

Study of sulfur dioxide oxidation in mini-packed bed reactor

Hanen NOURI^{#1}, Abdelmottaleb OUEDERNI^{*2}

Laboratory of Chemical Process and Industrial System (LR GPSI),
National School of Engineers of Gabes (ENIG), University of Gabes (UG),
Omar Ibn Elkhattab Street, 6029 Gabes, TUNISIA

¹hanennouri@gmail.com

Abstract— The conversion of sulfur dioxide into sulfur trioxide is a reaction which interests not only the industry of sulfuric acid production but also the processes of pollution control of certain gas effluents containing SO₂. This reaction was conducted in a tubular packed bed reactor using vanadium pentoxide as catalyst. Experiments were performed with different molar ratio of sulfur dioxide to oxygen and reaction temperature.

Fluid flow description inside the packed bed reactor was performed by using the free fluid and porous media flow model. This model was solved by the commercial software COMSOL Multiphysics 4.1. Pressure and velocity profiles inside the reactor were theoretically obtained.

Keywords— Packed bed, oxidation, heterogeneous catalysis, modeling.

I. INTRODUCTION

Sulfuric acid is one of the most important chemicals in the world. It is produced via the contact process in a gas phase catalytic oxidation reaction. In this process, a gas mixture containing sulfur dioxide and air is passed over a catalyst, which oxidizes SO₂ to SO₃[1]. Only two types of catalysts gained widespread commercial acceptance. These are platinum and vanadium pentoxide. Today, the dominating catalyst is vanadium pentoxide due to its lower cost and greater availability [1]. This catalyst consists of 4-9 wt% vanadium pentoxide V₂O₅, being the active component, together with alkali metals as promoters[2]. The oxidation of SO₂ is an exothermic reaction with fast reaction kinetics and high reaction enthalpy (-99 kJ/mol).

Due to the negative reaction enthalpy the equilibrium conversion decreases with rising temperature. However, with rising temperature the reaction rate increases but the equilibrium is shifted towards lower SO₃ concentration. So, an effective control of the temperature is very important. That is why, recent studies have been oriented to use microstructured reactor to conduct such exothermic reaction due to its outstanding heat transfer performance[1]. In fact, microstructured reactors represent a new approach of processes

development that has attracted the attention of many researchers in several engineering processes. Microreactors, as the name implies, involve reaction chamber whose dimensions are typically in the range of micrometers with volumetric capacity in the range of micro liters[3]. The possibility of reduction in dimensions with small volumes of reaction zone would allow application of high temperature or concentration with significant ease of process control and thermal management. The main advantage of microstructured reactors is their high surface to volume ratio in the range of 10000-50000 m²/m³ compared to more traditional chemical reactors [4]. This ratio enhances mass and heat transfer and thus an improvement in the conversion ratio. Heat transfer is also increased since the heat transfer coefficient is inversely proportional to the diameter of the channel; its value for microstructured reactors is around 10kW/(m².K), far higher than traditional reactors. The energy and economic gains are significant because the high heat transfer allows utilizing the full potential of catalysts during highly endothermic or exothermic reactions and avoiding hot-spots formation. In addition, the small inventories of reactants and products lead to inherent safety during the reactor operation. It has been reported that microstructured reactors run safely under conditions, which lay in the explosion regime. Small reactor dimensions facilitate the use of distributed production units at the place of consumption. This avoids the transport and storage of dangerous materials [5]. For these reasons, Pfeifer et al.[6] demonstrated the basic principle of producing SO₃ with pure oxygen in a one pass process without stepwise cooling or quenching. The goal is to reach a sufficiently high SO₃ concentration in a microstructured reactor being part of a compact plant installed on site.

It is proposed in our laboratory to take advantage of this new type of structures in the context of development of chemical reactors. That's why a micro channeled reactor is being developed but before using it we suggest to study the kinetic reaction and the influence of operating conditions in a tubular packed bed reactor. So, the aim of this work is to conduct the

conversion of sulfur dioxide to sulfur trioxide in a tubular packed bed reactor with different SO₂ inlet content and reaction temperatures and to study the flow rate and particle size effect. Numerical simulations with COMSOL Multiphysics were performed to describe the fluid flow in the reactor.

II. EXPERIMENTAL

The conversion of sulfur dioxide to sulfur trioxide had been conducted in a mill-packed bed reactor. The reactor is a stainless steel tube of internal diameter of 4 mm and 10 cm in length. The catalyst used in this study is the vanadium oxide with total surface area determined with liquid nitrogen adsorption by an autosorb1 Quantachrome according to Brunauer ,Emmetand Teller(SBET) of 4.041 m²/g and a total pore volume of 4.256E-3 cc/g. The catalyst was crushed sieved and particles of sizes of 500µm were introduced into the reactor. The particles of catalysts are fixed between two metallic grids. Approximately 200 mg of catalyst was used in most runs. The reactor was positioned in an electric furnace capable of reaching 1000 °C, and equipped with a temperature controller. Type K thermocouple was fitted in the catalyst bed to measure the reactor temperature. Pure nitrogen, oxygen and sulfur dioxide were metered by mass flow controller type Brooks, mixed in a micro mixer and preheated until the temperature of activation of catalyst before passing in the reactor. The reaction product were analyzed by iodometric method.

III. MODELLING

It is essential to study the hydrodynamics behavior and the flow in the catalytic bed. That is why a numerical simulation with the commercial software COMSOL Multiphysics 4.1 had been performed for the tubular packed bed reactor. The model couples the free fluid and porous media flow through the Navier-Stokes equations and Brinkman's extension of Darcy's law[8] .

The stationary Navier-Stokes equations describe the fluid flow in the free-flow regions:

$$\nabla \cdot [-\eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T + P\mathbf{I})] = -\rho(\mathbf{u} \cdot \nabla)\mathbf{u} \quad (1)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2)$$

In the porous bed, we used the Brinkman equations:

$$\nabla \cdot \left[-\frac{\eta}{\varepsilon_p} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T + P\mathbf{I}) \right] = -\frac{\eta}{\kappa} \mathbf{u} \quad (3)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (4)$$

In the above equations, η denotes the viscosity of the fluid (Ns/m²), ε_p is the porosity (dimensionless), \mathbf{u} the velocity (m/s), ρ the density (kg/m³), p the pressure (Pa), and κ the permeability (m²).

A constant velocity profile is assumed at the inlet boundaries:

$$\mathbf{u} = \mathbf{u}_{in} \quad (5)$$

The boundary condition for the Navier-Stokes equations at the outlet were

$$\mathbf{t} \cdot \mathbf{u} = 0 \quad (6)$$

$$p = 0 \quad (7)$$

where \mathbf{t} is any tangential vector to the boundary.

For the kinetic study, we coupled the hydrodynamics equations with transport of diluted species presented by the equation below:

$$\nabla \cdot (-D_i \nabla c_i) + \mathbf{u} \cdot \nabla c_i = R_i \quad (8)$$

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i \quad (9)$$

for the rate expression we used the modified equation of Calderbank based on the Langmuir-Hinshelwood concept.

$$R = \frac{K_1 P_{O_2} P_{SO_2} \left(1 - \frac{P_{SO_3}}{P_{SO_2} \sqrt{P_{O_2} K_P}}\right)}{22,414 \left(1 + K_2 P_{SO_2} + K_3 P_{SO_3}\right)^2} \quad (10)$$

where : R: kmol SO₂/kg cat hr

and temperature influence on constants expressed by:

$$K_1 = \exp\left(12,160 - \frac{5473}{T}\right)$$

$$K_2 = \exp\left(-9,953 + \frac{8619}{T}\right)$$

$$K_3 = \exp\left(-71,745 + \frac{52596}{T}\right)$$

$$K_P = \exp\left(-10,68 + \frac{11300}{T}\right)$$

COMSOL implements finite elements methods for solving partial differential equations and it uses the GMRES (Generalized Minimal Residual) method to solve the linearized equations. In the reactor, an unstructured mesh was generated . The number of elements was 57209 and the prescribed converging tolerance was 0.001.

IV. RESULTS AND DISCUSSION

A. Experimental Results

The temperature plays a significant role in gas heterogeneous catalysis because these reactions are generally limited by heat and mass transfers, it is thus imperative to take into account the parameter temperature, to adjust it and to control it according to the studied reaction. A series of experiments was undertaken to four contents of SO₂ (10%, 15%, 20% and 30%) and for a total volume flow of 2 ml/s.

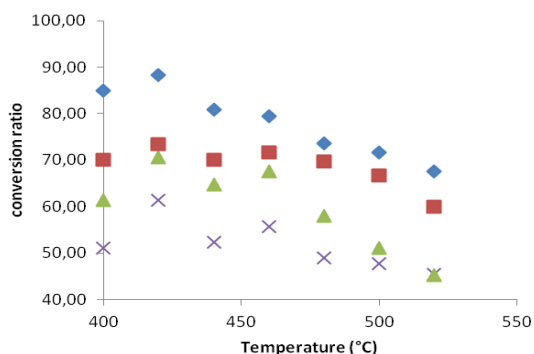


Fig. 1 Influence of temperature on conversion rate for various contents of SO_2

It can be seen that SO_2 conversion decreases with the SO_2 inlet content and that the increase in the temperature of 400°C to 450°C allows an improvement of conversion into SO_3 up to a value almost of 90% for a content of sulfur dioxide of 10%. After this value, the effect of the temperature becomes harmful and induced a fall of conversion rate. This result is well expected since the thermodynamics of this reaction which shows that the evolution of SO_2 conversion rate is increasing up to a precise value of the temperature from which it decrease according to the evolution of the equilibrium curve. This is well explained by Figure 2 that represent the conversion of SO_2 as a function of temperature for different reaction rates. The dashed line represent the Optimal Temperature Progression. It is the path that can achieve the highest conversion with the minimum volume reactor.

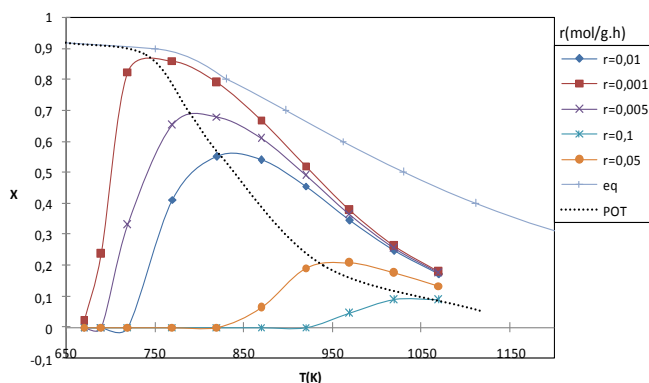


Fig. 2 Conversion of SO_2 as a function of temperature for different reaction rates

In addition to temperature, we studied the effect of flow rate and particle size in order to determine the limitation step.

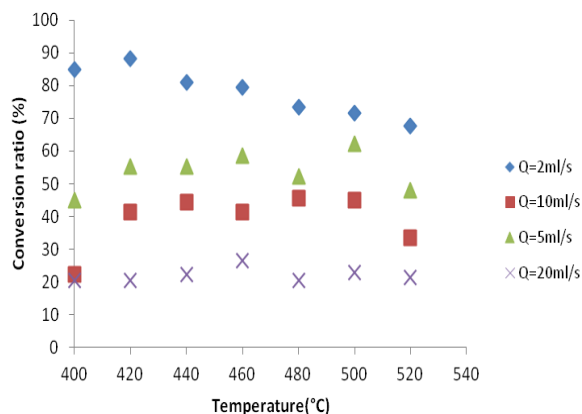


Fig. 3 Conversion of SO_2 as a function of temperature for different inlet flow rate ($\% \text{SO}_2=10$)

In figure 3, we tested the effect of the total inlet flow. We can see that the decrease of the inlet flow enhance the conversion ratio. A flow rate of 2 ml/s could achieve a conversion ratio of 90% in the packed bed.

B. Numerical study

The numerical resolution of the system of the equations allows us to have a theoretical model which describes the conversion of sulfur dioxide in a catalytic bed with vanadium pentoxide. This model allows us to simulate the reactor performance on the same operating conditions as the experiment.

For the hydrodynamic study, The model exemplifies the coupling of free and porous media flow in fixed bed reactors. Due to the symmetry only half of the reactor has to be considered. the flow within the reactor is laminar. COMSOL 4.1 solved the three dimensional Navier-Stokes equations for the flow through the reactor.

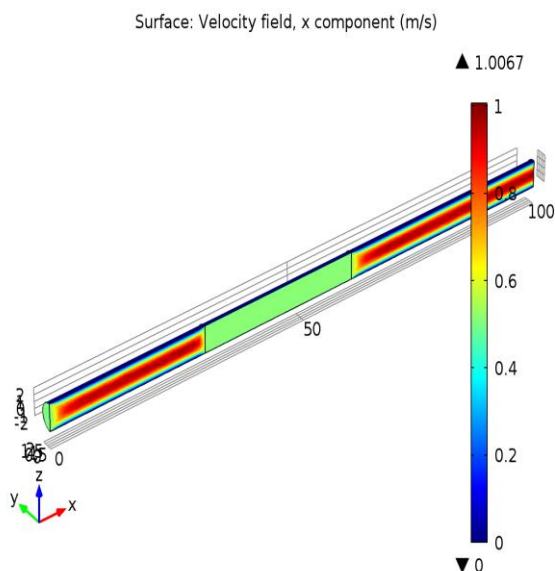


Fig 4: Magnitude of the velocity field in the free and porous reactor domains

Figure 4 shows the velocity profile of inert gas inside the packed bed reactor for a total gas flow of 20 ml/s. Due to the non-slip conditions, the velocity profile close to the wall becomes zero by definition, obtaining a maximum value in the middle of the free part of the reactor. In the catalyst bed, the velocity decreases until almost the half. The Figure 5 below shows the pressure drop, which occurs mainly across the porous bed.

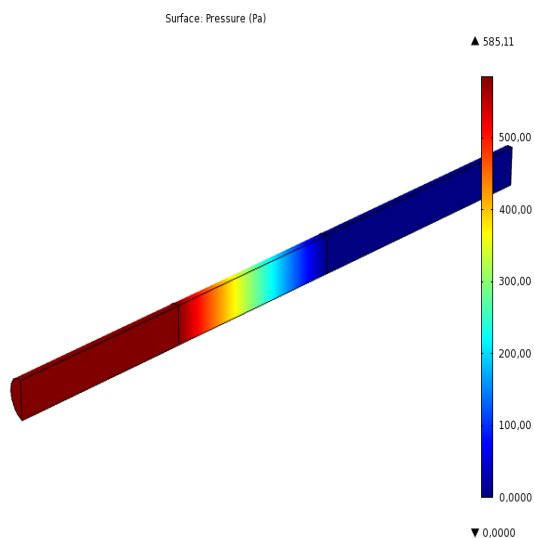


Fig 5: The pressure drop across the reactor.

V. CONCLUSIONS

This work is interested in the oxidation of sulfur dioxide in a tubular mill-packed bed reactor. This reaction had been performed for different sulfur dioxide content and temperature reaction. The catalysts used were particles of commercial

vanadium pentoxide. Experimental data show that the conversion ratio of SO_2 decrease with the inlet content of sulfur dioxide and increase with reaction temperature until an optimum equal to 450°C , above this value the conversion is limited by the equilibrium curve.

Numerical simulations by COMSOL Multiphysics were performed to describe the fluid flow in the reactor. Good agreement between the model predictions and the experimental results is achieved.

References

- [1] W. Benzinger, A. Wenka, R. Dittmeyer, Kinetic modelling of SO_2 oxidation with Pt in a microstructured reactor, *Applied Catalysis A: General* 397 (2011) 209-217
- [2] P. Pfeifer, T. Zscherpe, K. Haas-Santo, R. Dittmeyer, Investigations on a Pt/TiO₂ catalyst coating for oxidation of SO_2 in a microstructured reactor for operation with forced decreasing temperature profile, *Applied Catalysis A: General* (2010)
- [3] Kolb G., Hessel V., "Microstructured reactors for gas phase reactions", *Chemical Engineering Journal*, 98, 2004.
- [4] Gokhale S., Tayal R., Jayaraman V., Kulkarni B.,. *Microchannel Reactors: Applications and Use in Process Development*. International journal of Chemical Reactor Engineering, 3, 2005.
- [5] Renken A. and Kiwi-Minsker L., 2005. Microstructured reactors for catalytic reactions. *Catalysis today*, 110.
- [6] P. Pfeifer, K. Haas-Santo, J. Thormann, K. Schubert, *Chim. Oggi* 25 (2) (2007) 42-46
- [7] Froment F; Bichoff B. , *Chemical reactor analysis and design*, deuxième édition, (2002) 494
- [8] COMSOL Multiphysics 4.1 User's Guide. 2010.