

Analysis of Heat, Mass Transport, and Momentum Transport Effects in Complex Catalyst Shapes for Gas-Phase Heterogeneous Reactions Using COMSOL Multiphysics

Anuradha Nagaraj¹ and Patrick L. Mills^{2*}

¹Department of Electrical Engineering and Computer Science, Texas A&M University-Kingsville

²Department of Chemical and Natural Gas Engineering, Texas A&M University-Kingsville

*Corresponding author: 700 University Blvd, MSC 188, Kingsville, TX 78363, Patrick.Mills@tamuk.edu

Introduction

The global chemical industry generates a gross income of more than \$US 2 trillion each year that is distributed across more than 1000 corporations with a spectrum of more than 70,000 user end-products. Chemical and inorganic products produced from gas-phase heterogeneous reactions over solid porous catalysts represent the largest contributor to these metrics and are identified with a range of important processes in the bulk chemical manufacturing, fine chemical, petroleum refining, pharmaceutical, and biomaterials industries. Because catalyst and reactor system performance dictates the product separation and recycle stream requirements in any process scheme, a notable amount of research and development effort has been spent on creating new catalyst products with improved measures of performance, such as activity, conversion, selectivity, space-time yield, resistance to deactivation, mechanical integrity, and ease of recycle for the active catalyst metal ingredients.

Catalyst size and shape are two interlinked parameters that have received notable attention by catalyst scientists and engineers since these directly affect the catalyst effectiveness or so-called catalyst utilization in addition to observed pressure drop, rate of catalyst attrition, and catalyst mechanical integrity, to name a few. Determination of the preferred catalyst size and shape parameters requires careful optimization since tradeoffs exist in how the observed reaction rate and other measure of performance may be affected by altering one or both of these parameters. For example, in a catalytic system that exhibits notable intraparticle diffusional limitations, reducing the particle size decreases the effective path length for diffusion of reactants and products and results in a higher observed reaction rate owing to a higher catalyst effectiveness factor. However, smaller catalyst particles produce a higher pressure drop over a packed bed due to a lower bed voidage when compared to a larger particle, thereby requiring additional compressor power to transport the same molar flow rate of gas. Consequently, any improvement in the space-time yield of the desired product could be offset by larger capital and operating costs associated with gas compression. Similarly, removal of catalyst material from the center region of the pellet, such as in a hollow cylinder shape, would also reduce the effective path length for diffusion and would increase the catalyst effectiveness factor. However, the net amount of active ingredient would be decreased so the reaction rate per unit volume of reactor could either increase or decrease, depending upon how the rate based on the weight of active ingredient compared to the rate based on the pellet volume.

The above problem of catalyst size and shape optimization is actually specific to a particular process technology since the interaction between intrinsic kinetics and transport effects for a given chemistry produces unique numerical values for the observed reaction rates for a given set of local species bulk concentrations and temperature. Consequently, the characteristic times for species diffusion, thermal energy transport, and reaction will define the extent to which the intrinsic kinetics are impacted by transport effects. Similarly, catalyst packed-bed pressure drop, or more generally, gas phase momentum transport, is also process-specific since the parameters that affect it, such as gas superficial velocity, gas viscosity, and gas density, depend upon the required gas mean residence time to achieve the target conversion as well as the local gas composition. In addition, the catalyst process history and activity are also integral part of this analysis since the catalyst morphology and nature of the local catalyst sites always exhibit temporal behavior in any real process environment with time constants that can easily vary over several orders-of-magnitude. While some general conclusions regarding optimal catalyst size and shape can be developed

without considering a specific catalytic reaction, the results will generally depend upon the particular catalytic chemistry and the process conditions under which it operates. For this reason, optimization of catalyst size and shape should generally be analyzed for each reaction system application of interest.

The primary objective of this work is to analyze the performance of various heterogeneous catalyst shapes that have been proposed for the oxidation of SO_2 to SO_3 used in the manufacture of sulfuric acid. This application is selected since various commercial sulfuric acid catalyst manufacturers offer a variety of catalyst shapes for use in adiabatic multi-stage reactor systems, although technical details on why a specific shape is preferred over another are generally lacking. In 2001, world-wide production of sulfuric acid was 165 million tones with a value of more than \$8 billion with principal uses being in fertilizer manufacturing, ore processing, chemical synthesis, wastewater processing, and oil refining. The global demand for sulfuric acid has been forecast to grow at an average of 2.6% per year from 2005 – 2010. However, this demand does not account for catalyst replacement at existing facilities and commissioning of new conversion processes, which is one application where new catalyst shapes could be introduced. Hence, an opportunity exists to bring new engineering analysis to an important technology that has a rich and long history.

To analyze catalyst performance for complex catalyst shapes, the governing multi-dimensional forms of the conservation equations that define species, thermal, and momentum transport in the porous catalyst structure must first be solved for a given SO_2 oxidation kinetic rate law. Next, the resulting local values for species concentrations are then used to evaluate the catalyst effectiveness factor by integration over the catalyst control volume. The hydrodynamics of gas flow over a given catalyst shape, or an ensemble of catalysts, can also be analyzed to provide insight into the impact of shape on pressure drop. COMSOL Multiphysics is particularly suited for these types of analysis due to its ability to solve user-defined models in an arbitrary control volume. Previous efforts by other authors on catalyst shape analysis have employed special-purpose finite element or boundary element codes, although the case of SO_2 oxidation to SO_3 has not been analyzed to the authors' knowledge.

Use of COMSOL Multiphysics

COMSOL Multiphysics was used to simulate the performance of various catalyst shapes for the case of SO_2 oxidation to SO_3 . The simplest shapes are actually one-dimensional in space and correspond to non-isothermal diffusion and reaction in either an infinite slab, an infinite cylinder having a circular cross-section, or a sphere. Analysis of performance of these simpler shapes is useful since it provides a reference point for more complex shapes.

a. System geometry. Diagrams for some of catalyst shapes that have been proposed for SO_2 oxidation to SO_3 are illustrated in Figure 1. These were constructed using the drawing tools provided in COMSOL Multiphysics, but they could also be imported from another compatible drawing software package or generated using MATLAB. Both 2-D and 3-D shapes are provided to show that the analysis requires a consideration of all three spatial dimensions. This is the case since the characteristic height, width, and length of a given shape affects heat, mass transport and momentum transport. In addition, an initial voidage distribution is created when catalysts are dumped from a sack or other catalyst shipping container into a commercial-scale reactor system to create a randomly packed bed. The fashion in which the external surfaces of particles interact with each other will ultimately impact the voidage distribution.

The catalyst shapes shown here are not exhaustive, but provide a perspective of the types of shapes that have been proposed in various patents. In the case of catalyst shapes involving multiple lobes, the shape parameters include the number and shape of the lobes, the characteristic dimension of a given lobe, the distance from the lobe center to true particle center, and the diameter of the hollow region. The lobes shown here are based upon either a circle or a triangle, although this is not a restriction and other more complex shape functions could be used.

b. Model equations. The model equations given here correspond to the one-dimensional cases, which include the infinite slab, solid or hollow cylinder, or sphere. The extension of these to multiple space dimensions is relatively straightforward and will be described in the final paper.

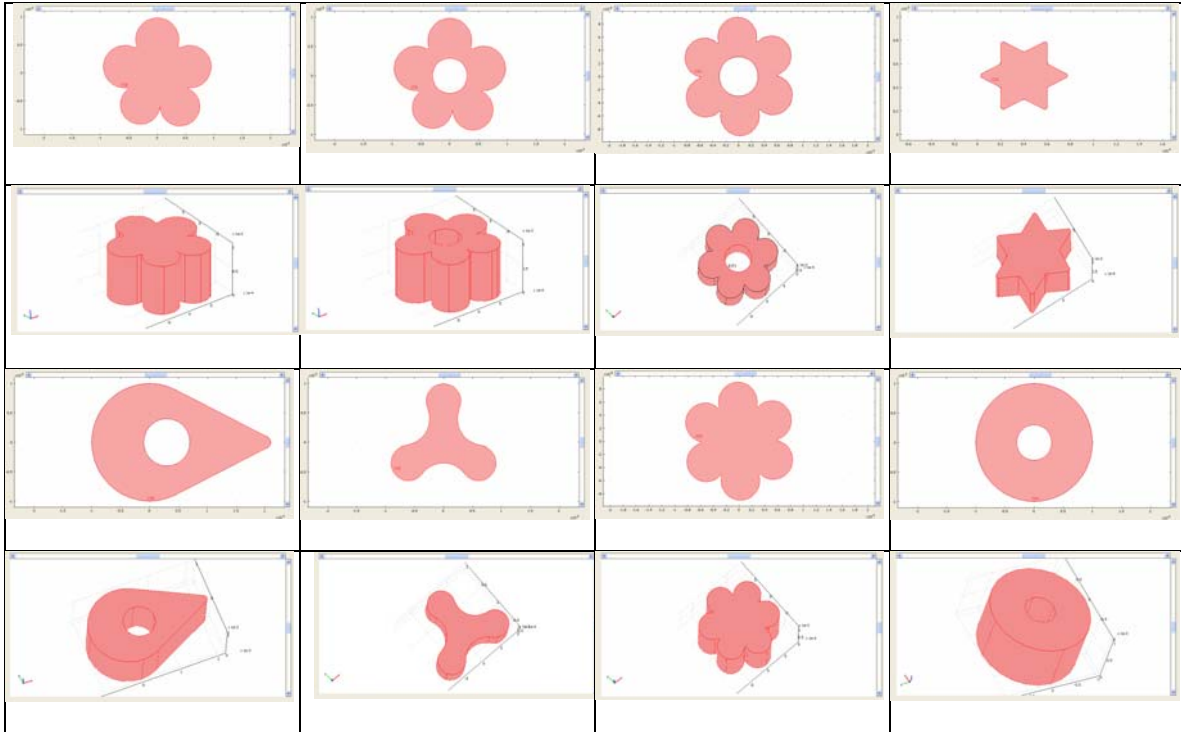
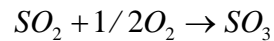


Figure 1. Illustration of various catalyst shapes.

The primary reaction is the selective oxidation of SO_2 to SO_3 which is typically conducted using air as the O_2 source. This behavior is unusual for an industrial system since the primary reaction is often accompanied by multiple side reactions.



The reaction kinetics for SO_2 oxidation to SO_3 have been the subject of numerous studies. A detailed summary of the literature will be provided in the final paper. One intrinsic kinetic model that captures the observed experimental behavior over a reasonable temperature range is defined below by a Langmuir-Hinshelwood dual-site type of mechanism involving the dissociation of O_2 in terms of the partial pressures of the SO_2 , O_2 , and SO_3

$$r_{SO_2} = \frac{k' P_{SO_2} P_{O_2}^{1/2} (1 - \beta)}{(1 + K_{SO_2} P_{SO_2} + K_{SO_3} P_{SO_3})^2}$$

Here, the parameter that accounts for the reversible reaction is:

$$\beta = P_{SO_3} / (K_p P_{SO_2} P_{O_2}^{1/2})$$

where K_p is the equilibrium constant.

The single reaction defined above can be written in more general form as one that involves a mixture of n chemical species where only the first m participate in the reaction. In this particular case, $n = 4$ corresponding to SO_2 , O_2 , SO_3 and N_2 but $m = 3$ since the latter is present as an inert specie since it does not undergo any molecular transformations. The reaction stoichiometry given above can then be generally written as

$$\sum_{i=1}^m \nu_i A_i = 0$$

where A_i represents the i^{th} species and the stoichiometric coefficients ν_i are negative for reactants and positive for products. Here, $\nu_1 = -1$, $\nu_2 = -1/2$, and $\nu_3 = 1$ corresponding to SO_2 , O_2 , and SO_3 , respectively.

The governing equations for conservation of species and energy in 1-D are:

$$\frac{1}{z^\alpha} \frac{d}{dz} (z^\alpha N_i) = \nu_i r \quad \text{for } i = 1, \dots, m$$

$$\frac{1}{z^\alpha} \frac{d}{dz} (z^\alpha N_i) = 0 \quad \text{for } i = m+1, \dots, n$$

Here, the variable N_i denotes the molar flux of the i^{th} species, r denotes the specific reaction rate on a catalyst volume basis, and the parameter $\alpha = 0, 1$ or 2 corresponds to an infinite slab, cylinder, or sphere, respectively. The first equation applies to SO_2 , O_2 , and SO_3 ($m = 3$) while the second equation applies to nitrogen ($m = n = 4$) since it is inert and does not participate in the reaction.

The governing equations for conservation of energy in 1-D is

$$k^e \frac{1}{z^\alpha} \frac{d}{dz} \left(z^\alpha \frac{dT}{dz} \right) = \Delta H_r r$$

Here, k^e denotes the effective thermal conductivity of the porous catalyst solid, T denotes the local temperature, and ΔH_r is the heat of reaction.

If the dusty gas model of Mason and Evans is used to describe the mass fluxes, then the following constitutive relation must be satisfied

$$\frac{N_i}{D_i^e} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j N_i - x_i N_j}{D_{ij}^e} = -\frac{1}{RT} \frac{dP_i}{dz} - \frac{x_i}{RT} - \frac{x_i}{RT} \frac{B_0 P}{\mu D_i^e} \frac{dP}{dz}$$

The key parameters that appear in the above equation include the mole fraction x_i of the i^{th} species, the permeability B_0 of the porous catalyst, the partial pressure P_i of the i^{th} species, the local total pressure P , the gas viscosity μ , the effective Knudsen diffusivity D_i^e of the i^{th} species, and the effective binary diffusivity D_{ij}^e of the i^{th} species in the j^{th} species.

The expression for the fluxes can be used to eventually derive a system of second order, nonlinear ordinary different equations along with appropriate boundary conditions that define a fairly rigorous model for non-isothermal diffusion and chemical reaction in a porous catalyst. Solution of the model equations generates local values for the species partial pressures and catalyst particle temperature from which the catalyst effectiveness factor can be evaluated for a given set of kinetic constants and other model parameters. The details will be provided in the final paper along with related version for 2-D and 3-D catalyst geometries.

Preliminary Results

COMSOL Multiphysics was used to solve the above 1-D model as well as other 2-D and 3-D models of the catalyst. A complicating factor in the case of the 2-D and 3-D models is defining appropriate values for the permeability parameter B_0 that appears in the dusty gas model since these have not been measured for typical industrial catalysts owing to the complex “skin” and other morphological effects that occur during catalyst manufacturing using extrusion technology. This work was still in progress at the time of this writing but the results will be presented at the COMSOL Users Conference.

Conclusions

COMSOL Multiphysics provides a powerful numerical platform for simulation of 1-D, 2-D, and 3-D models for complex catalyst shapes. These models provide a systematic approach for creating optimal catalyst shapes for a given chemistry that can be readily modified for a given application. These models can be readily coupled to global reactor models that allow the performance of pilot and commercial scale adiabatic reactors to be analyzed with a detailed accounting of various complex hydrodynamic effects and transport-kinetics interactions.