H_2SO_4 Catalysis: Perspective and Opportunities for Reducing SO_2 Emissions Using Particulate and Monolith Catalysts

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Introduction. Development of next-generation chemical processes that have zero emissions is a key environmental objective for sustainable development. The manufacture of H_2SO_4 by the air oxidation of SO_2 to SO_3 is an important technology where an opportunity exists for new catalyst development and process innovation by reducing emissions of unconverted SO_2 in process reactor tail gases owing to the sheer number (> 1500) and scale (ca. 500 to 4500 metric tons/day) of typical plants. The global supply of H_2SO4 is projected to grow from 200 MM tonnes in 2006 to more than 258 MM tonnes in 2015 with a value of > $10 MMM [1]. An opportunity exists to develop new innovations in environmental catalysis and reaction engineering for an important technology that has a rich and long history with sustained economic growth. Best Available Control Technologies (BACT) for controlling SO_2 emissions from stack gases involves additional processing resulting are cost intensive and well-studied. However, emissions control technologies using front-of-pipe technology, such as new catalyst technology, improved reactor designs, and process operational strategies have greater potential to be more economical versus end-of-pipe scrubbing technologies.

From a catalyst design perspective, specification of catalyst composition, catalyst size, catalyst shape and internal pore structure are interlinked parameters that have received notable attention by catalyst scientists and engineers since these properties affect the catalyst effectiveness factor, bed pressure drop, rate of catalyst attrition, catalyst mechanical integrity, catalyst life, amongst other key measures of performance. It is evident that specification of preferred catalyst design parameters requires careful optimization since tradeoffs exist in how the observed reaction rate and other measures of performance may be affected by altering one or both of these parameters.

The primary objective of this study is three-fold: (1) to review the current H_2SO_4 catalysts utilized in the oxidation of SO_2 to SO_3; (2) to evaluate monolith catalysts as potential candidates as SO_2 oxidation

catalysts; and (3) to develop modeling framework to compare reactor designs for both particulate and monolith catalysts under typical multi-pass convertor operation that can be used as the starting basis for process optimization.

Methods. Typical commercial H_2SO_4 catalyst compositions consist of silica support, vanadium and possibly metal promoters. The current state-of-the-art of both particulate and monolithic catalysts based upon recent open and patent literature will be reviewed.

COMSOL Multiphysics is used to model non-isothermal diffusion, reaction and transport effects in both various particulate and monolith catalyst geometries with compositional and temperature dependence of all model parameters. This builds upon our previous work [2] on modeling of transport-kinetic interactions in SO_2 oxidation commercial catalysts shapes, such as solid and hollow cylinders and various types of multi-lobe catalyst shapes. There is a knowledge gap in monolith modeling for SO_2 oxidation to SO_3 since the only open literature on modeling on monoliths was the numerical model developed by Bespalov *et al.* in 1991 [3]. Therefore, it is important to develop advanced models for better understanding of the transport-kinetic interactions that occur between the monolith channel and monolith microstructures that can be created by various catalyst synthesis protocols.

In this work, a new model is described that accounts transport-kinetic interactions for SO_2 oxidation in monolith catalysts that is valid for process conditions encountered in typical commercial-scale multi-pass convertor operation. The reaction kinetic model is based upon the work of Collina *et al*. [4] since it accounts for the dependence of the SO_2 oxidation rate on the partial pressures of SO_2, O_2, and SO_3 with inhibition by both SO_2 and SO_3. The reaction rate and adsorption equilibrium parameters in this model are valid from 420 to 550^{o}C, which is within the commercial operating range of most convertors. COMSOL Reaction Engineering Lab is used to study various adiabatic reactor designs for SO_2 converter performance under ideal plug flow conditions, while a more advanced COMSOL Multiphysics model is described that accounts for non-ideal gas and thermal energy interphase and intraphase transport effects.

Results and Discussion. Typical adiabatic 4-pass converter profiles are shown in Figure 1. These are based upon COMSOL Reaction Engineering Lab to describe adiabatic reactor performance with ideal plug flow of the gas. These results provide the incentive for developing new catalyst technology because the maximum SO_2 conversion possible is 99.7%, which is adequate to meet current EPA regulations for SO_2 emissions. However, it does not meet the anticipated future need to design H_2SO_4 plants with SO_2 emissions < 100 ppm, or even < 10 ppm.

Additional results that compare the performance of particulate versus monolithic catalyst shapes using typical process conditions will be presented and discussed, thereby showing the incentive for development of monolithic catalyst with higher activity and reduced emissions.

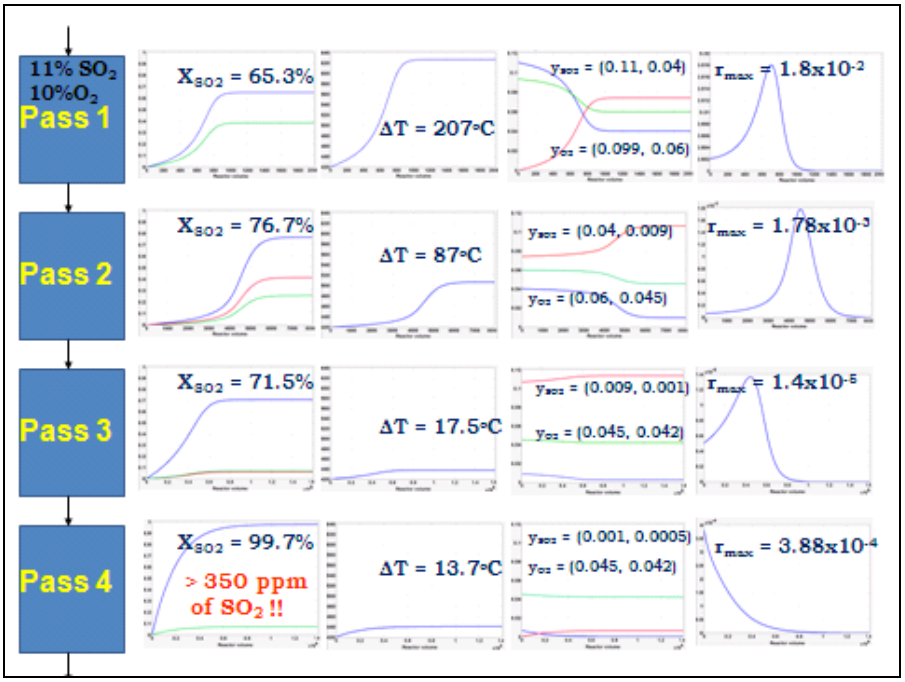


Figure 1. Adiabatic 4-pass converter profiles

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