Fast Estimation of Reaction Rates in Catalysts and Sorbents

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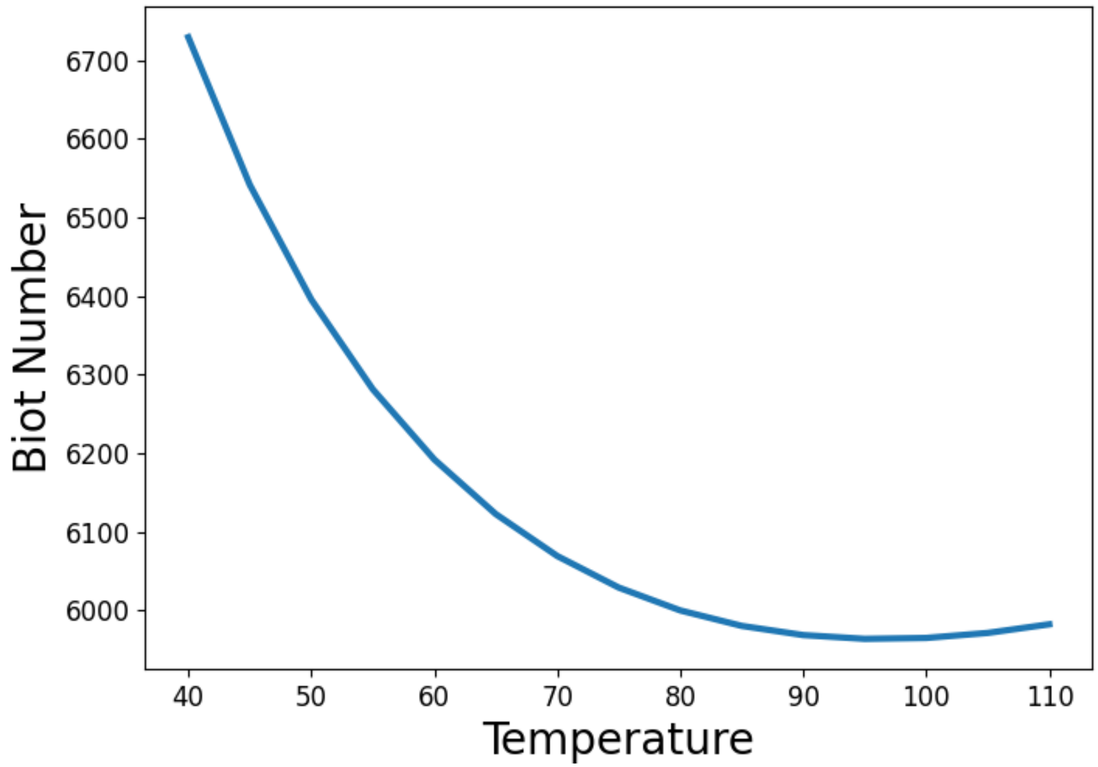
Motivation

- Catalysts
  - Isomerization
  - Hydrogenation
  - Catalytic cracking
  - Chemical looping
- Sorbents
  - Separations
  - Sour gas removal
  - Post-combustion carbon capture

A pilot-scale chemical looping reactor at NETL
Source: https://netl.doe.gov/node/7478

Intraparticle Dynamics are Important in Solid Sorbents



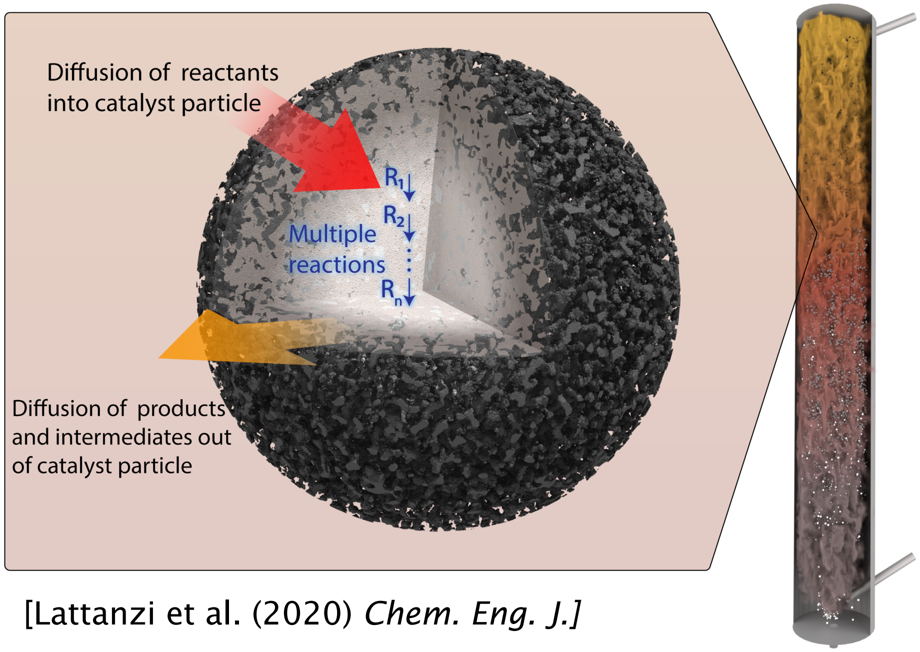
$$\mathrm{Bi}_m = \frac{\text{Surface Mass Transfer Rate}}{\text{Internal Mass Diffusivity}} = \frac{hL}{\mathcal{D}_{\text{eff}}}$$

Objectives

1. Capture intraparticle effects in CFD-DEM without adding additional costs
2. Account for non-spherical effects

A range of industrial catalysts in pellet form
Source: https://en.wikipedia.org/wiki/Catalysis

Outline



[Lattanzi et al. (2020) *Chem. Eng. J.*]

- **Mathematical Framework**
- Particle Geometries
- MEVlib
- FCC example (CFD—DEM)
- Future work:
  CO_2 adsorption

More Details in our 2 Recent Papers

"Beyond the effectiveness factor: Multi-step reactions with intraparticle diffusion limitations"
Lattanzi, A.M., Pecha, M.B., Bharadwaj, V.S., Ciesielski, P.N.
Chemical Engineering Journal, 2020

"Fast estimation of reaction rates in spherical and non-spherical porous catalysts"
Wakefield, J.P., Lattanzi, A.M., Pecha, B., Ciesielski, P.N., and Capecelatro, J.
Chemical Engineering Journal, Submitted, 2022.

MEV – Multi-step Effectiveness Vector

$$\eta = \frac{\text{Observed Reaction Rate}}{\text{Intrinsic Reaction Rate}}$$

Governing Equations Inside the Particle

Consider N reacting species with mass fractions $Y_1, \ldots, Y_N$.

$$\frac{\partial}{\partial t}\left(\epsilon\rho_g Y_i\right) + \nabla\cdot\left(\boldsymbol{u}\epsilon\rho_g Y_i\right) = \nabla\cdot\Big(D_i\nabla\left(\epsilon\rho_g Y_i\right)\Big) + \dot{\omega}_i$$

$$\dot{\omega}_i = -\underbrace{\sum_{j=1}^{N}\psi k_{ij}\epsilon\rho_g}_{\phi_i^2} Y_i + \sum_{j=1}^{N}\underbrace{\psi k_{ji}\epsilon\rho_g}_{\phi_{ij}^2} Y_j$$

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B.C. $\frac{1}{\mathrm{Bi}}\hat{\nabla}Y_i\cdot\mathbf{n} + Y_i = Y_{i,\infty}$

Steady State Equations

$$-\hat{\nabla}^2 Y_i + \phi_i^2 Y_i - \sum_{j=1}^{N} \phi_{ij}^2 Y_j = 0$$

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$$\longrightarrow$$

$$-\nabla^2 \hat{Z} + a^2 \hat{Z} = 0 \quad \text{in } \widehat{\Omega}$$

$$\beta \nabla \hat{Z} \cdot \mathbf{n} + \hat{Z} = 1 \quad \text{on } \partial\widehat{\Omega}$$

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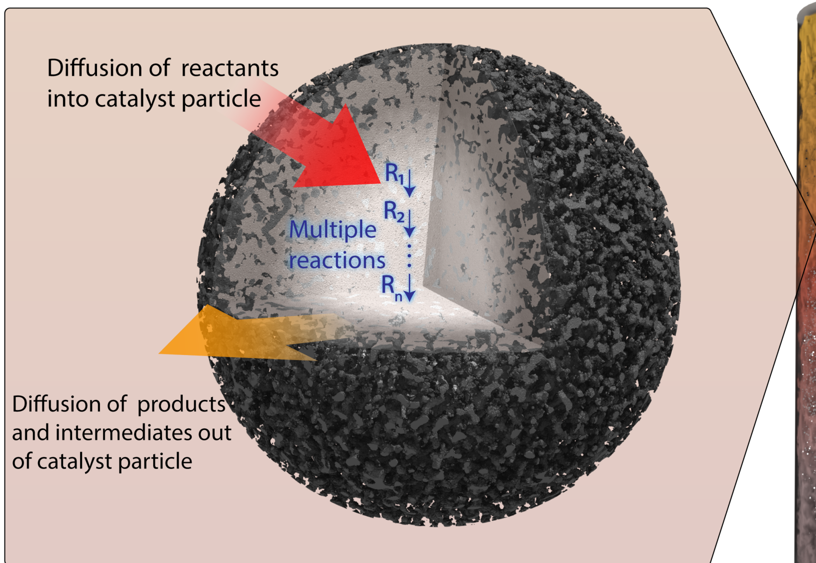
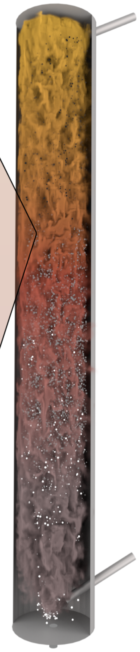
$$\eta = \frac{1}{\mathrm{VOL}} \int_{\Omega} Z \, \mathrm{d}V$$

Outline



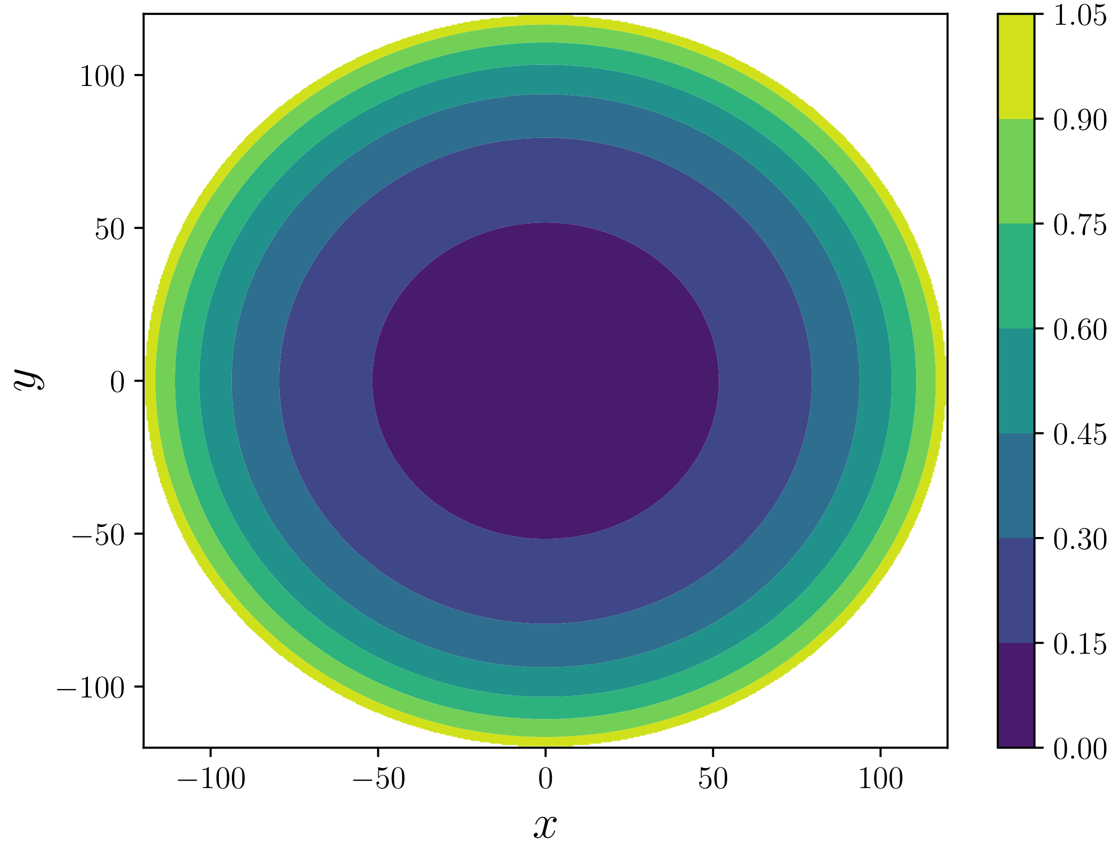
[Lattanzi et al. (2020) *Chem. Eng. J.]*



- Mathematical Framework
- **Particle Geometries**
- MEVlib
- FCC example (CFD—DEM)
- Future work:
  CO_2 adsorption

Sphere

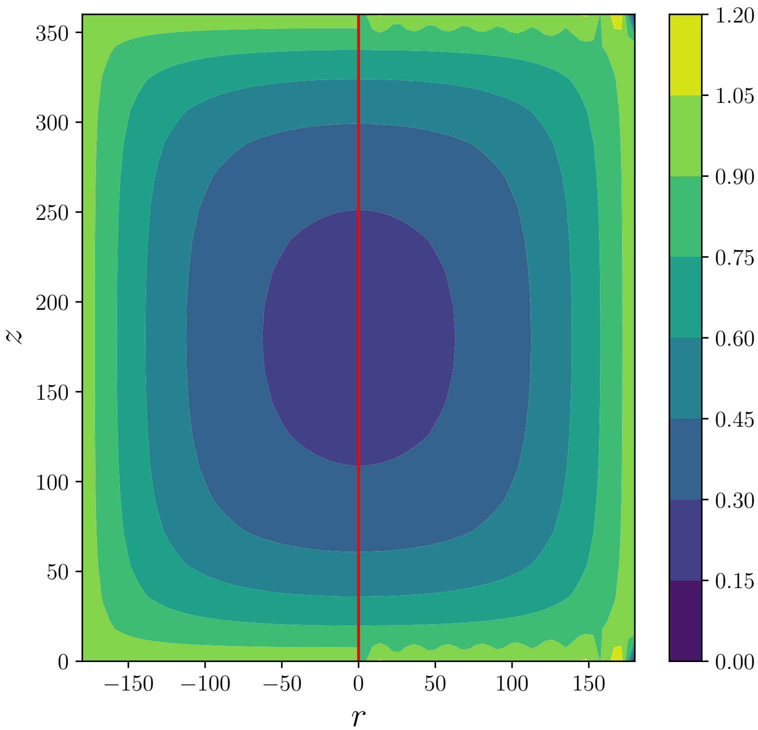
$$\eta = \frac{3}{aR}\left(a\beta + \frac{aR\tanh(aR)}{aR - \tanh(aR)}\right)^{-1}$$

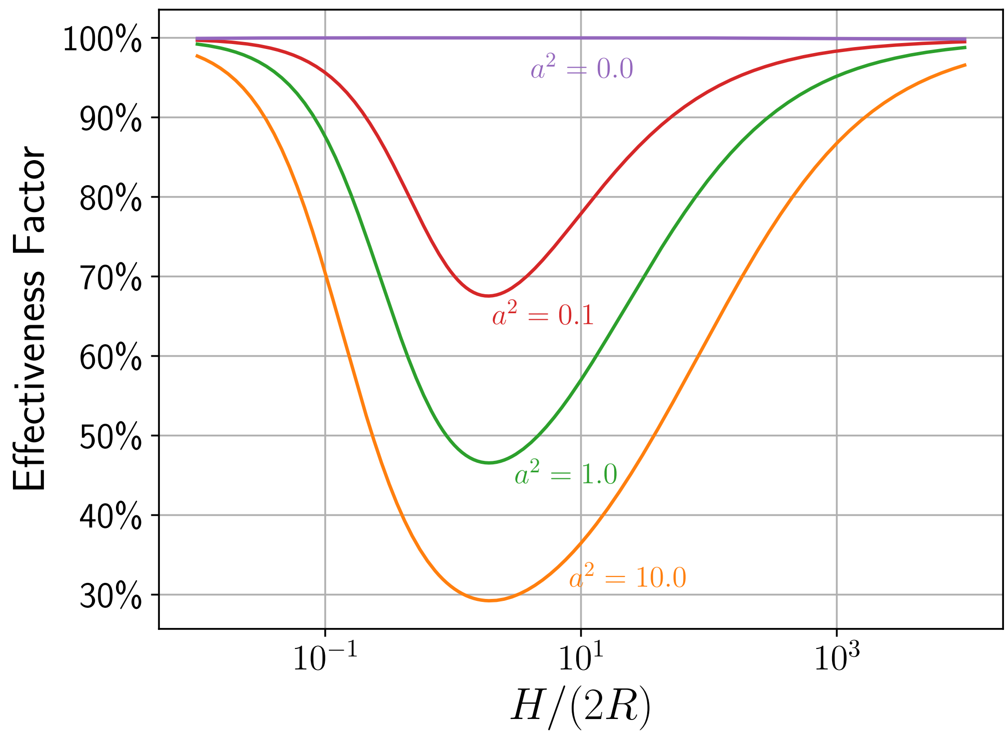


Cylinder

$$\eta = \sum_{n=0}^{N} \frac{16}{\pi^2 R \gamma_n (2n+1)^2} \frac{I_1(\gamma_n R)}{I_0(\gamma_n R)} + \sum_{k=1}^{K} \frac{8}{H \delta_k \alpha_k^2} \tanh\left(\delta_k \frac{H}{2}\right)$$

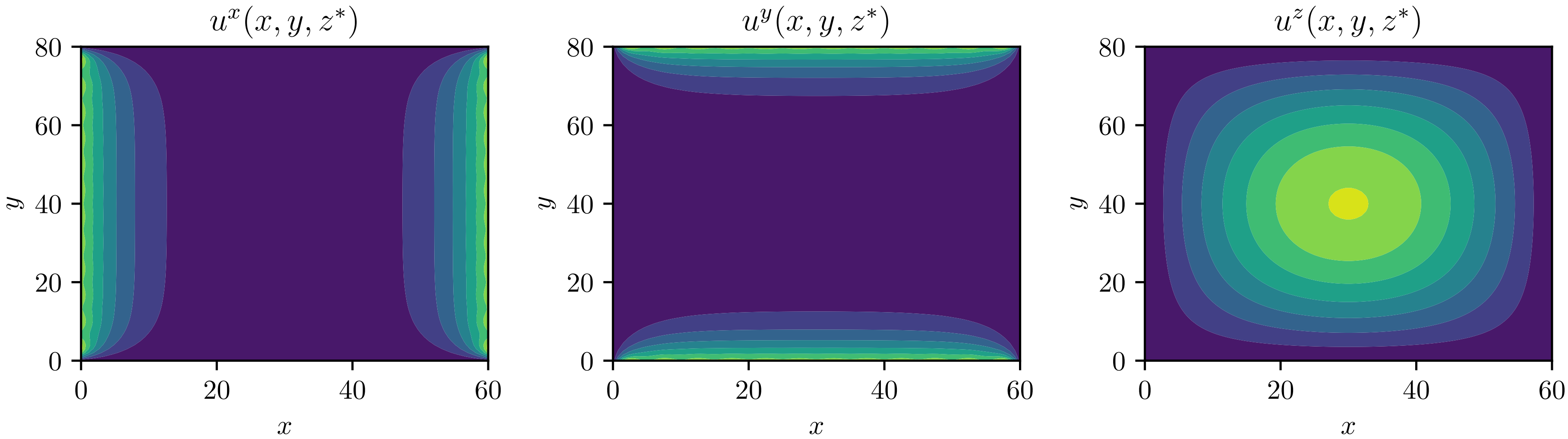
$$\gamma_n = a^2 + \left(\frac{\pi(2n+1)}{H}\right)^2 \qquad \delta_k = a^2 + \left(\frac{\alpha_k}{R}\right)^2$$





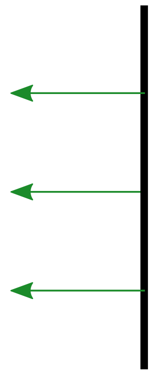
Rectangular Prism

$$\eta = \sum_{m,n} \frac{32}{\beta_{m,n}\pi^4 \ell_{p,x}} \frac{1}{(2m+1)^2(2n+1)^2} \tanh\left(\beta_{m,n}\frac{\ell_{p,x}}{2}\right)$$



Arbitrary Shapes

Half Plane Solution

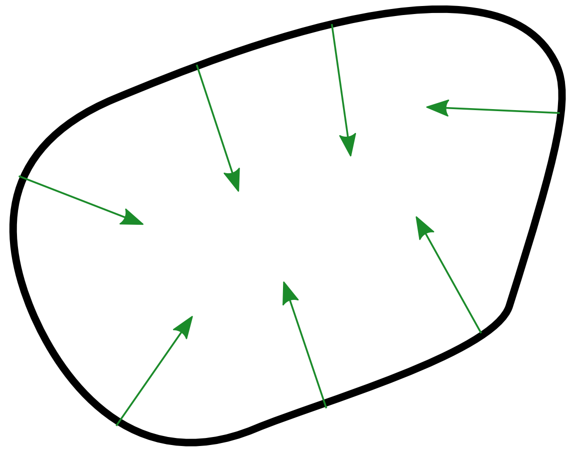


$$-v_{xx} + a^2 v = 0 \quad \text{for } x < 0$$
$$\beta v_x + v = 1 \quad \text{at } x = 1$$

has solution

$$v(x) = \frac{e^{ax}}{1 + a\beta}$$

Surface Area Estimate



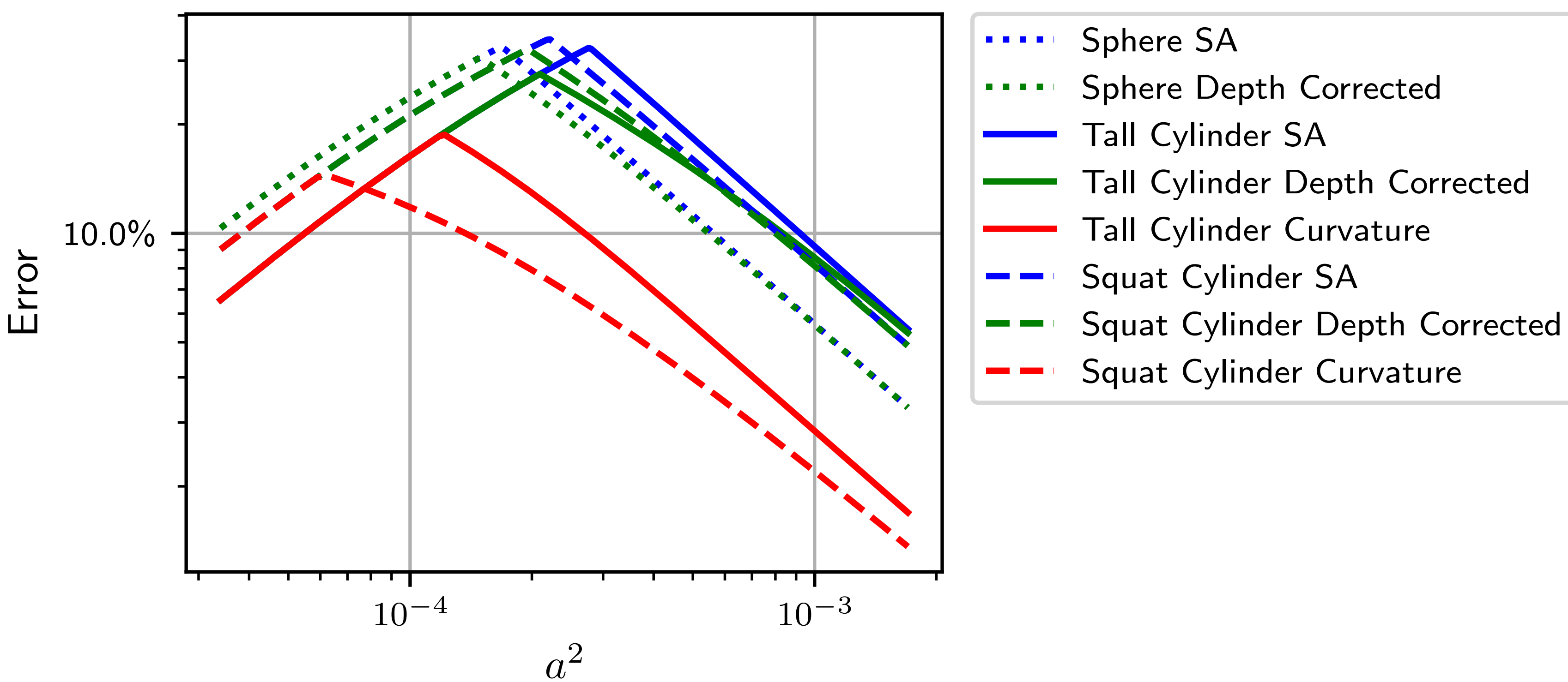
$$\int_\Omega \hat{Z}\, \mathrm{d}V \approx \int_{\partial\Omega} \int_{-\infty}^{0} v(x)\, \mathrm{d}x\, \mathrm{d}S$$

$$= \frac{1}{a(1 + a\beta)} \int_{\partial\Omega} \mathrm{d}S$$

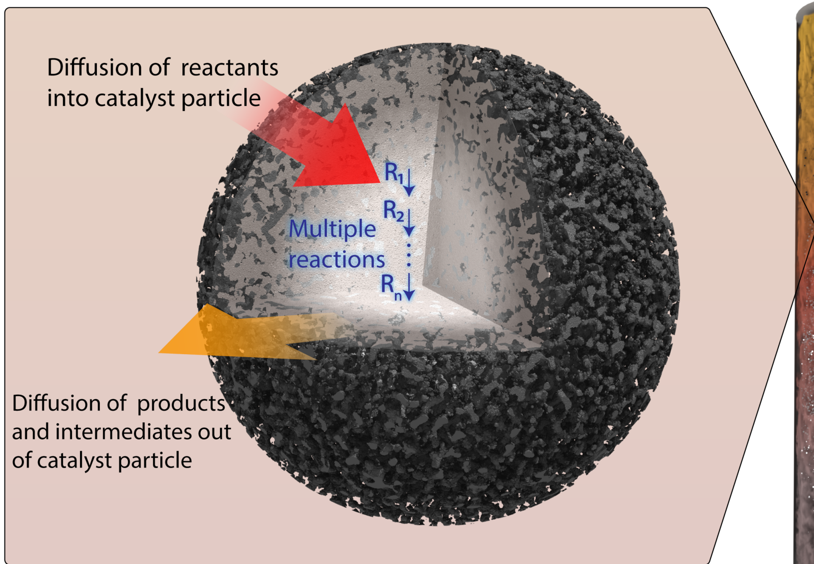
Arbitrary Shapes

Curvature Corrected Estimate

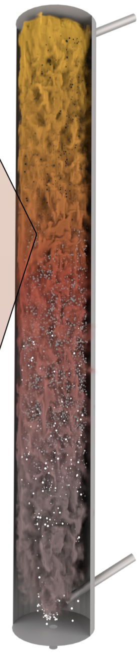
$$\eta = \frac{\mathrm{SA}}{\mathrm{VOL}} I_a\left(\sqrt{\frac{\mathrm{SA}}{4\pi}}\right) \qquad I_a(R) = \frac{1}{(Ra)^2}\left(\beta + \frac{R\tanh(Ra)}{Ra - \tanh(Ra)}\right)^{-1}$$



Outline



[Lattanzi et al. (2020) *Chem. Eng. J.]*



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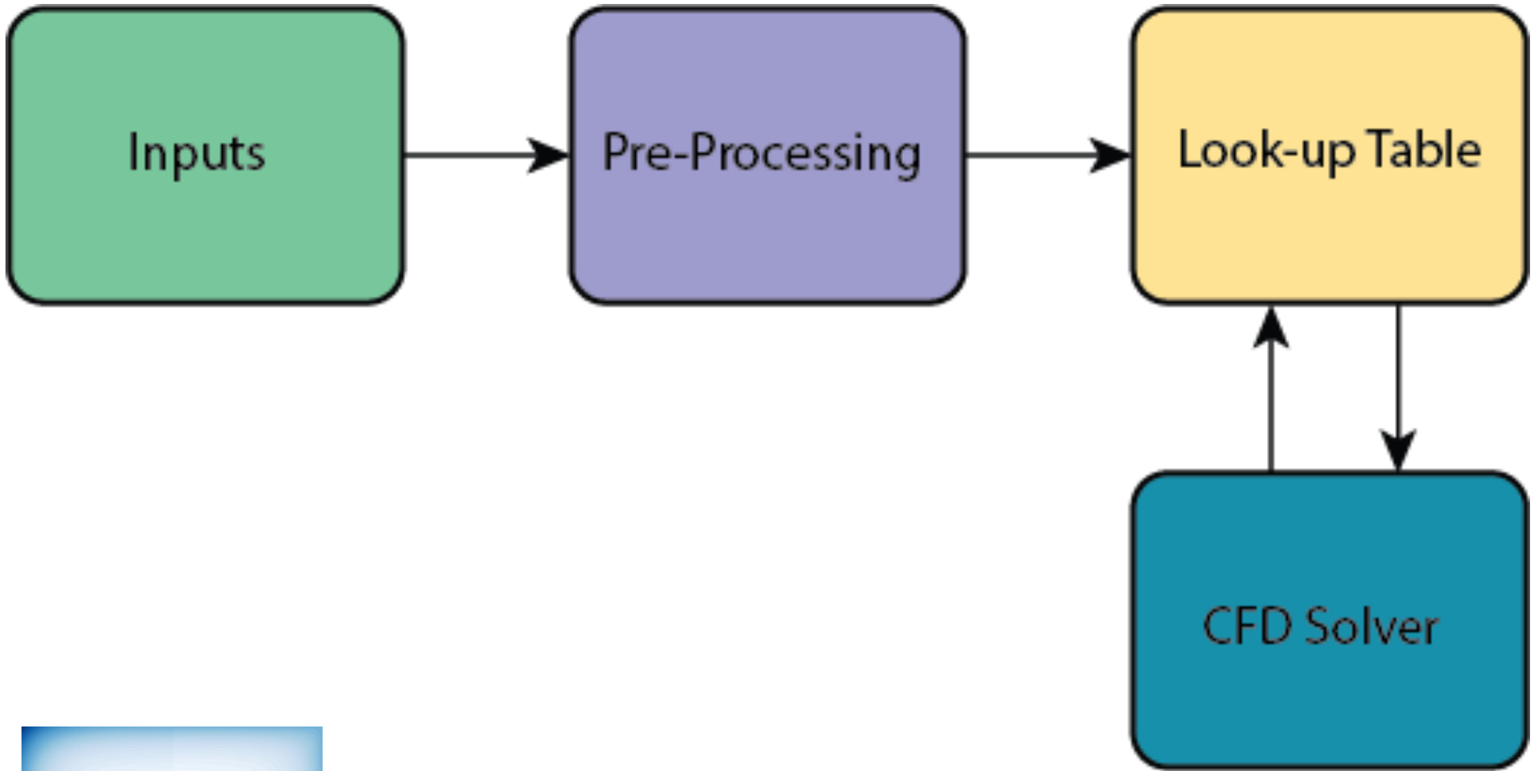
- **FCC example (CFD—DEM)**
- Future work:
  CO_2 adsorption

MEVlib

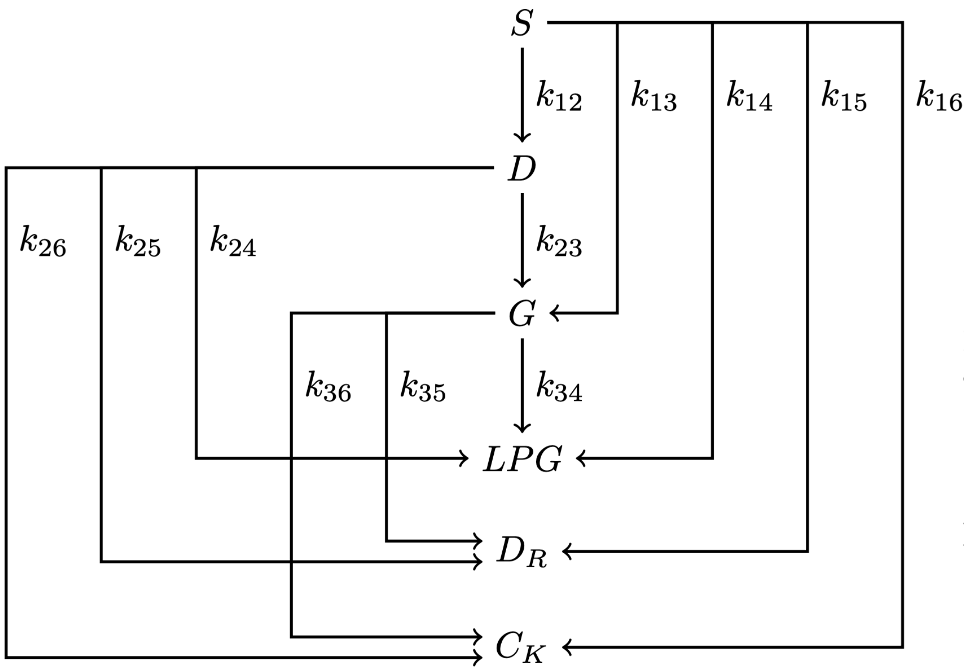


MEVlib

https://github.com/johnpwakefield/mevlib

Fluidized Catalytic Cracking

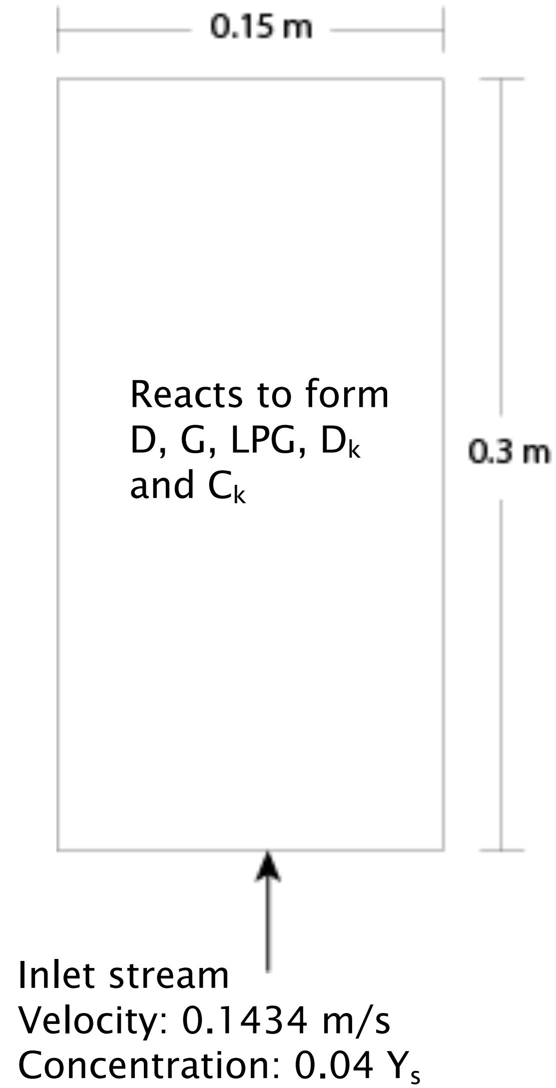
Component	Structure	Lump
Feed Oil	$C_{35}H_{20}$	S
Diesel	$C_{18}H_{14}$	D
Gasoline	C_8H_{18}	G
Liquid Petroleum Gas	C_4H_6	LPG
Dry Gas	CH_4	D_R
Coke	-	C_K



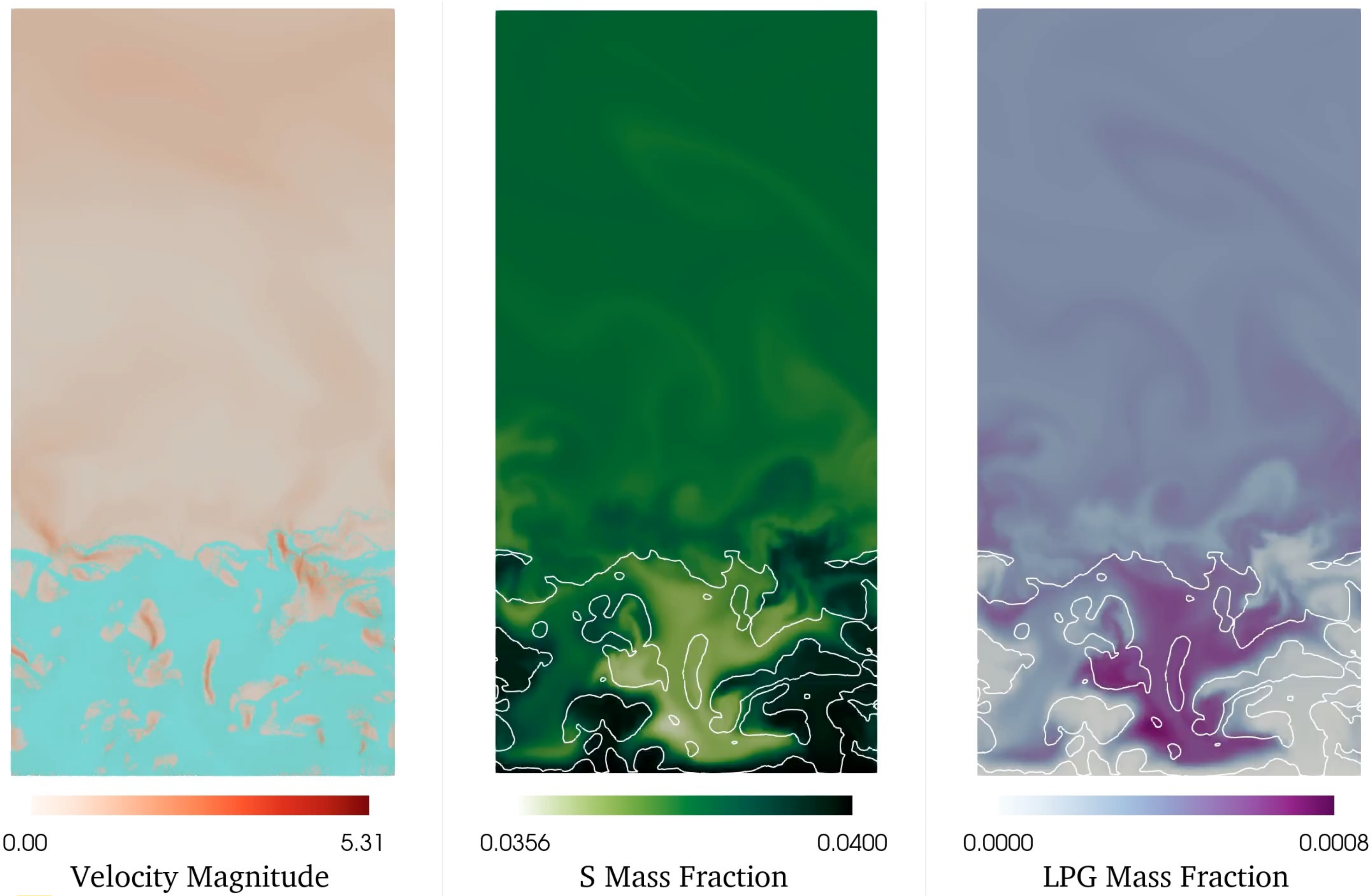
Properties and kinetics from Xiong et al. and Lattanzi et al.

Fluidized Catalytic Cracking

Reactor Specifications	
Solver	NGA with Lagrangian Particle tracking
Reactor	Fluidized Bed
Mesh	384 x 768
Number of Particles	212552



Fluidized Bed Reactor with Intraparticle Reactions



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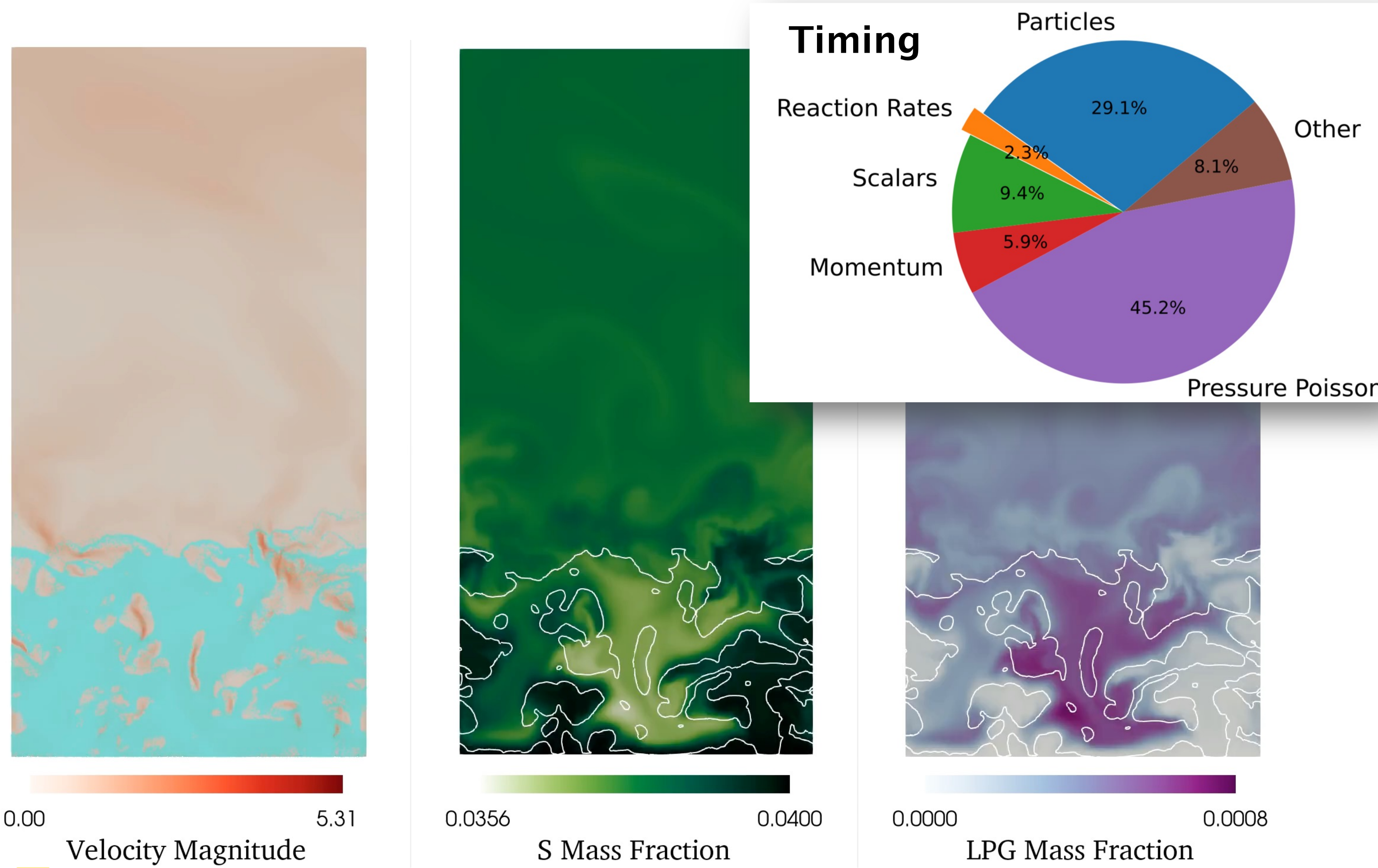

Summary and Future Work

- **MEVlib**
  - Brings together solutions for various shapes
  - Generates look-up tables in a preprocessing step to improve computational efficiency
  - Demonstrated with CFD—DEM
  - Next step: Extend MEVlib to fully support complex reversible reactions

- **Adsorption**
  - Extend the presented framework for post-combustion carbon capture with amine-impregnated sorbent

Questions?

Post-Combustion Carbon Capture

$$\frac{\partial}{\partial t}\left(\epsilon\rho_g Y_i\right) + \nabla\cdot\left(\boldsymbol{u}\epsilon\rho_g Y_i\right) = \nabla\cdot\left(D_i\nabla\left(\epsilon\rho_g Y_i\right)\right) + \dot{\omega}_i$$

$$2\mathrm{R_2NH} + \mathrm{CO_2} \rightleftharpoons \mathrm{R_2NH_2^+} + \mathrm{R_2NCO_2^-}$$

$$R(c,q) = k\left(\left(1 - \frac{2q}{q_s}\right)^2 RTc - \frac{1}{K}\frac{q^2}{q_s^2}\right)$$

$$\varepsilon_s\frac{\partial c}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) - \rho_s R(c,q) \qquad \frac{\partial q}{\partial t} = R(c,q)$$

Governing Equations

$$\frac{\partial c'}{\partial Fo} = \frac{1}{r'^2}\frac{\partial}{\partial r'}\left(r'^2\frac{\partial c'}{\partial r'}\right) - \phi^{*2}(1-2q')^2c' + \frac{\phi^{*2}}{\beta}q'^2$$

$$\frac{\partial q'}{\partial \omega} = (1-2q')^2c' - \frac{q'^2}{\beta}$$

$$\omega = \frac{tkRTc_b}{q_s} \qquad Fo = \frac{D_p t}{\varepsilon_s L^2} \qquad \phi^* = L\sqrt{\frac{\rho_s kRT}{D_p}} \qquad \beta = bc_bRT$$

Analytical Effectiveness Factor

- Driessen et al. make the simplifying assumption

$$\frac{c}{c_b} = \frac{q}{q_{surf}}$$

$$\phi_{ads} = L\sqrt{\frac{\rho_s kRT}{D_p}(1-2q')}$$

$$\eta_{ads} = \frac{3}{\phi_{ads}^2}(\phi_{ads}\coth(\phi_{ads}) - 1)$$