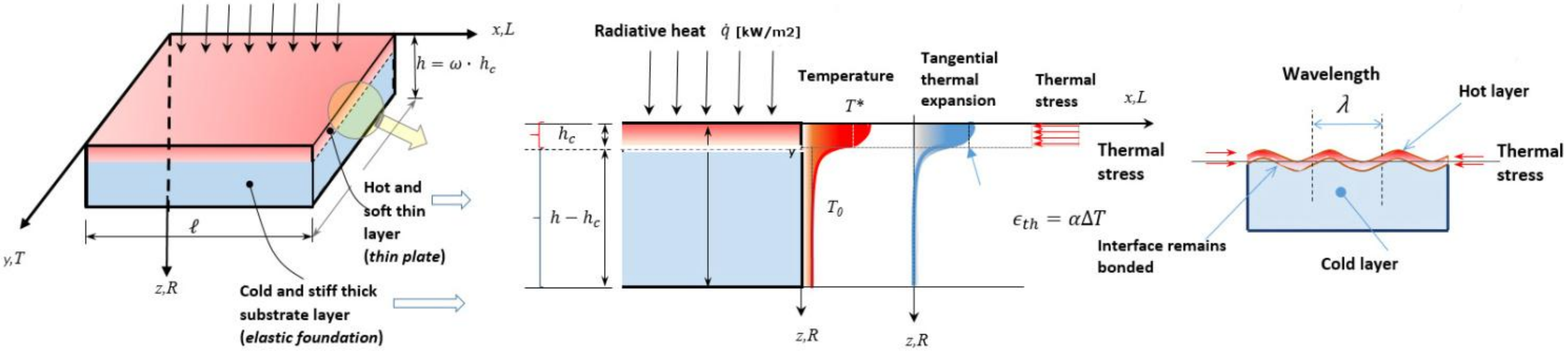
[1] Wang et al. Fire Safety J. 54 (2012)

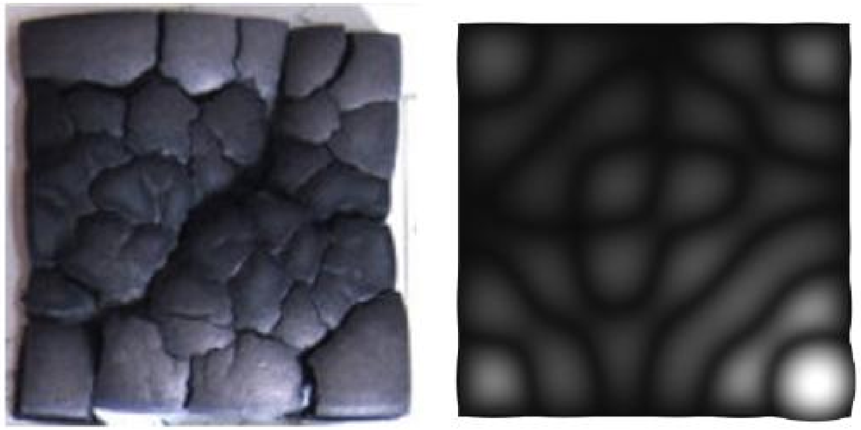
[2] Hu et al. Proc Comb Inst 35 (2015)

Discontinuities and small-scale 3D phenomena

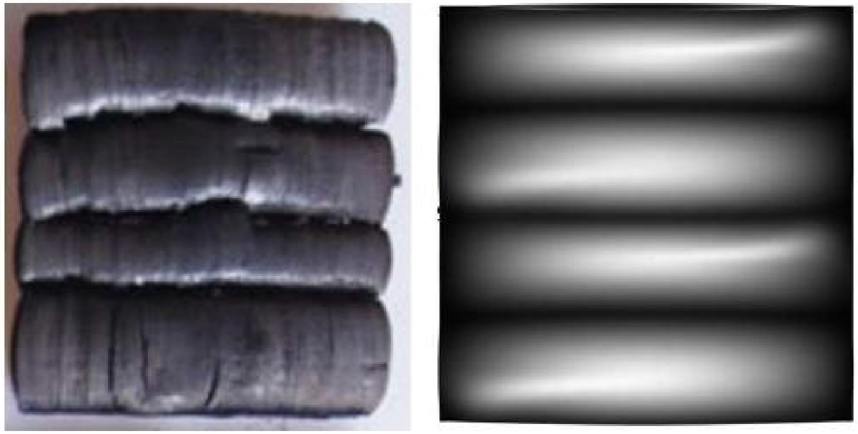


Pyrolysis meets solid mechanics





isotropy (MDF)



orthotropy (FIR)

[1] Baroudi et al. Comb. Flame 182 (2017)

[2] Li et al. IAFSS 12 (2017)

Possible MaCFP topics

1D Pyrolysis

- Basic charring / non-charring material tests cases
- Internal gas transfer
- Determination of the heat of reaction
- Intumescense
- Internal radiation distribution and spectra

2D / 3D Pyrolysis

- Role of 2D/3D conduction in flame spread
- Anisotropic gas transfer
- Coupling with CFD and complex geometries
- Coupling of pyrolysis and solid mechanics