Transport-Kinetic Interactions for SO_2 Oxidation to SO_3 in Particulate and Monolith Catalysts

COMSOL Conference 2014
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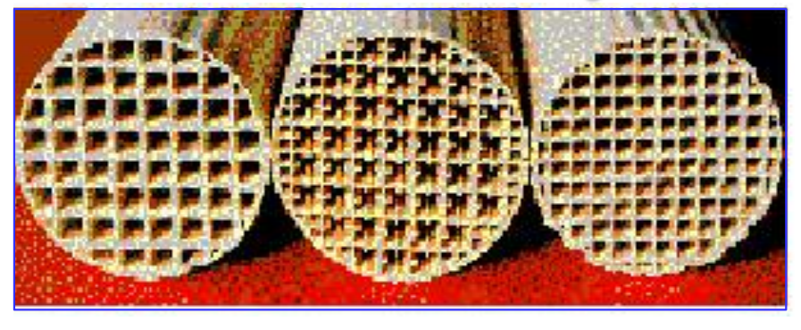
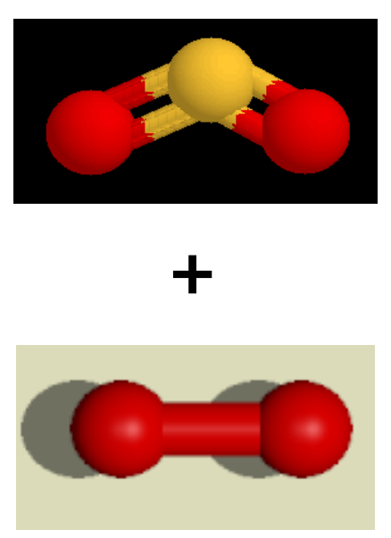
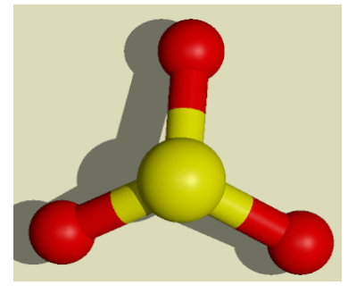
Monolith Catalysts



SO_2 Oxidation Catalysts





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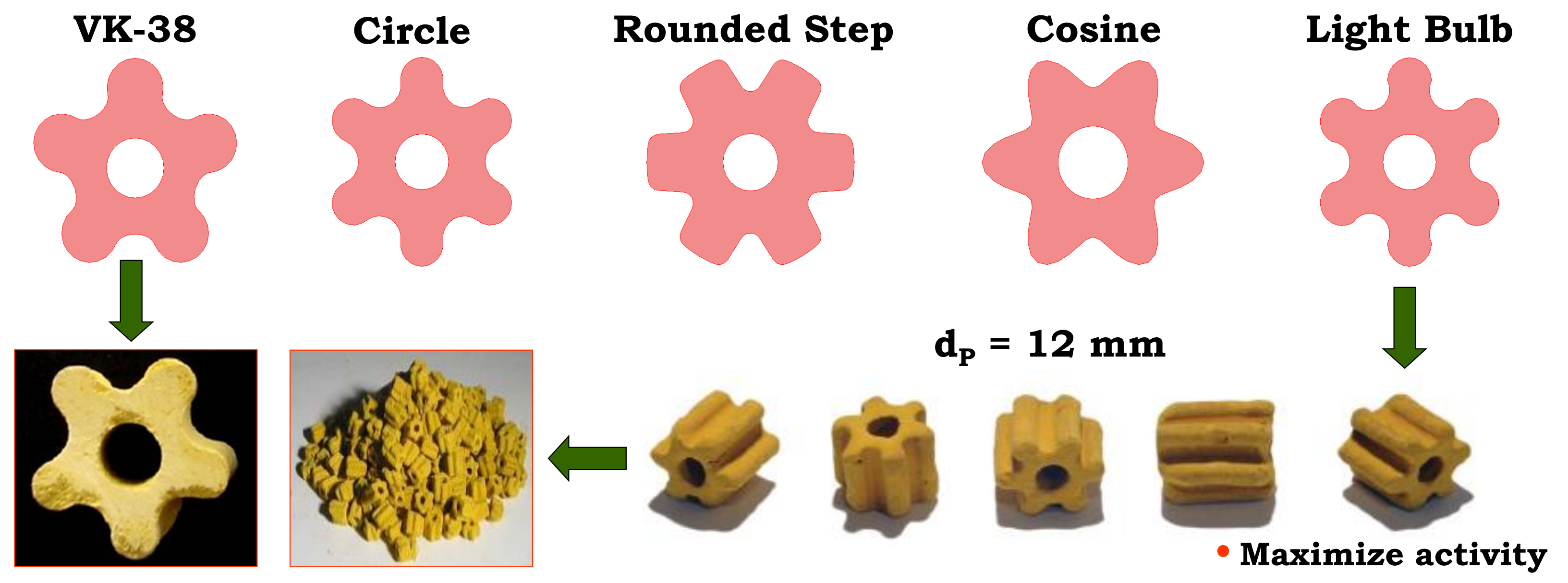
SO_2 Oxidation Convertor

Introduction

Transport-kinetic interactions in commercial porous catalyst shapes used for SO_2 oxidation are analyzed using the Wilke, Wilke-Bosanquet, Maxwell-Stefan, and Dusty-Gas flux models. Particle effectiveness factors derived from the various flux models can differ for otherwise identical values for kinetic and transport parameters. Development of new catalysts having higher activity, lower pressure drop, and adequate crush strength to meet the anticipated reduction in SO_2 emissions from H_2SO_4 manufacturing plants will potentially benefit by using this more realistic approach for particle-scale shape modeling.

Catalyst Particle Shapes



- Maximize activity
- Minimize ΔP

Transport-Kinetics Particle Model

Species Mass Balance:

$$\nabla \bullet N_i = \upsilon_i \, r \, \rho_P$$

where i = SO_2, O_2, SO_3 & N_2

Energy Balance:

$$\nabla \bullet \bar{q} = -(\Delta H_{rxn}) \, r \, \rho_p$$

SO_2 Oxidation Kinetics:

$$r = \frac{k_1 \, p_{O2} \, p_{SO2} \left(1 - \dfrac{p_{SO3}}{p_{SO2} \sqrt{p_{O2}} \, K_P}\right)}{22.414\left(1 + K_2 \, p_{SO2} + K_3 p_{SO3}\right)^2}$$

(Collina *et al*, 1971)

T = 420 to 590°C

Diffusion Flux Models

Wilke Model

$$N_i = \left(-D_{ei,m} \nabla C_i\right) \quad where \quad D_{ei,m} = \frac{1}{\left(\sum_{j=1, j\neq i}^{n} \left(x_j / D_{ij}^e\right)\right)}$$

Wilke-Bosanquet Model

$$N_i = \left(-D_{i,eff} \nabla C_i\right) \quad where \quad \frac{1}{D_{i,eff}} = \frac{1}{D_{ei,m}} + \frac{1}{D_{ei,k}}$$

Maxwell-Stefan Model

$$N_i = \frac{-\nabla C_i + \sum_{j=1, j\neq i}^{n} \dfrac{x_i N_j}{D_{ij}^e}}{\sum_{j=1, j\neq i}^{n} \dfrac{x_j}{D_{ij}^e}}$$

Dusty-Gas Model

$$N_i = \frac{\sum_{j=1, j\neq i}^{n} \dfrac{x_i N_j}{D_{ij}^e} - \dfrac{C_i v^*}{D_{ei,k}} - \nabla C_i}{\sum_{j=1, j\neq i}^{n} \dfrac{x_j}{D_{ij}^e} + \dfrac{1}{D_{ei,k}}}$$

Effectiveness Factor

$$\eta = \frac{\int_0^{V_P} r(c,T)\, dV}{r(C_S, T_S)\, V_P}$$

Dimensionless Velocity

$$V^* = -\frac{\varepsilon \, d_{pore}^2}{32 \, \tau \, \mu} \nabla P$$

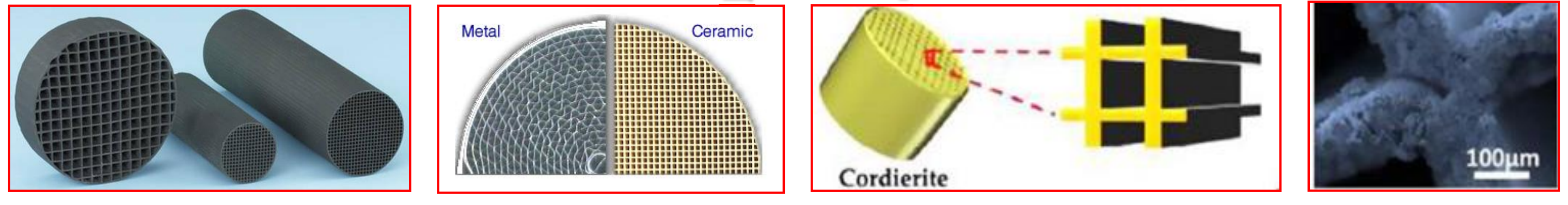
d_{pore} = 638 nm
ε = 0.44
τ = 2.7

*Reference: M. E. Davis, (1982) *Chem. Eng. Sci.*, 37(3) pp 447-452

Objectives

- Review the current state-of-the art in modeling transport-kinetic interactions for catalyst particle shapes utilized in the SO_2 oxidation.
- Develop a rigorous modeling framework that accounts for diffusion and non-isothermal reaction in various realistic 3-D commercial catalyst shapes using different flux models.
- Employ this framework to compare the performance of these various catalyst shapes under typical multi-pass convertor operation.

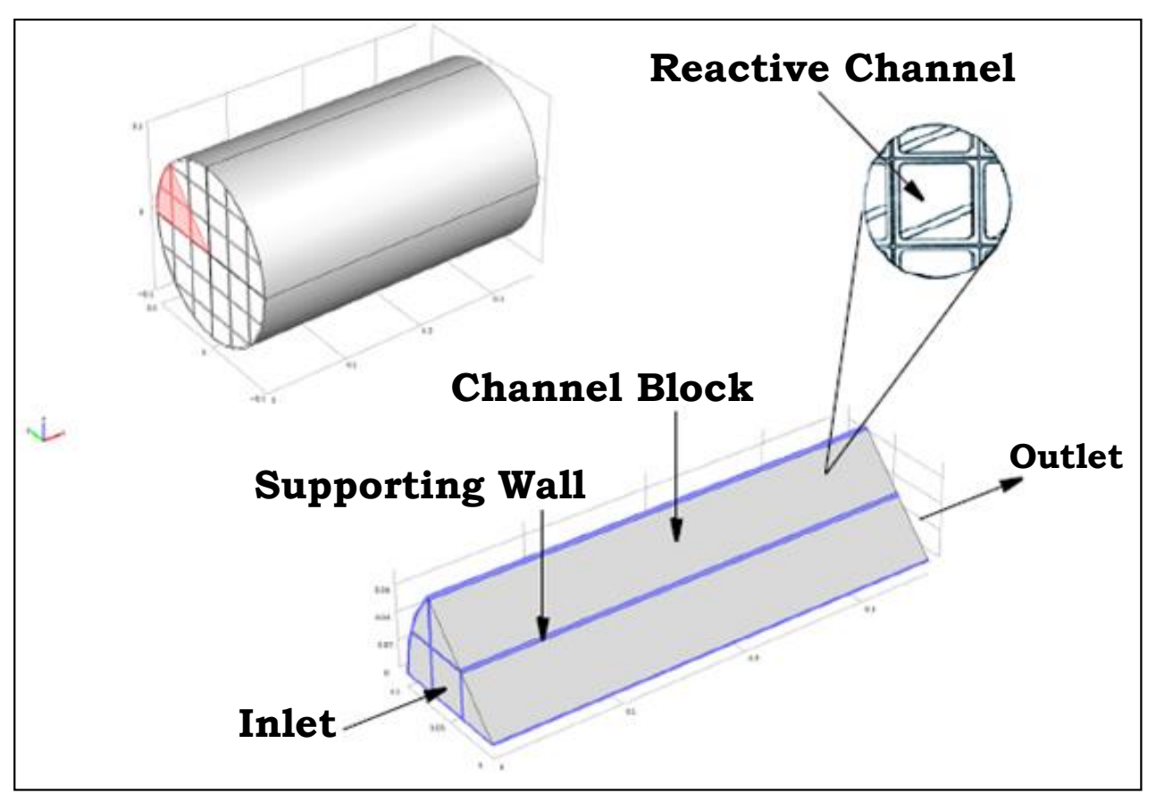
Monolith H_2SO_4 Catalysts



Modeling of SO_2 Oxidation in Honeycomb Structures

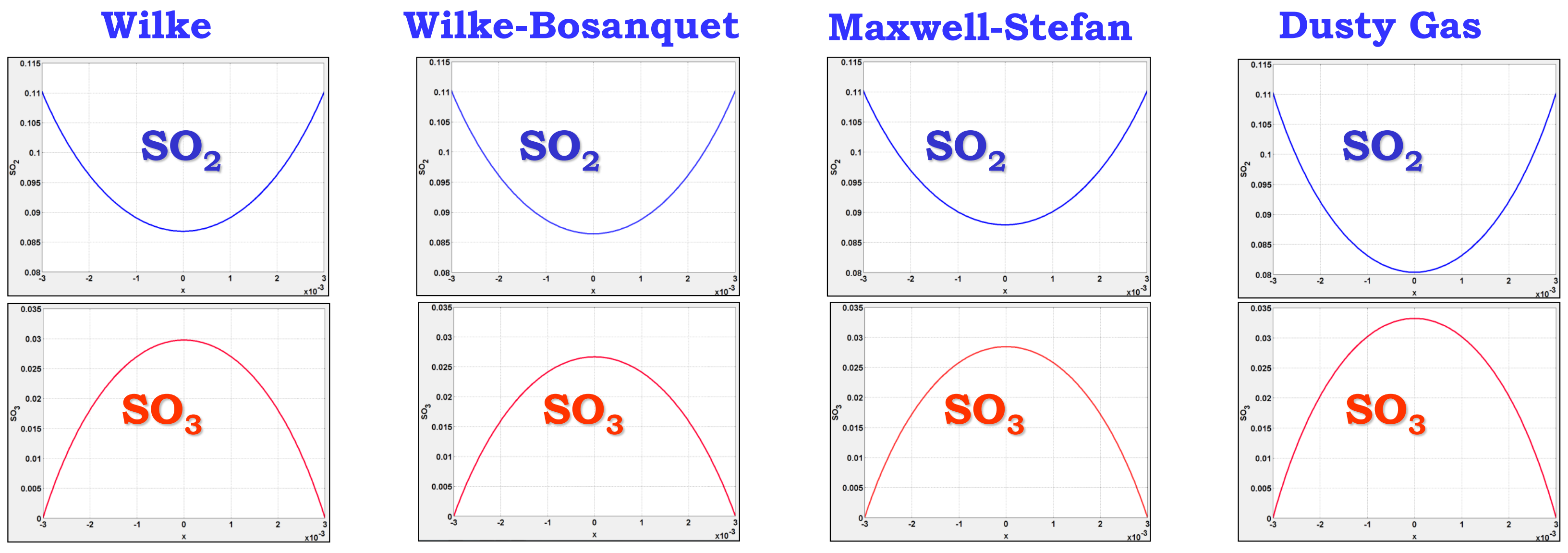
- In 1991, Bespalov and coworkers* at Moscow Chemical Engineering Institute developed a numerical model for SO_2 oxidation in monolith catalysts.
- This is the only known open literature on SO_2 oxidation modeling for a monolith.
- An opportunity ALSO exists to **develop advanced models** for the purpose of design and analysis.

*Bespalov, A.V. *et al.*(1991) Zhurnal Prikladnoi Khimii, 64(10) pp 2048 - 2053

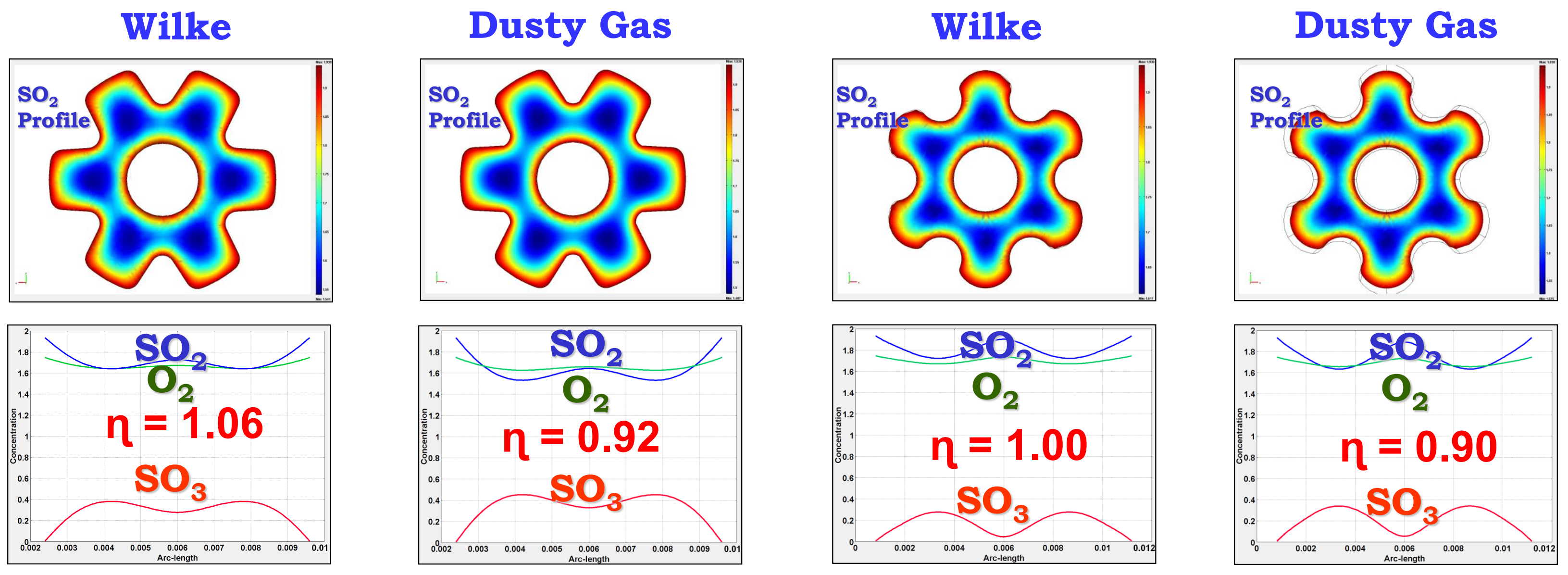


Results

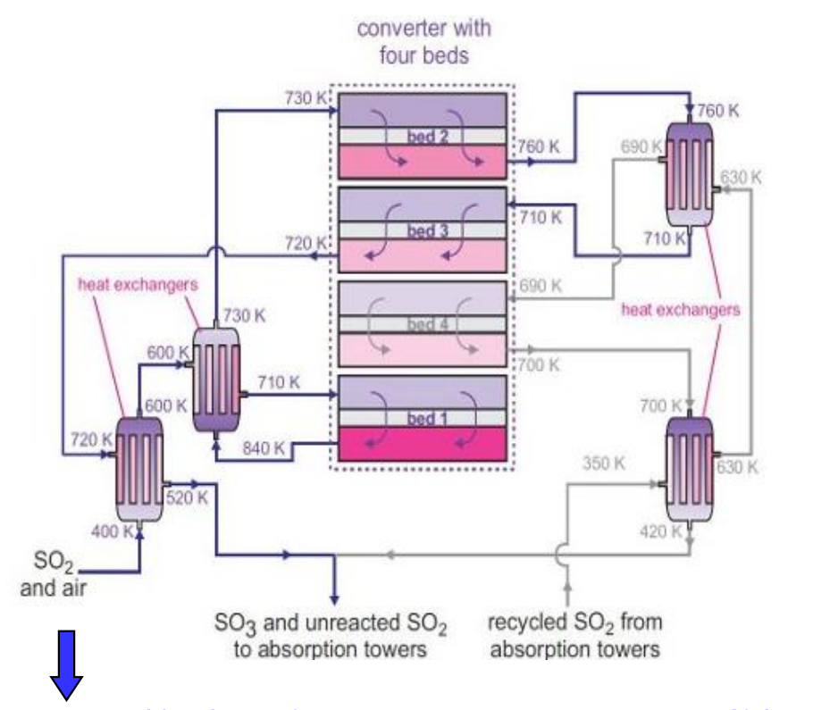
1-D Catalyst **T_0 = 420°C 11% SO_2 9%O_2**



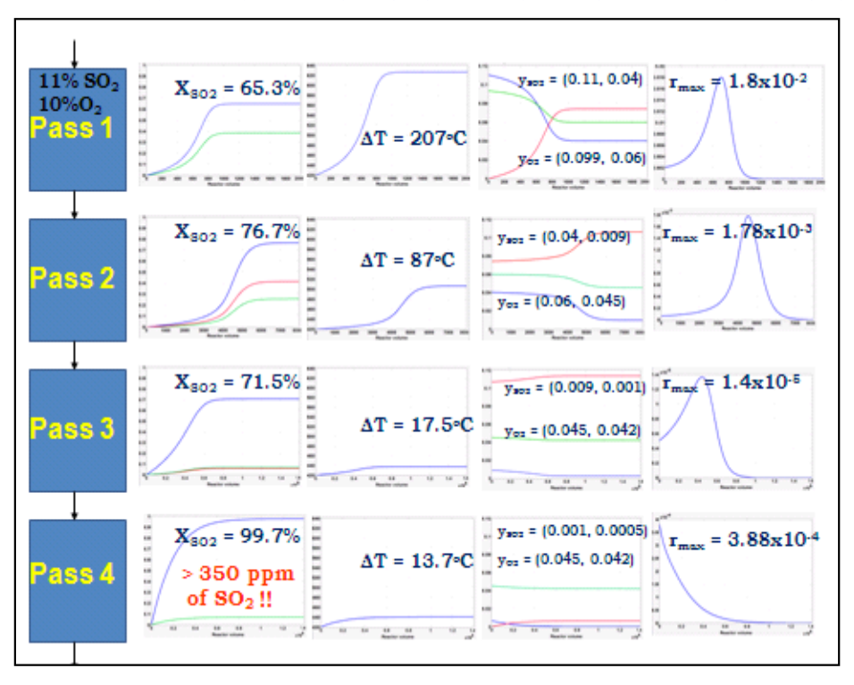
2-D Rounded Step Shape **2-D Light Bulb Shape**



Commercial Multi-Pass Convertor



1-D Adiabatic Converter Profiles

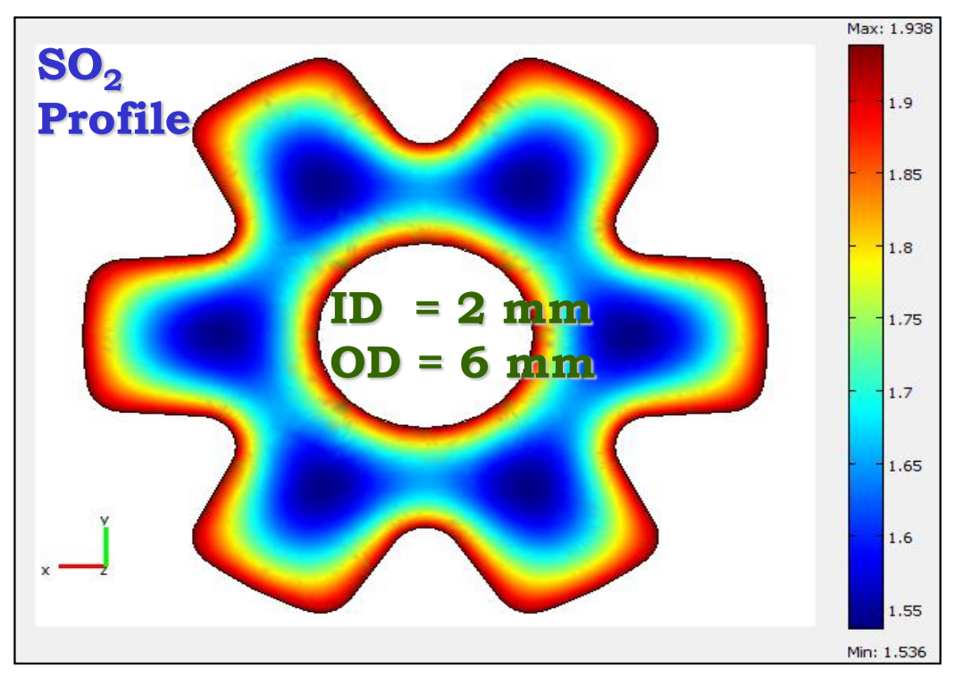


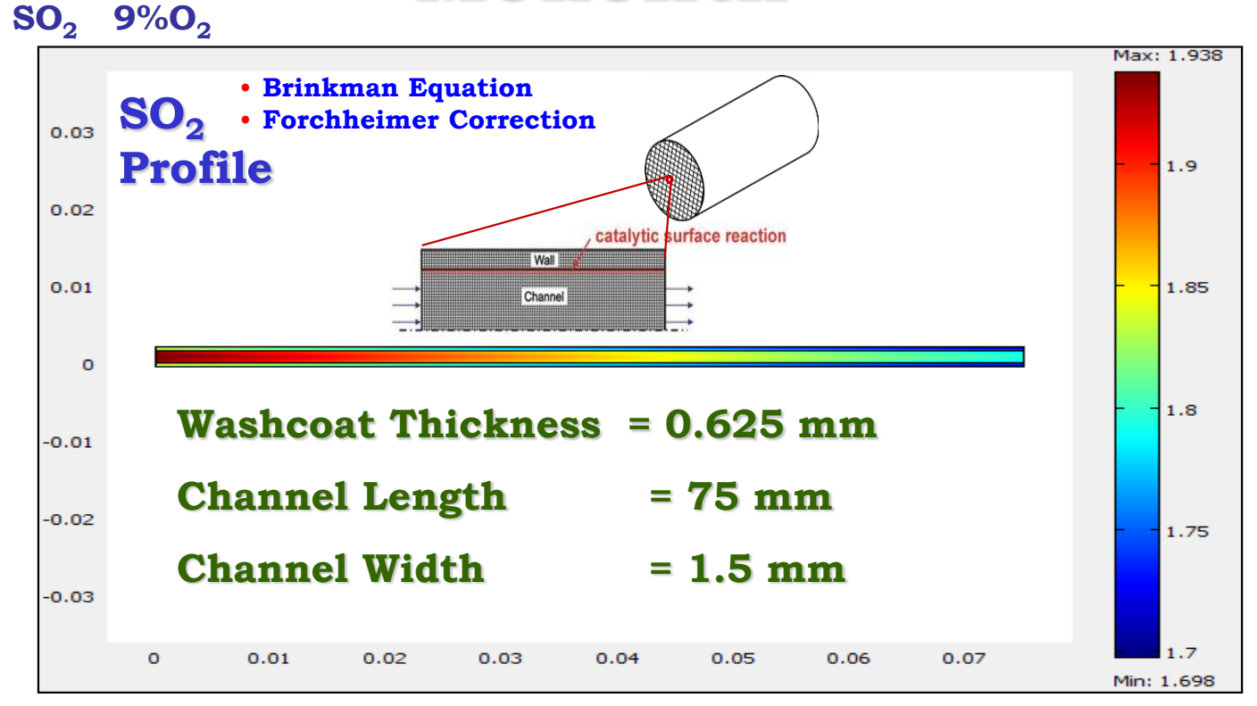
Particulate *vs* Monolith Catalysts

Particulate

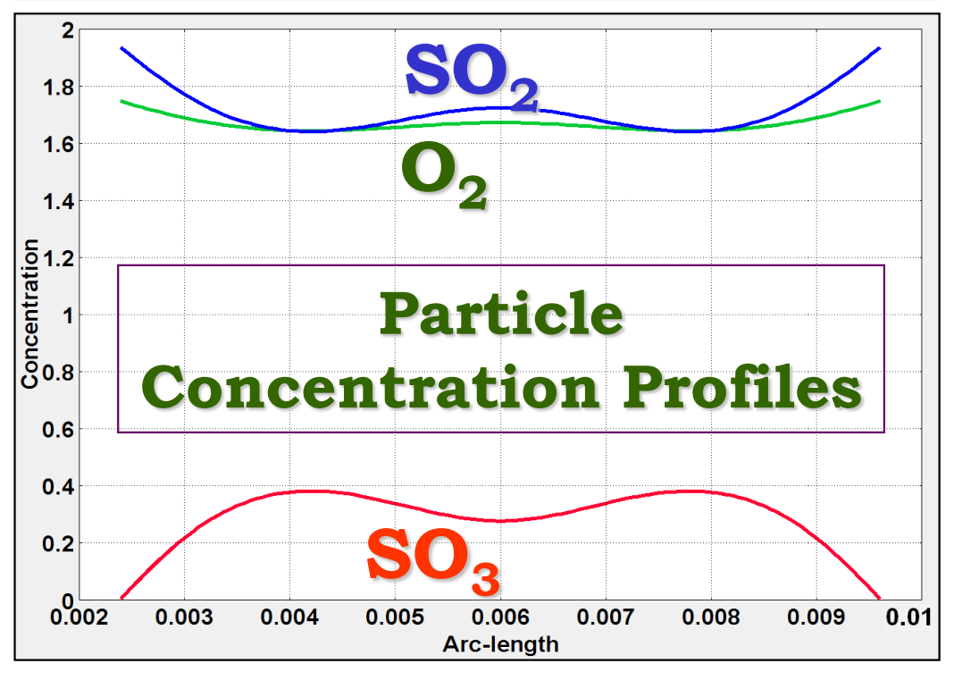
Inlet Conditions
T_B = 420°C
11% SO_2 9%O_2

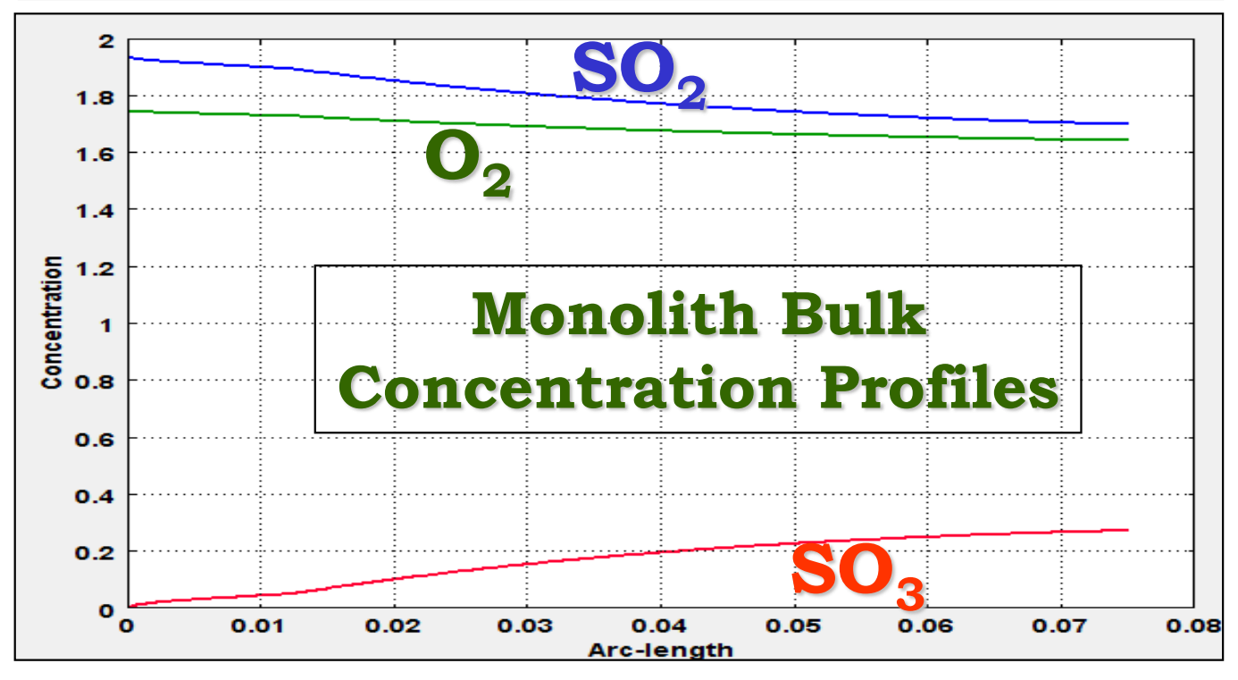
Monolith





Washcoat Thickness = 0.625 mm
Channel Length = 75 mm
Channel Width = 1.5 mm





CONCLUSIONS The Wilke model produces results that closely approximates those for the Dusty Gas Model for a uniform macroscopic pore structure for a given shape. However, the effectiveness factor varies with shape so it should be optimized in view of other factors, *i.e.*, ΔP and crush strength. Detailed data on pore structure would be captured by the Dusty Gas Model. Monoliths provide another potential catalyst platform for SO_2 oxidation. Detailed models that account for transport-kinetic interactions can provide rationale approaches for comparing traditional particulate *vs* monolith reactor performance.