COMSOL Conference 2014 Boston

Session: Transport Phenomena

Boston Marriott Newton
Boston, MA

Commonwealth Ballroom 4
2:45 PM – 4:15 PM

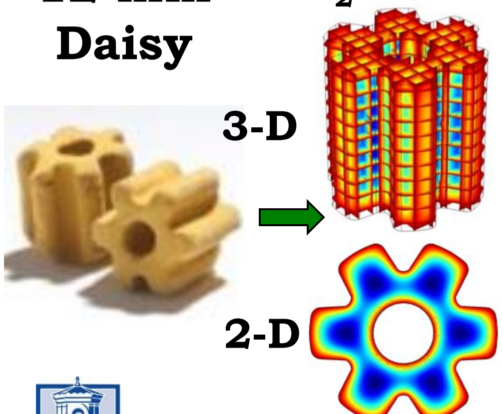
October 9, 2014

Moderator : William Clark

H_2SO_4 Catalysis: Perspective & Opportunities for Reducing SO_2 Emissions

12 mm Daisy

SO_2 Profiles



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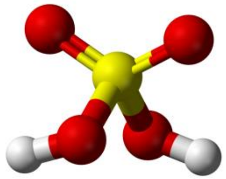
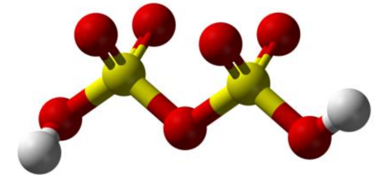
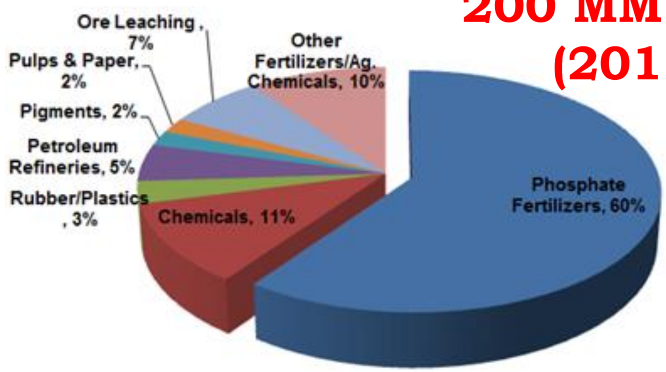


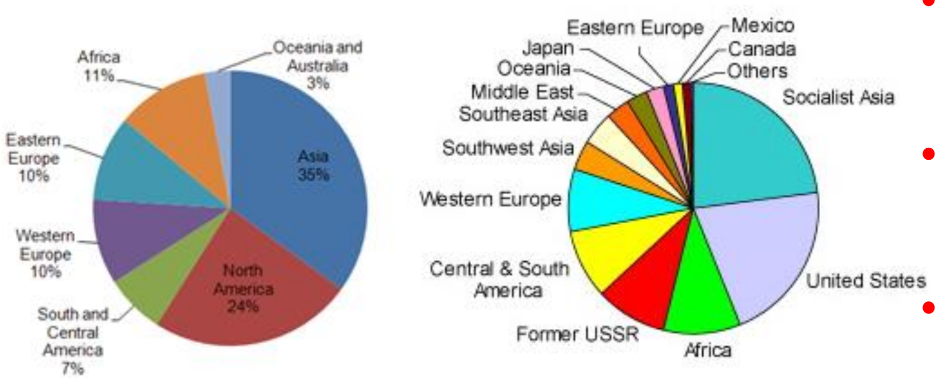
Sulfuric Acid (H_2SO_4) - Demand & Production -



200 MM Tons (2011)



Global H_2SO_4 Demand by Application



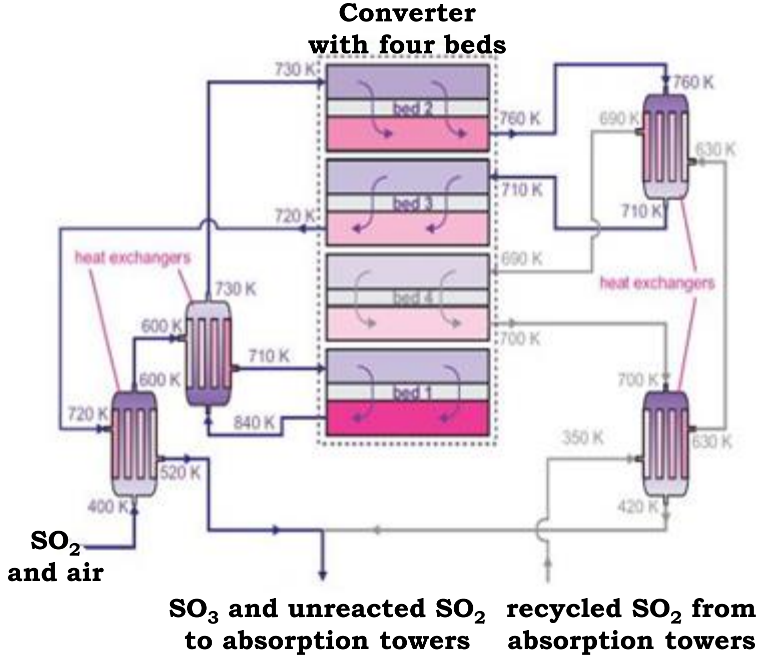
Global H_2SO_4 Production and Consumption*

- H_2SO_4 is the chemical with the highest total annual production on a global basis.
- World H_2SO_4 production/consumption in 2011 was estimated as 200 MM tons, or about $US 25-30 MMM.
- The USA is the largest **consumer** and China is the largest **producer** of H_2SO_4
- Global H_2SO_4 demand has increased by 58% from 1990 to 2011.
- H_2SO_4 is considered as a good indicator of a nation's industrial strength.
- The commercial importance of H_2SO_4 is the subject of various annual and biannual conferences (*e.g.*, Sulphur and Sulphuric Acid Conferences). **(http://www.crugroup.com/events/sulphur)**

A. A . Kiss, C. S. Bildea, et al. (2010).
"Dynamic modeling and process optimization of an industrial sulfuric acid plant." Chemical Engineering Journal **158**(2): 241-249

SO_2 Oxidation Reactor Technology

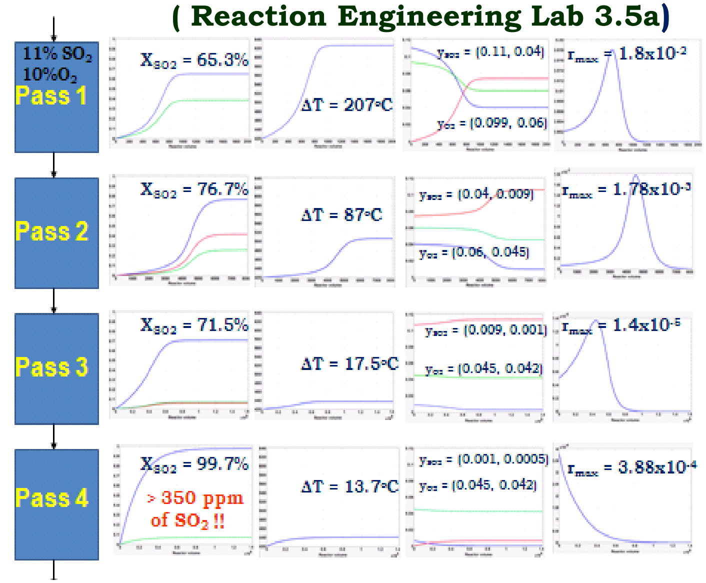
Commercial Multi Bed Convertor



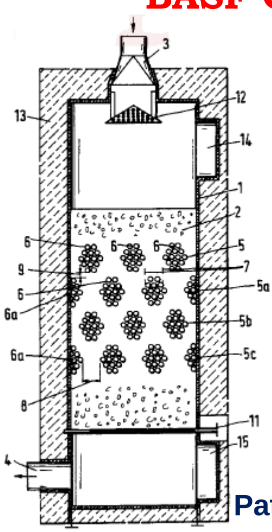
Convertor Conversion & Temperature Profiles

1-D Pseudo-homogeneous T(z) C(z) Adiabatic Plug-flow

(Reaction Engineering Lab 3.5a)



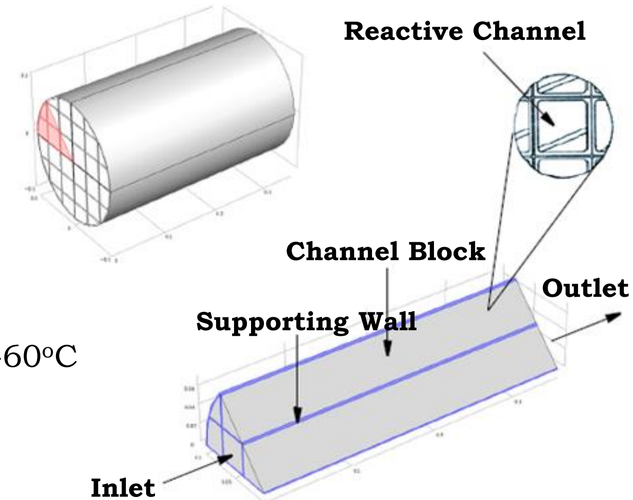
BASF Contact Reactor



- Quasi-isothermal catalytic SO_2 oxidation
- Contacting trays
- Cooling tubes
- 2 to 12 volume % of SO_2
- Temperature range is 400 – 460°C

Patent : US00xxxx402A

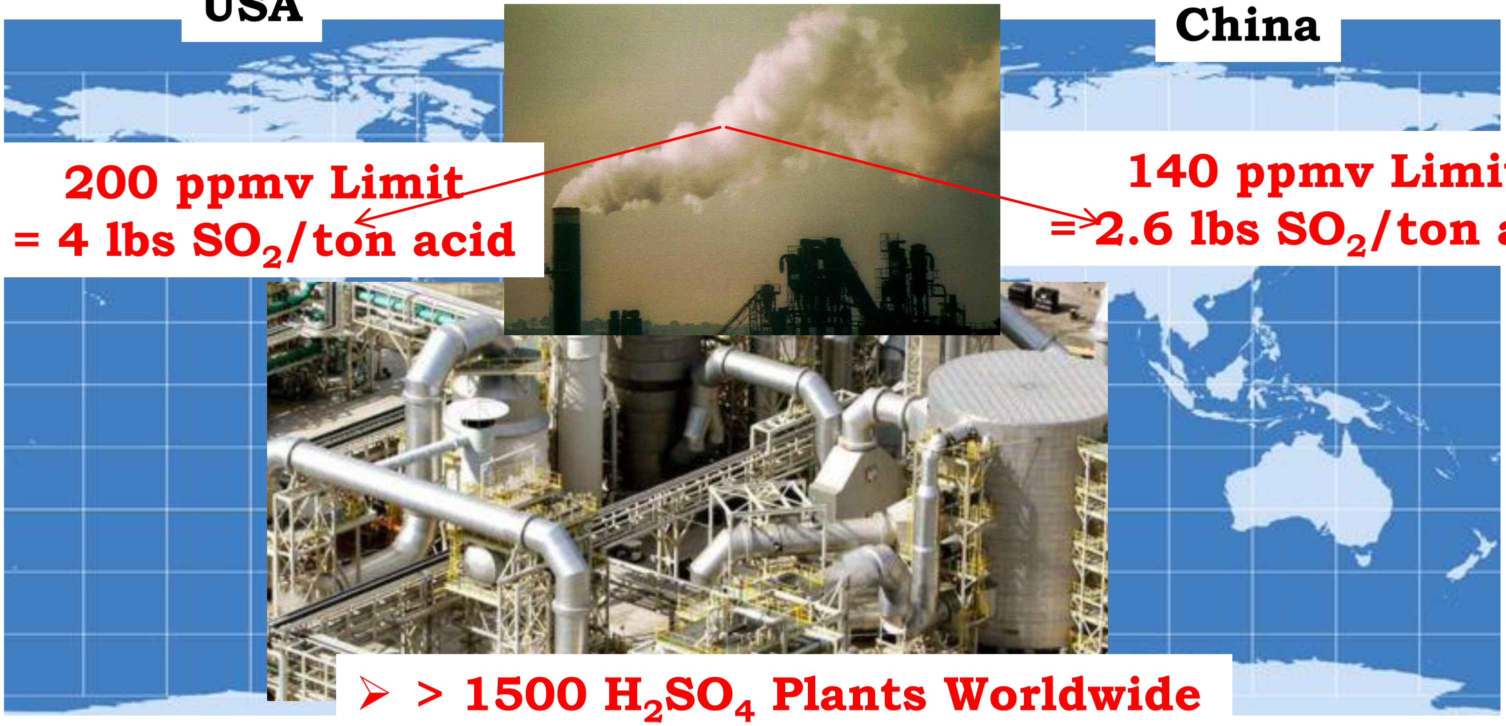
Monolith Reactor



- Honeycomb structure
- Metallic or ceramic support
- Circular, triangular or square cross sections
- Parallel and long channels
- Lower pressure drop

Motivation for Research

Global SO_2 Emissions
2700 Metric Tons/day



USA

200 ppmv Limit
= 4 lbs SO_2/ton acid

China

140 ppmv Limit
= 2.6 lbs SO_2/ton acid

- **> 1500 H_2SO_4 Plants Worldwide**
- **~750 to 1000 tons acid/day**

Target for new plants, or replacement catalysts in existing plants: 2.5 to 4 lbs SO_2/ton acid, but may vary depending on EPA limits

Image Courtesy: www.dupont.com

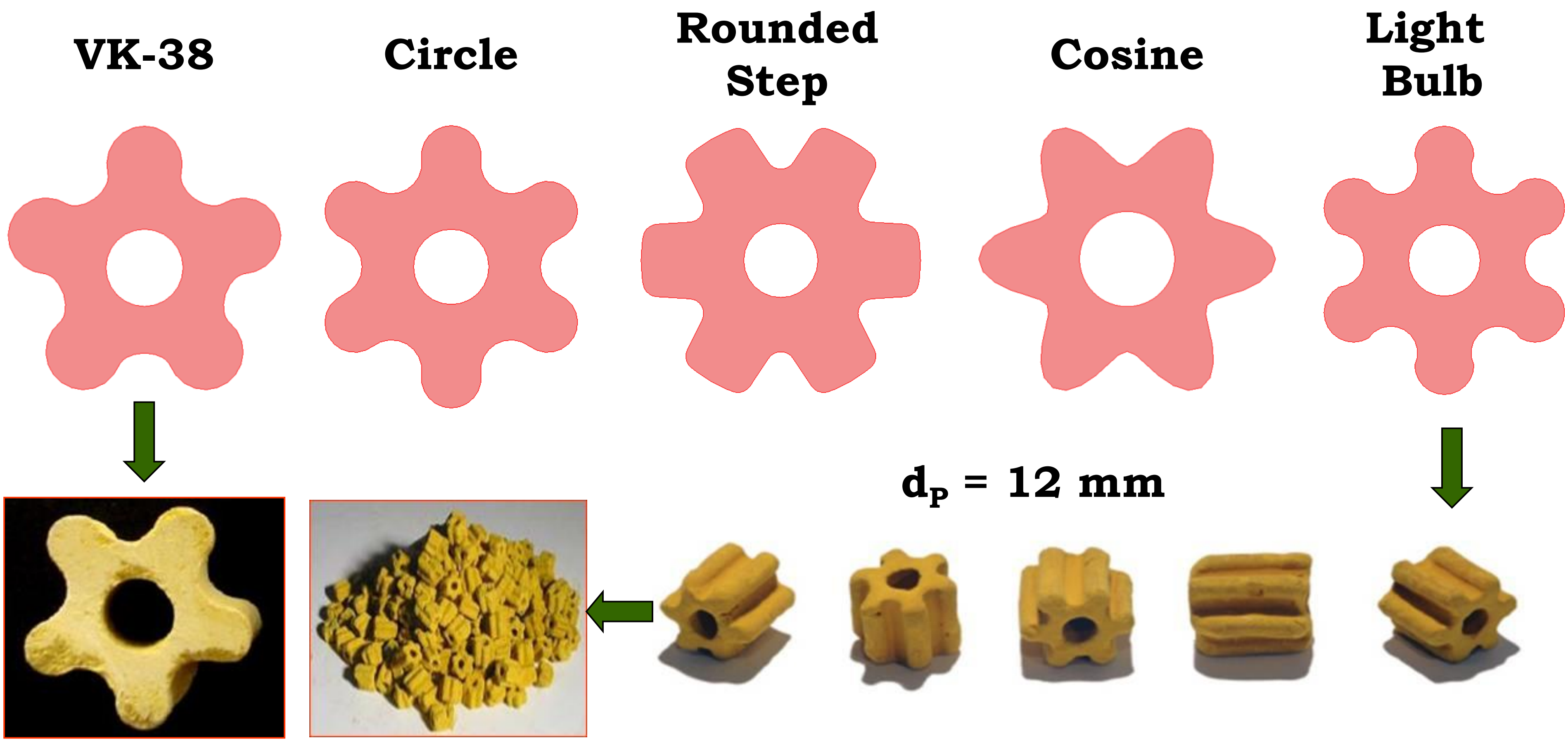
Best Available Control Technologies (BACT) for H_2SO_4 Plants

- Control technologies without additional processing [Front-End Fix; Less Expensive]
  - **New Catalyst Technology**
  - Converter Size/Arrangement/Catalyst Loading.....
  - Operating Parameters (feed gas composition, quality of cooling efficiency, etc.)

- Control technologies with additional processing [End-of-Pipe Fix; More Capital Intensive]
  - Single or Dual Absorption Operation
  - Waste Management (recycle of weak H_2SO_4 using activated carbon)
  - Scrubbing (removal using H_2O_2-based solvent)

Reference: Frank, N.A. *Clean air act requirements for sulfuric acid plants in the USA*. Paper presented at Sulfur 2011 conference, Houston, November 7-10, 2011

Multi-Lobe Catalyst Technology



- **Prior art based on multi-lobe shapes considering activity, attrition resistance and dusting during catalyst loading and extended process operation**

Reference: A. Nagaraj and P. L. Mills (2008). Analysis of heat, mass transport, and momentum transport effects in complex catalyst shapes for gas-phase heterogeneous reactions using COMSOL multiphysics. COMSOL Conference 2008 Boston, MA.

COMSOL Modules

- **Particulate Modeling**
  - **Heat Transfer by Conduction**

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k\nabla T) = Q + h(T_{ext} - T) + C({T^4}_{amb} - T^4)$$

  - **Diffusion**

$$\frac{\partial \mathbf{c}_i}{\partial t} + \nabla \cdot (-D_i \nabla \mathbf{c}_i) = R_i$$

- **Monolith Modeling**
  - **Brinkman Equation (Flow in Porous Media)**

$$\frac{\rho \partial \mathbf{u}}{\varepsilon \partial t} + \left(\frac{\eta}{\kappa} + Q\right)\mathbf{u} = \nabla \cdot \left[-p\mathrm{I} + \frac{1}{\varepsilon}\left\{\eta\left(\nabla \mathbf{u} + (\nabla \mathbf{u})^{\mathrm{T}}\right) - \left(\frac{2}{3}\eta - \kappa_{dv}\right)(\nabla \cdot \mathbf{u})\mathrm{I}\right\}\right] + \mathbf{F}$$

  - **Diffusion**

$$\frac{\partial \mathbf{c}_i}{\partial t} + \nabla \cdot (-D_i \nabla \mathbf{c}_i) = R_i$$

  - **Convection and Diffusion**

$$\frac{\partial \mathbf{c}_i}{\partial t} + \nabla \cdot (-D_i \nabla \mathbf{c}_i) = R_i - \mathbf{u}\nabla \mathbf{c}_i$$

Typical Expressions

Global Expressions

Name	Expression	Unit
p_so2	abs(c_so2*Rg*Tp/10^6)	
p_o2	abs(c_o2*Rg*Tp/10^6)	
p_so3	abs(c_so3*Rg*Tp/10^6)	
r_so2_f	k1_v*p_o2*p_so2/(22.414*(1+K2_v*p_so2+K3_v*p_so3)^2)	[]
r_so2_b	k1_v/Kp_v*p_o2^0.5*p_so3/(22.414*(1+K2_v*p_so2+K3_v*p_so3)^2)	
r_so2	r_so2_f - r_so2_b	
r_so2_comsol	r_so2*10^6/3600*rho_cat	
Ct	P/Rg/Tp*10^6	1/K
y_so2	c_so2/Ct	K·mol/m^3
y_o2	c_o2/Ct	
y_so3	c_so3/Ct	
y_n2	1-y_so2-y_o2-y_so3	
kg_SO2_case2	jD_case2*GG/(M_mix_case2*Pf_SO2_case2*Sc_SO2_case2^(2/3))	[]
kg_O2_case2	jD_case2*GG/(M_mix_case2*Pf_O2_case2*Sc_O2_case2^(2/3))	[]
kg_SO3_case2	jD_case2*GG/(M_mix_case2*Pf_SO3_case2*Sc_SO3_case2^(2/3))	[]
Q_rxn	dhr_avg*r_so2_comsol	[]
r	sqrt(x^2)	m
e_factor	integral_rate/(r_so2_comsol_max*volume)/2	
k1_v	exp(12.16-5473/Tp)	
K2_v	exp(-9.953+8619/Tp)	
K3_v	exp(-71.745+52596/Tp)	[]
Kp_v	exp(-71.745+52596/Tp)	[]
D_SO2_O2_v	(k*(Tp)^1.75/(P*(v_SO2^(1/3)+v_O2^(1/3))^2)*(1/m_SO2+1/m_O2)^0.5)*particle_voidage/particle_tortuosity*10^-4	[]
D_SO2_SO3_v	(k*(Tp)^1.75/(P*(v_SO2^(1/3)+v_SO3^(1/3))^2)*(1/m_SO2+1/m_SO3)^0.5)*particle_voidage/particle_tortuosity*10^-4	[]
D_SO2_N2_v	(k*(Tp)^1.75/(P*(v_SO2^(1/3)+v_N2^(1/3))^2)*(1/m_SO2+1/m_N2)^0.5)*particle_voidage/particle_tortuosity*10^-4	[]
D_O2_SO3_v	(k*(Tp)^1.75/(P*(v_O2^(1/3)+v_SO3^(1/3))^2)*(1/m_O2+1/m_SO3)^0.5)*particle_voidage/particle_tortuosity*10^-4	[]
D_O2_N2_v	(k*(Tp)^1.75/(P*(v_O2^(1/3)+v_N2^(1/3))^2)*(1/m_O2+1/m_N2)^0.5)*particle_voidage/particle_tortuosity*10^-4	[]
D_SO3_N2_v	(k*(Tp)^1.75/(P*(v_SO3^(1/3)+v_N2^(1/3))^2)*(1/m_SO3+1/m_N2)^0.5)*particle_voidage/particle_tortuosity*10^-4	[]
D_SO2_v	((y_o2-(y_so2*-0.5/-1))/D_SO2_O2_v)+((y_so3-(y_so2*1/-1))/D_SO2_SO3_v)+((y_n2-(y_so2*-1/-1))/D_SO2_N2_v)	[]
D_O2_v	((y_so3-(y_o2*1/-0.5))/D_O2_SO3_v)+((y_so2-(y_o2*-1/-0.5))/D_SO2_O2_v)+((y_n2-(y_o2*-1/-0.5))/D_O2_N2_v)	[]
D_SO3_v	((y_n2-(y_so3*1/1))/D_SO3_N2_v)+((y_so2-(y_so3*-1/1))/D_SO2_SO3_v)+((y_o2-(y_so3*-0.5/1))/D_O2_SO3_v)	[]
D_N2_v	((y_so2-(y_n2*-1/1))/D_SO2_N2_v)+((y_o2-(y_n2*-0.5/1))/D_O2_N2_v)+((y_so3-(y_n2*1/1))/D_SO3_N2_v)	[]
Dk_SO2_v	particle_voidage/particle_tortuosity*(9700*rm*(Tp/m_SO2)^0.5)*10^-4	[]
Dk_O2_v	particle_voidage/particle_tortuosity*(9700*rm*(Tp/m_O2)^0.5)*10^-4	[]
Dk_SO3_v	particle_voidage/particle_tortuosity*(9700*rm*(Tp/m_SO3)^0.5)*10^-4	[]
Dk_N2_v	particle_voidage/particle_tortuosity*(9700*rm*(Tp/m_N2)^0.5)*10^-4	[]
De_SO2	(1+(B0*P*1.01325e5)/(Dk_SO2_v*Mu_mixture))/(D_SO2_v+1/Dk_SO2_v)	[]
De_O2	(1+(B0*P*1.01325e5)/(Dk_O2_v*Mu_mixture))/(D_O2_v+1/Dk_O2_v)	[]
De_SO3	(1+(B0*P*1.01325e5)/(Dk_SO3_v*Mu_mixture))/(D_SO3_v+1/Dk_SO3_v)	[]
De_N2	(1+(B0*P*1.01325e5)/(Dk_N2_v*Mu_mixture))/(D_N2_v+1/Dk_N2_v)	[]

OK Cancel Apply Help

Partial pressures

Reaction rate

Molar Fractions

Kinetic rate constants

Binary, knudsen and effective diffusivities

Transport-Kinetics Particle Model

Species Mass Balance:

$$\nabla \bullet \boldsymbol{N}_i = \upsilon_i \, r \, \rho_p$$

where i = SO_2, O_2, SO_3 and N_2

and ν_i = -1, - ½, 1 and 0

Energy Balance:

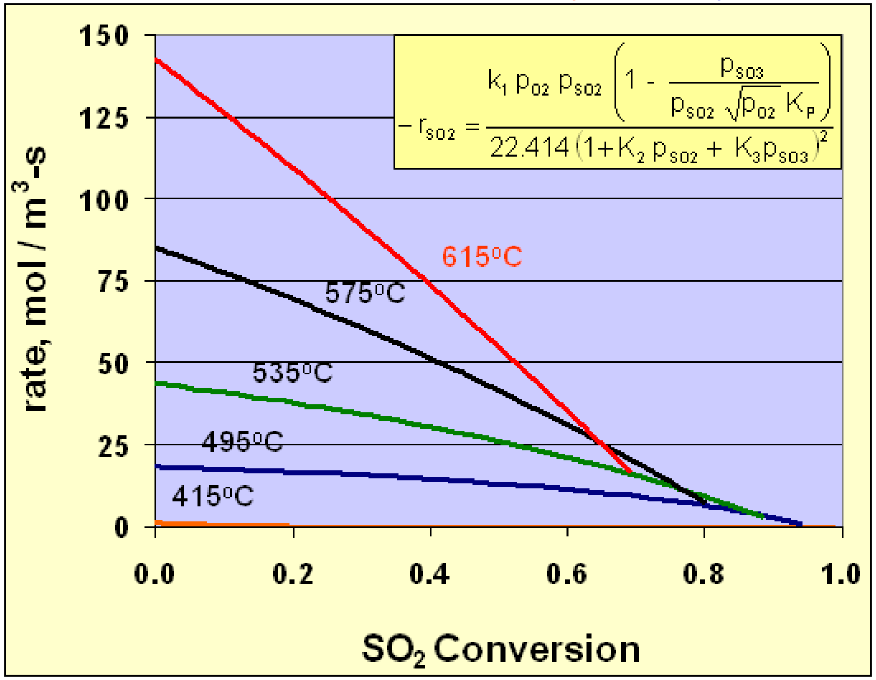
$$\nabla \bullet \bar{q} = -(\Delta H_{rxn}) \, r \, \rho_P$$

SO_2 Oxidation Kinetics:

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

$$SO_2 + \tfrac{1}{2} \, O_2 \rightleftarrows SO_3$$

Hougen-Watson Mechanism
RLS = Adsorbed SO_2 & O_2



- Statistical Design
- K-V salt catalyst on silica
- ca. 59 Data Points
- 420°C < T < 590°C; P_T = 1 atm

Diffusion Flux Models

Wilke Model

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

Wilke-Bosanquet

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

Maxwell-Stefan

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

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

d_{pore} = 638 nm

ε = 0.44

τ = 2.7

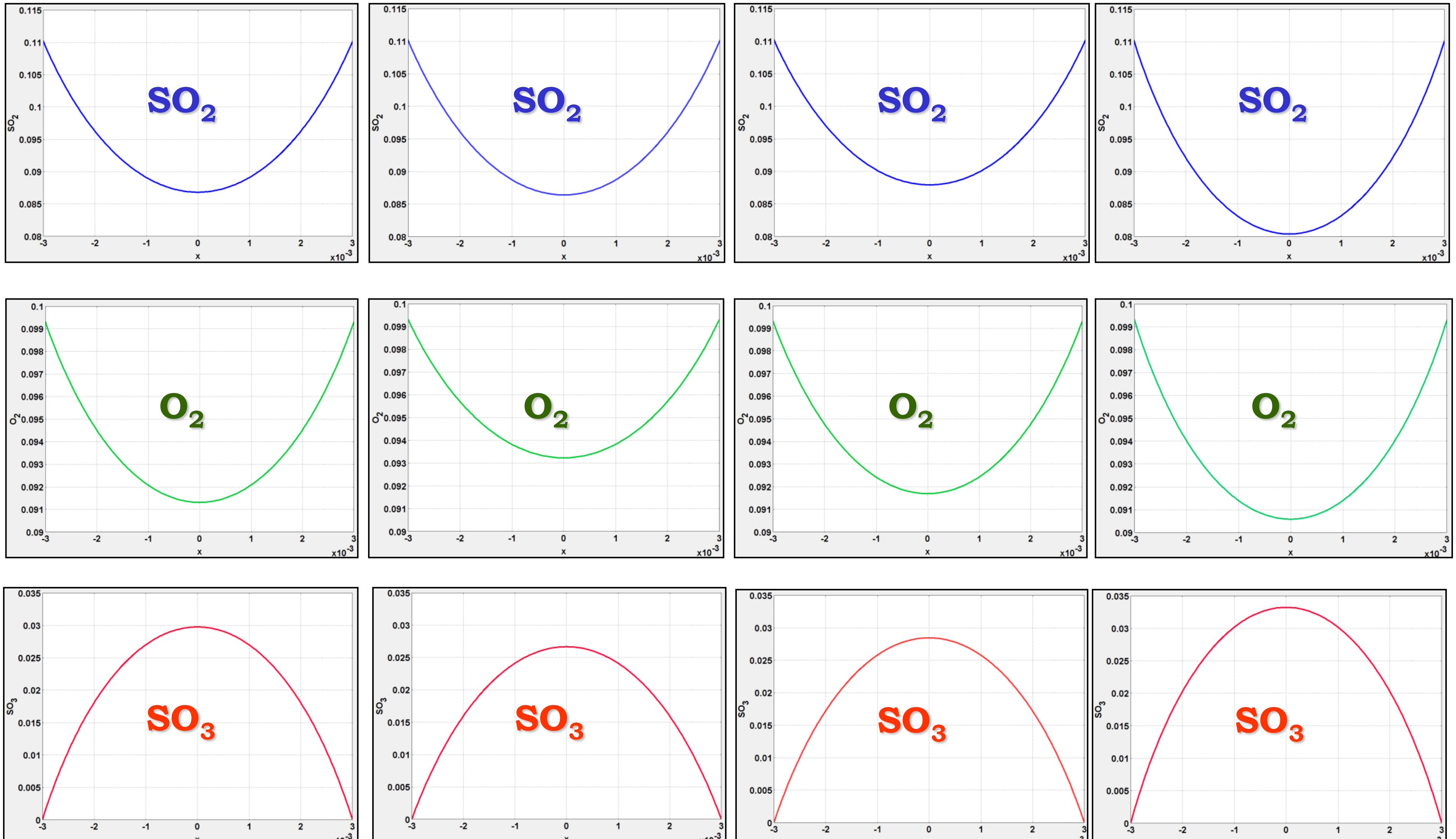
Dusty Gas

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

Profiles for 1-D Catalyst

6 mm "T-type" Cylinder $T_B = 420^oC$ 11% SO_2 9% O_2

Wilke | **Maxwell-Stefan** | **Wilke-Bosanquet** | **Dusty Gas**



SO_2 Concentration Profiles

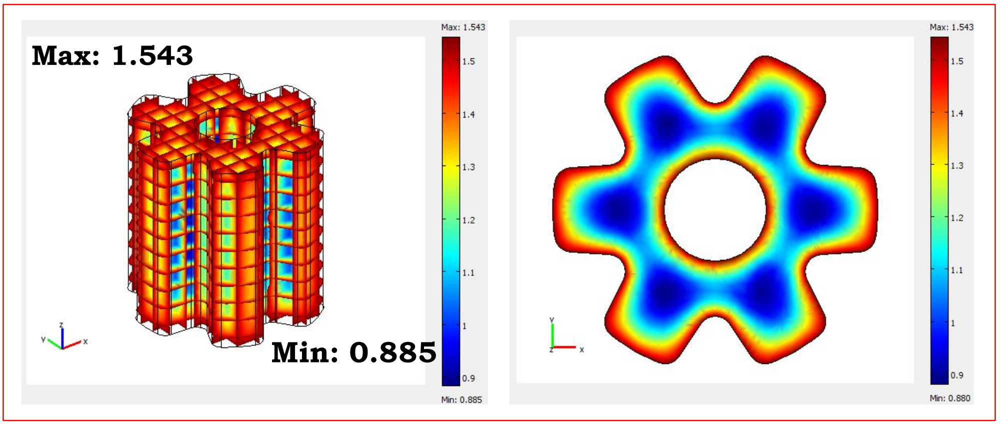
T_B = 435°C

9% SO_2 9.5% O_2

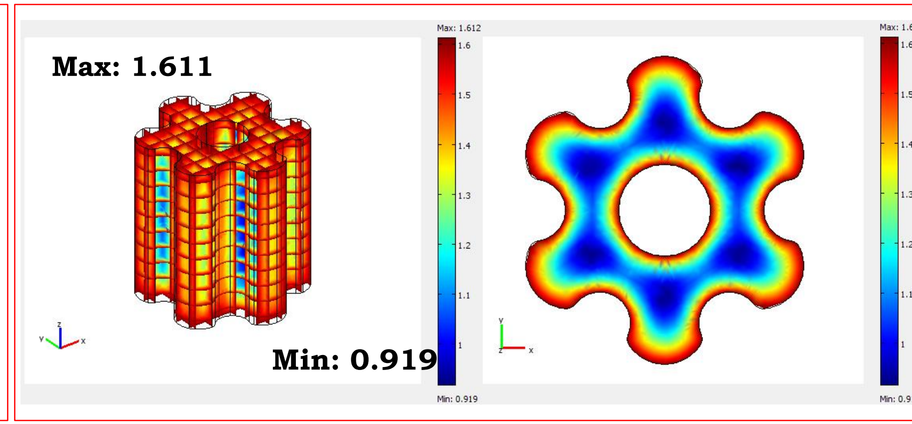
Wilke Model

η = 1.74

Rounded Step



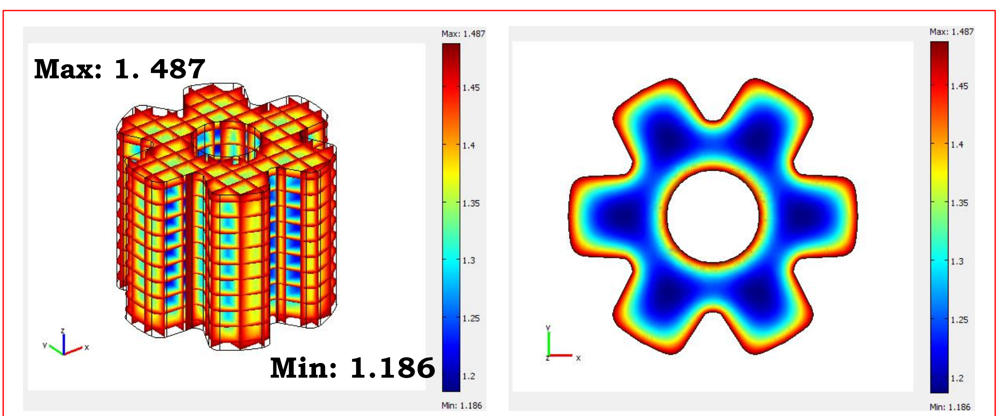
Light Bulb



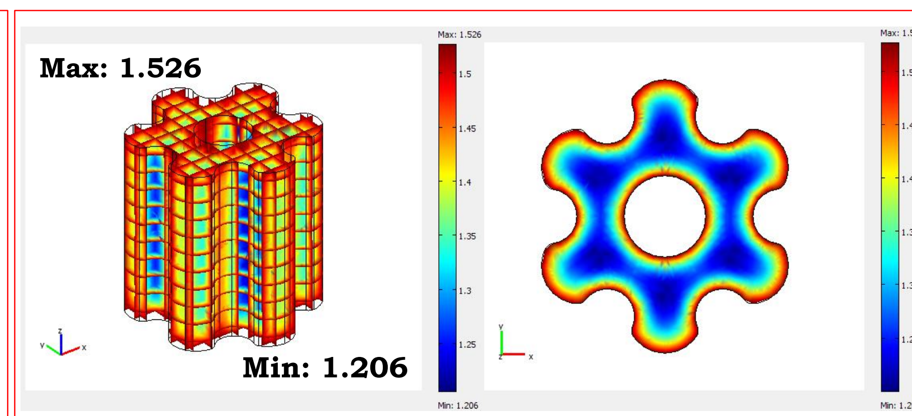
Dusty Gas Model

η = 0.83

Rounded Step



Light Bulb



Temperature Profiles

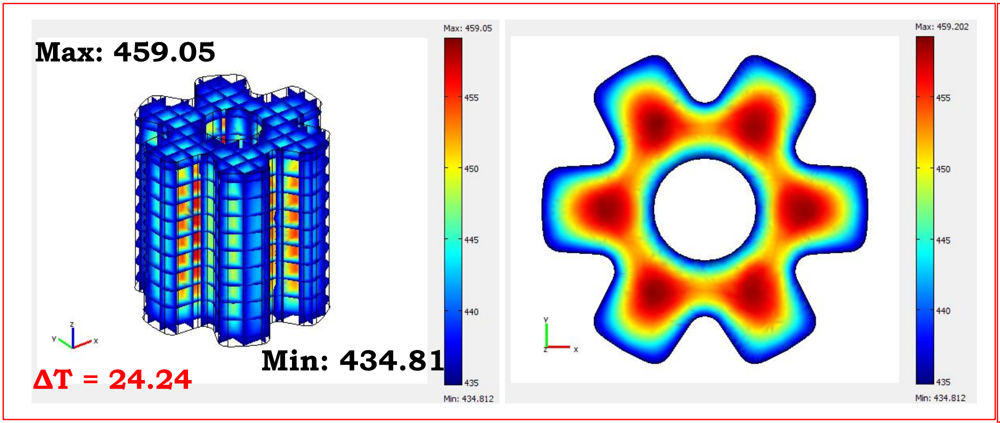
T_B = 435°C
9% SO_2 9.5%O_2

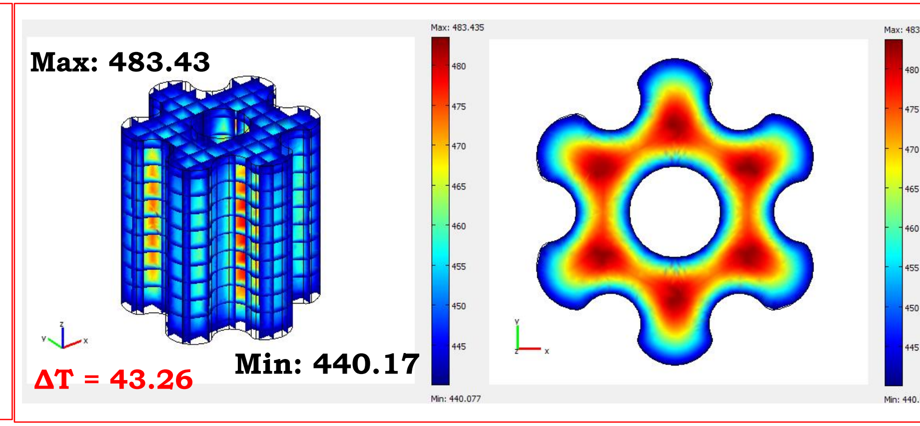
Wilke Model

η = 1.74

Rounded Step

Light Bulb





Dusty Gas Model

η = 0.83

Rounded Step

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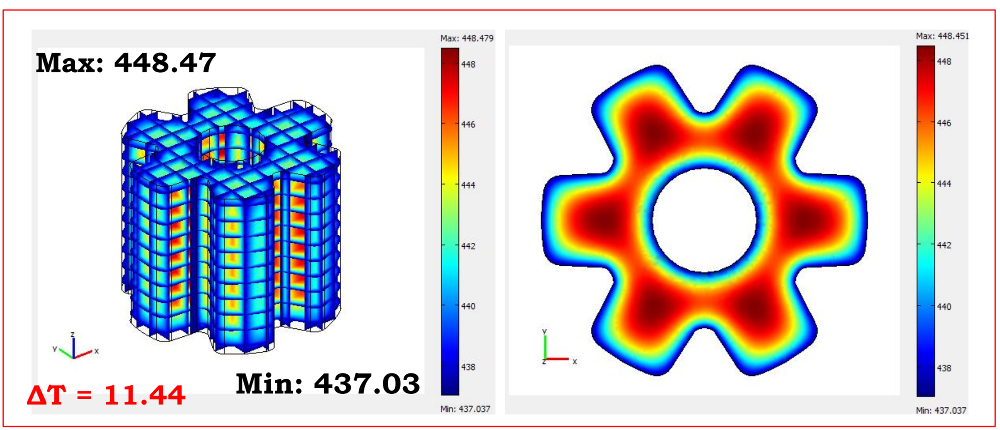
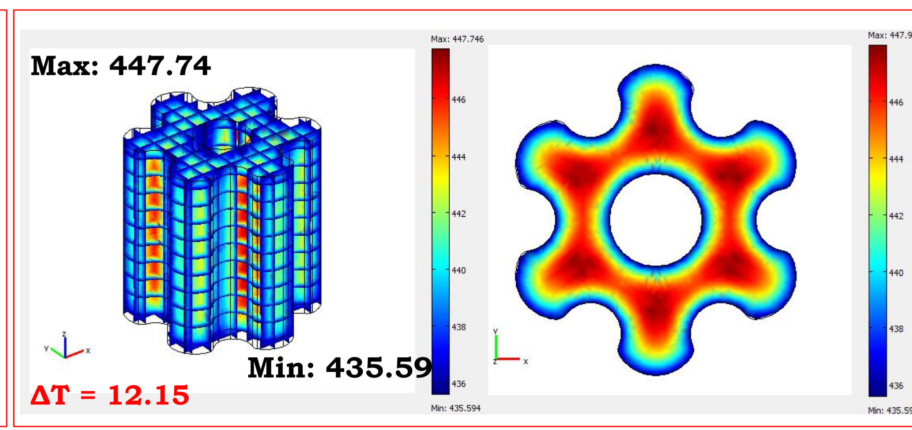


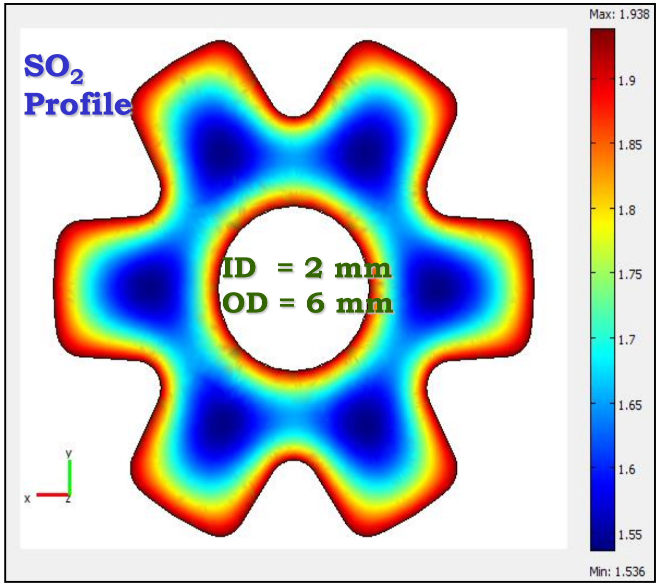


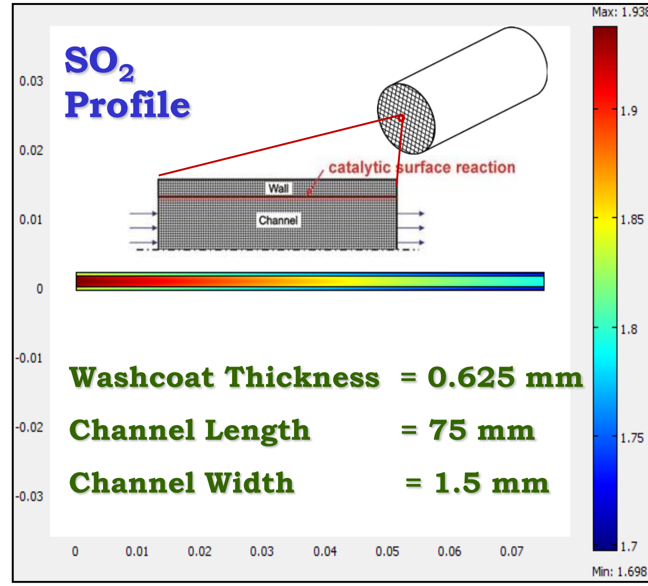
Particulate *vs* Monolith

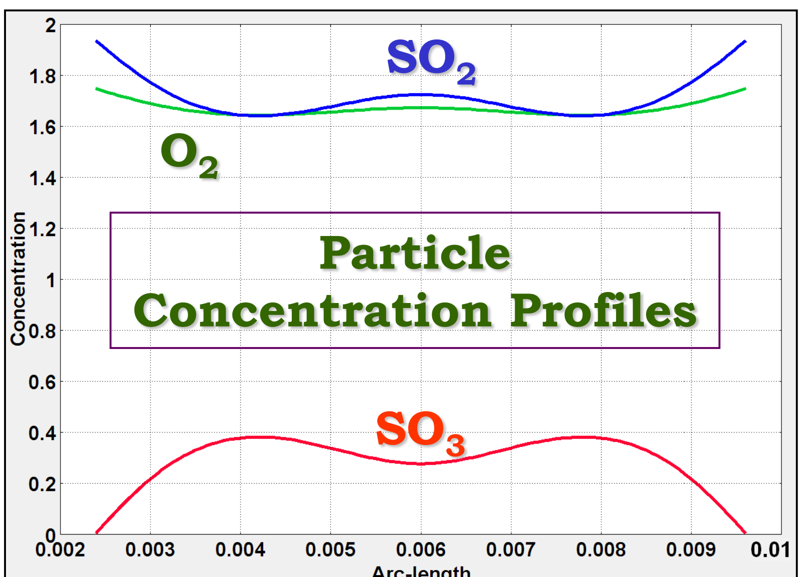
Particulate

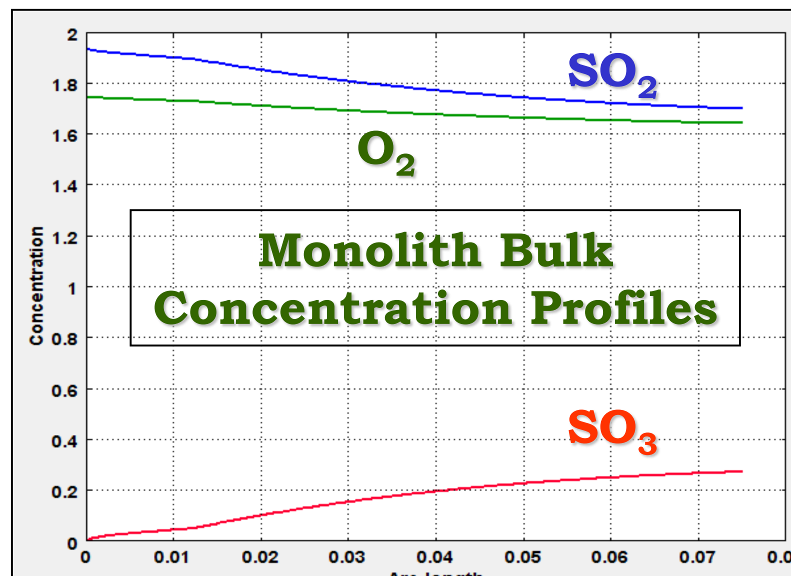
T_B = 420°C
11% SO_2 9% O_2

Monolith

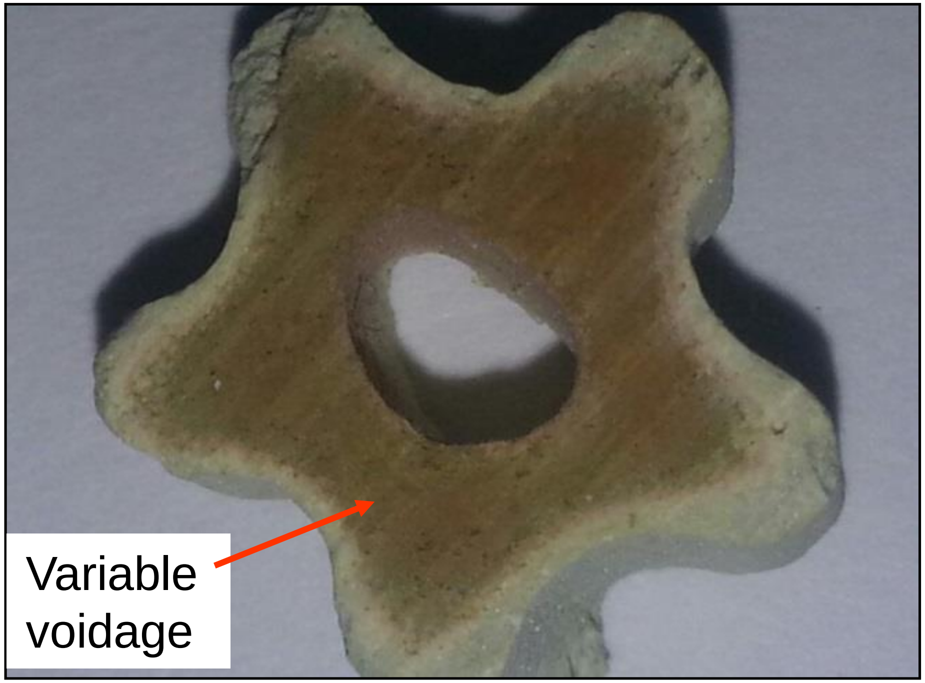


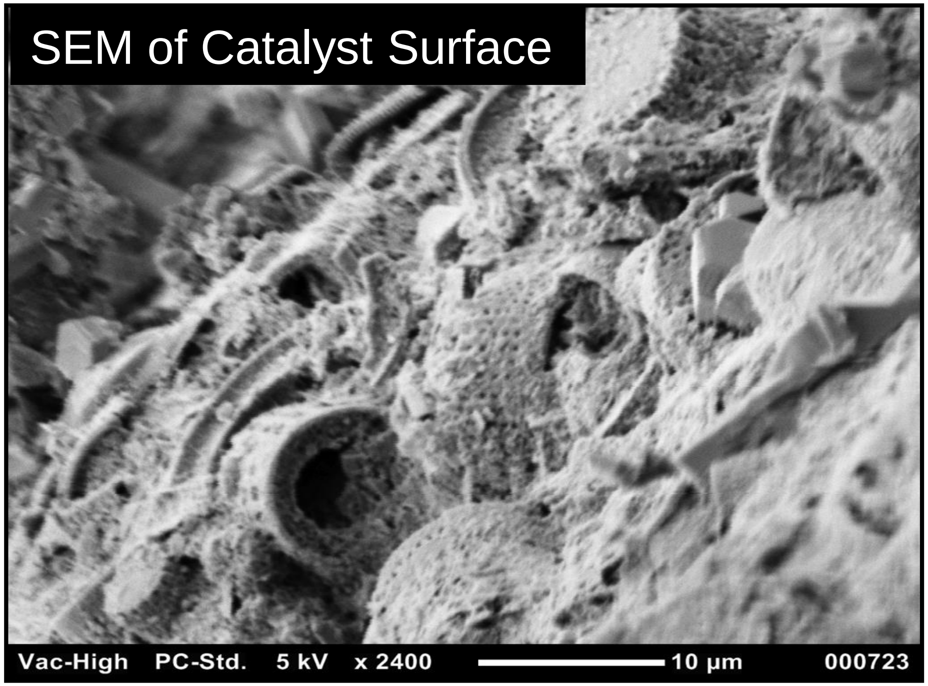






Modeling Results - Conclusion





Detailed knowledge of catalyst morphology, *e.g.*, 3-D PSD, and other supporting data is required to validate flux models

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Summary & Conclusions

- Models for sulfuric acid catalysis that account for various transport-kinetic interactions in particulates & monoliths can be solved using COMSOL Multiphysics

- These models provide a fundamental basis for synthesis of next generation particulate or monolith catalyst having higher activity and hence reduce environmental impact vs existing catalyst

- Monolith supports provide a potential catalyst platform for SO_2 oxidation catalysts having higher activity, lower ΔP, higher mechanical strength and reduced dust *vs* particulate catalysts. This is a work in progress that will be guided by COMSOL-based modeling tools.

- Data on 3-D catalyst pore structure from SEM image processing would allow more realistic predictions of catalyst performance