Effectiveness factor estimates for general catalyst geometries

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Diffusion Limitations in Catalyst Particles

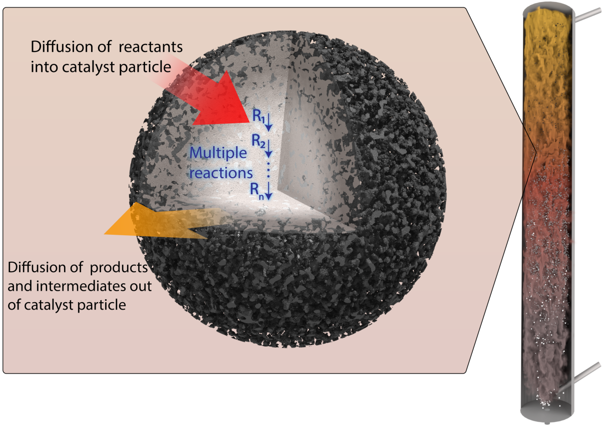


Image from Lattanzi et al, 2021.

- reaction rates are non-trivially temperature dependent
- effective rates may differ substantially from nominal rates
- it is straightforward to use modified reaction rates
- large numbers of particles
- many independent variables
  - particle shape
  - temperature
  - free stream concentration

Governing Equations

$$\cancel{\frac{\partial}{\partial t}(\epsilon\rho_g Y)} + \cancel{\nabla\cdot(\mathbf{u}\epsilon\rho_g Y)} = \nabla\cdot(D\nabla(\epsilon\rho_g Y)) - \underbrace{k\epsilon\rho_g Y}_{\dot{\omega}}$$

$$\nabla Y\cdot\boldsymbol{n} = \mathrm{Bi}\,(Y_\infty - Y)$$

$$\nabla^2 Y - \left(\sqrt{\frac{k}{D}}\right)^2 Y = 0$$

$$\frac{1}{\mathrm{Bi}}\nabla Y\cdot\boldsymbol{n} + Y = Y_\infty$$

- assume a single effective diffusivity D approximates diffusion through pores
- pores are small, so velocity is small and mass transport is diffusion dominated
- the time scale for reactions is small, approximate with the steady state solution

Why effectiveness factors?

If the reaction rate at a point in the particle is

$$\dot{\omega} = k\epsilon\rho_g Y$$

We want the total conversion rate

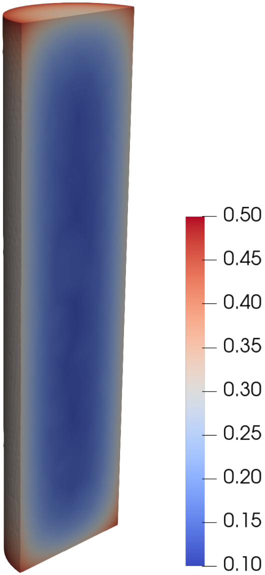
$$\int_\Omega \dot{\omega}\,\mathrm{d}V = k\epsilon\rho_g \int_\Omega Y\,\mathrm{d}V.$$

If we define the effectiveness factor η as

$$\eta = \frac{1}{Y_\infty V_p}\int_\Omega Y\,\mathrm{d}V$$

then the total conversion in the particle is

$$\frac{1}{V_p}\int_\Omega \dot{\omega}\,\mathrm{d}V = \eta\,k\,\epsilon\rho_g\,Y_\infty.$$

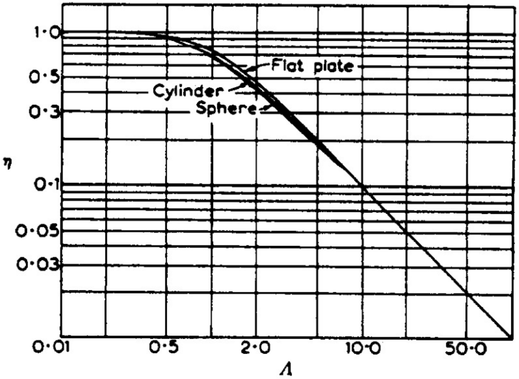


Sphere	$\eta = \frac{3}{ar_p}\left(a\mathrm{Bi}^{-1} + \frac{ar_p \tanh(ar_p)}{ar_p - \tanh(ar_p)}\right)^{-1}$
Cylinder	$\eta = \lim_{N,K\to\infty}\left(\underbrace{\sum_{n=0}^{N}\frac{16}{\pi^2 r_p p_n (2n+1)^2}\frac{I_1(p_n r_p)}{I_0(p_n r_p)}}_{A_N} + \underbrace{\sum_{k=1}^{K}\frac{8}{h_p q_k j_k^2}\tanh\left(q_k\frac{h_p}{2}\right)}_{B_K}\right)$
Rectangular Prism	$\eta = \sum_{d\in\{x,y,z\}}\sum_{m,n}\frac{32}{\beta_{d,m,n}\pi^4\ell_{p,d}}\frac{1}{(2m+1)^2(2n+1)^2}\tanh\left(\beta_{d,m,n}\frac{\ell_{p,d}}{2}\right)$ $\beta_{d,m,n}^2 = a^2 + \sum_{d'\neq d}\left(\frac{\pi(2m+1)}{\ell_{p,d'}}\right)^2$

Dimensional Quantities:

- geometry
  - chords $[L]$
  - volume $[L^3]$
  - surface area $[L^2]$
- k/D $[L^{-2}]$

$$\Lambda_a = 3\frac{V}{S}\sqrt{\frac{k}{D}}$$



Aris 1957

Chemical engineers worry about the *magnitude* of Λ_a rather than the precise value.

We aim to *quantify* the error in η.

Aris (1957)

$$\Lambda_a = \frac{3\,V}{S}\sqrt{\frac{k}{D}}$$

$$\frac{1}{\eta^{\mathrm{a}}} = \frac{1}{\eta_d^{\mathrm{a}}} + \frac{1}{\eta_b^{\mathrm{a}}}$$

where

$$\eta_d^{\mathrm{a}} = \frac{3}{\Lambda_a}\left(\coth \Lambda_a - \frac{1}{\Lambda_a}\right),$$

and

$$\eta_b^{\mathrm{a}} = \frac{3}{{\Lambda_a}^2}\,\mathrm{Bi}_a$$

Burghardt and Kubaczka (1996)

$$\Lambda_b = R_b\sqrt{\frac{k}{D}}$$

$$\frac{1}{\eta^{\mathrm{b}}} = \frac{1}{\eta_d^{\mathrm{b}}} + \frac{1}{\eta_b^{\mathrm{b}}}$$

where

$$\eta_d^{\mathrm{b}} = 2\,\frac{d+1}{\Lambda_b}\,\frac{I_{d+1}(\Lambda_b)}{I_d(\Lambda_b)}$$

and

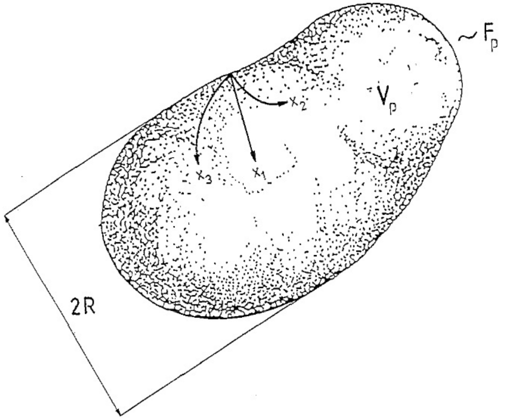
$$\eta_b^{\mathrm{b}} = 2\,\frac{(d+1)\,\mathrm{Bi}_b}{{\Lambda_b}^2}.$$

Burghardt and Kubaczka's Estimate - Inspiration

Bessel Functions

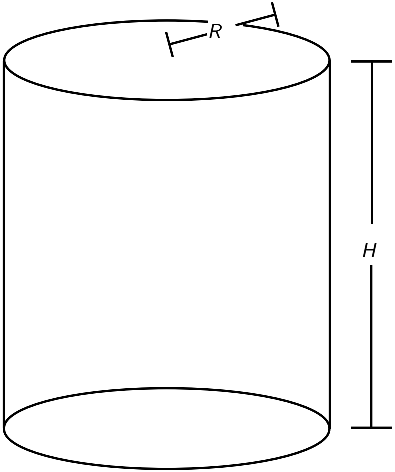
	η
Sphere	$\frac{3}{\Lambda_b}\frac{I_{3/2}(\Lambda_b)}{I_{1/2}(\Lambda_b)}$
Cylinder without Ends	$\frac{2}{\Lambda_b}\frac{I_1(\Lambda_b)}{I_0(\Lambda_b)}$
Slab	$\frac{1}{\Lambda_b}\frac{I_{1/2}(\Lambda_b)}{I_{-1/2}(\Lambda_b)}$
$d = \frac{S}{2\,V}R_b - 1$	$\frac{2(d+1)}{\Lambda_b}\frac{I_{d+1}(\Lambda_b)}{I_d(\Lambda_b)}$?

Effective Radius R_b



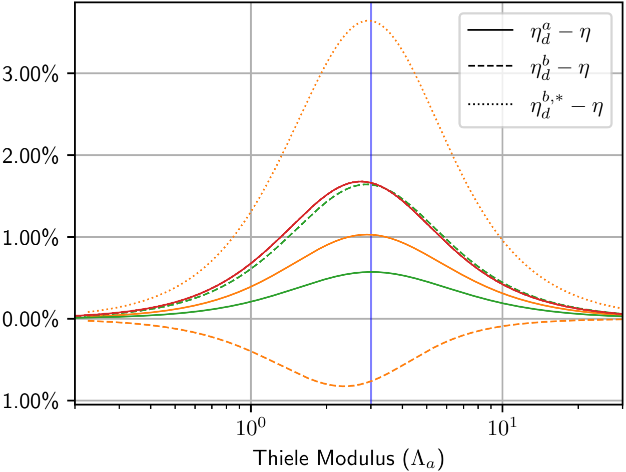
Burghardt 1996

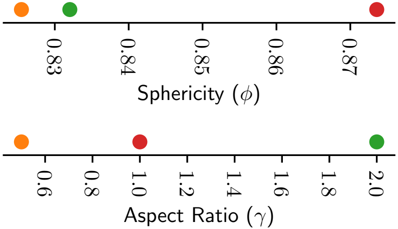
Cylinders



- very common catalyst shape
- aspect ratio $\gamma = \frac{H}{2R}$
- sphericity $\phi = \frac{\sqrt[3]{36\pi V}}{S}$

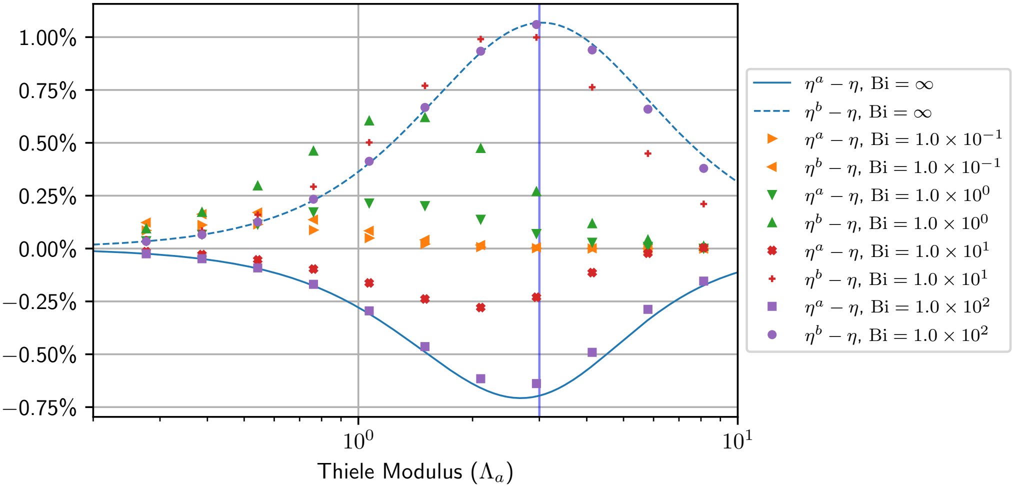
Cylinders at Infinite Biot Number





η_d^{a}	Aris-type
η_d^{b}	Burghardt-type, improved radius
$\eta_d^{\mathrm{b},*}$	Burghardt-type, original radius

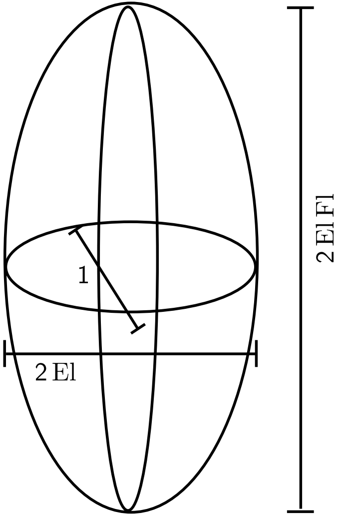
Cylinders, Finite Biot Number, $\gamma = 4$, $\phi \approx 0.734$



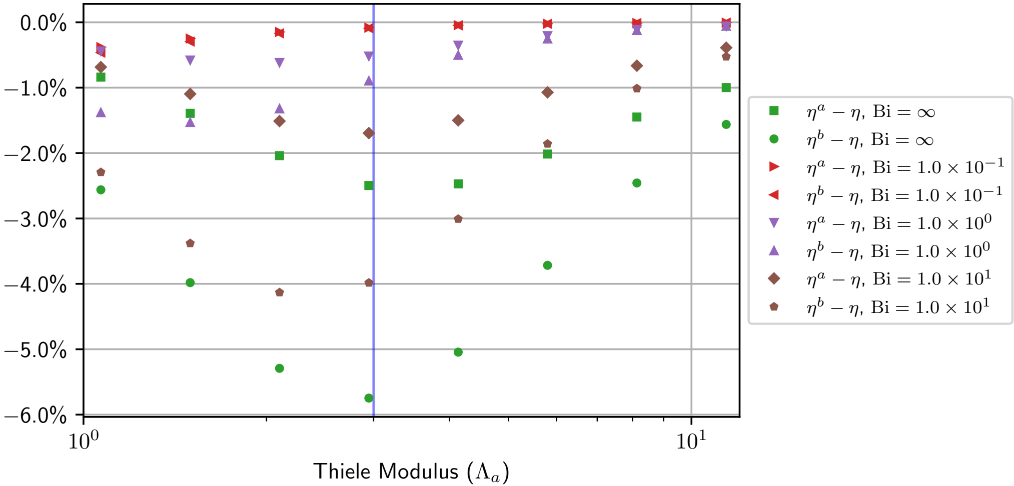
Ellipsoids

- sphere perturbation
- smooth

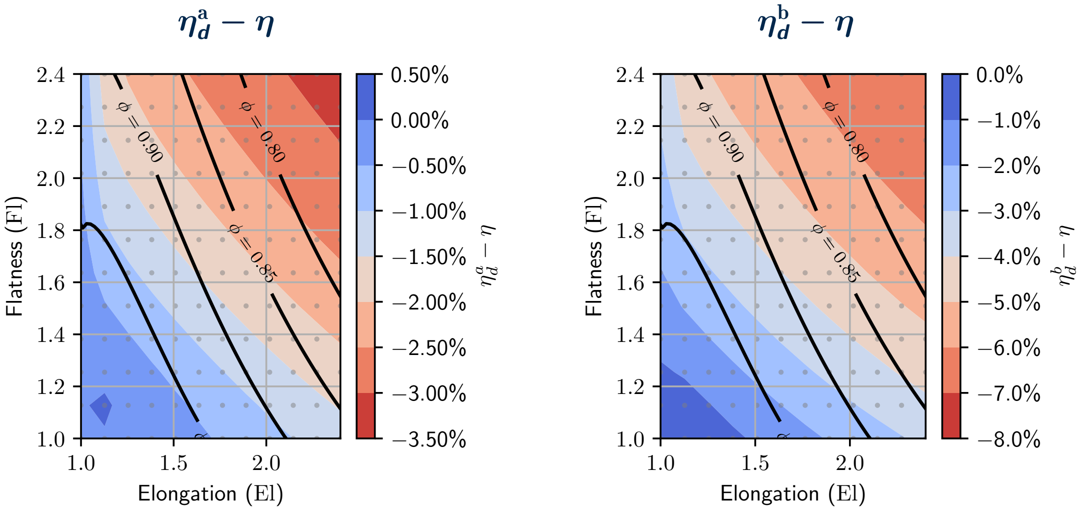
$$x^2 + \left(\frac{y}{\mathrm{El}}\right)^2 + \left(\frac{z}{\mathrm{El}\,\mathrm{Fl}}\right)^2 = 1$$



$\mathbf{El} = 2,\ \mathbf{Fl} = 2,\ \phi \approx 0.812$



Does error correlate with sphericity?



What about a general shape?

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Short communication

A simple method for particle shape generation with spherical harmonics

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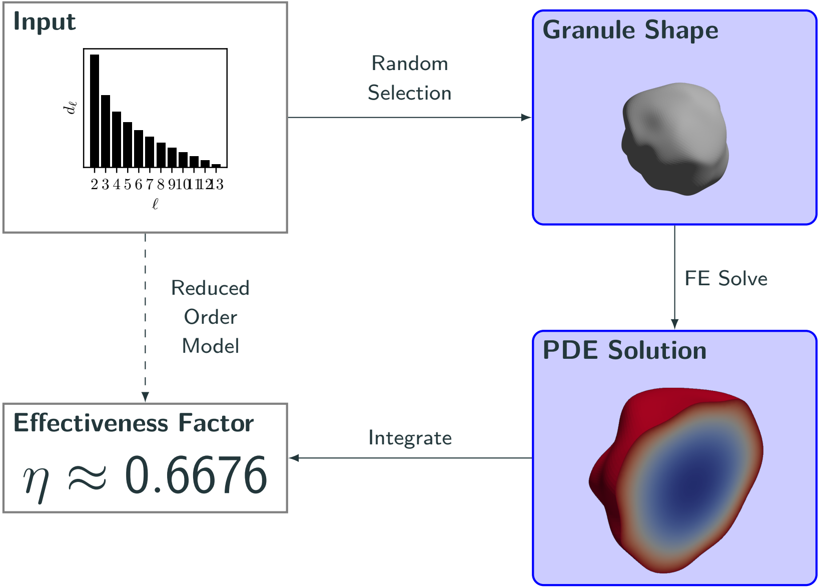
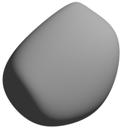
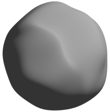
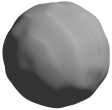
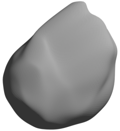
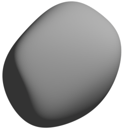
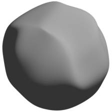
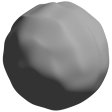
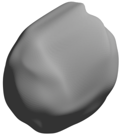
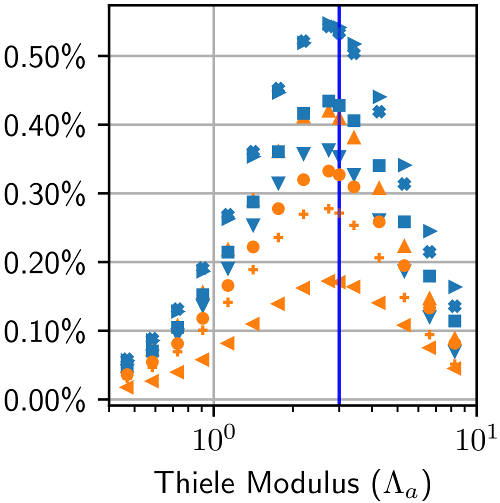
$$\begin{bmatrix} x(\theta,\phi) \\ y(\theta,\phi) \\ z(\theta,\phi) \end{bmatrix} = \begin{bmatrix} \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} c_x^m Y_l^m(\theta,\phi) \\ \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} c_y^m Y_l^m(\theta,\phi) \\ \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} c_z^m Y_l^m(\theta,\phi) \end{bmatrix}$$

Choose c_d^m at random in a manner that preserves certain metrics.

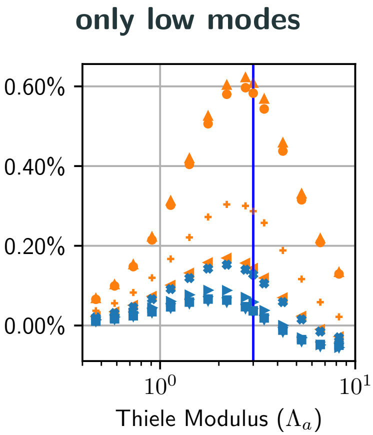

Input
d_ℓ
2 3 4 5 6 7 8 9 10 11 12 13
ℓ
Random Selection
Granule Shape
FE Solve
PDE Solution
Reduced Order Model
Integrate
Effectiveness Factor
$\eta \approx 0.6676$

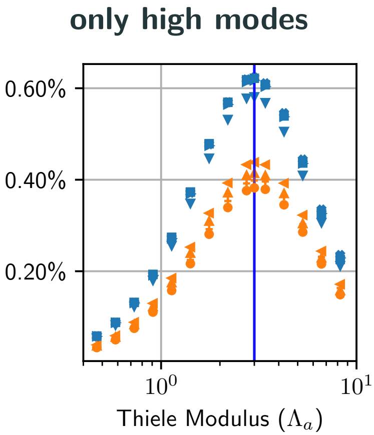
$2 \leq \ell \leq 5$	$6 \leq \ell \leq 10$	$11 \leq \ell \leq 15$	All ℓ
			
			

Random Granules



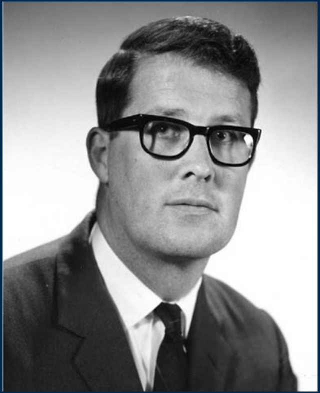
$\eta_d^{\mathrm{a}} - \eta_d$ (blue)
$\eta_d^{\mathrm{b}} - \eta_d$ (orange)





$\eta_d^{\mathrm{a}} - \eta_d$ (blue)
$\eta_d^{\mathrm{b}} - \eta_d$ (orange)

Use the Aris-type estimate, regardless of geometry.



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Thank you for listening.

Any questions?

(manuscript in preparation)

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