



Simulation of an industrial adiabatic multi-bed catalytic reactor for sulfur dioxide oxidation using the Maxwell–Stefan model

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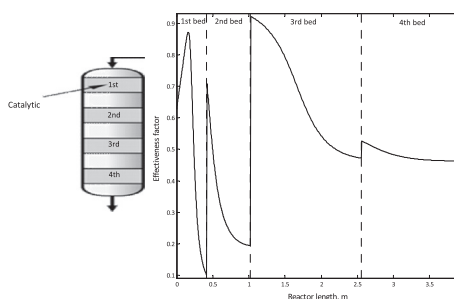
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HIGHLIGHTS

- A rigorous model was proposed for the analysis of a SO₂ oxidation catalytic reactor.
- The Maxwell–Stefan diffusional model was justified from thermodynamic correction factor matrix.
- The model allowed evaluating the reactor behavior with errors lower than 3%.

GRAPHICAL ABSTRACT

Catalytic performance – Effectiveness factor profiles in the multi-bed reactor.



ARTICLE INFO

Article history:

Available online 18 February 2015

Keywords:

SO₂ oxidation
Adiabatic reactor
Maxwell–Stefan diffusion model
Industrial reactor

ABSTRACT

In this work, a rigorous heterogeneous model for the analysis of an industrial adiabatic multi-bed catalytic reactor for sulfur dioxide oxidation was developed. It was based on the Maxwell–Stefan diffusional model, which was selected from the analysis of the Maxwell–Stefan diffusivity and the thermodynamic correction factor matrix. The reactor model, implemented in MatLab[®], allowed evaluating truthfully the behavior of each catalytic bed (e.g., concentration, conversion, pressure and temperature profiles) with errors lower than 3%. Additionally, the effectiveness factor variation along the reactor was estimated. Thus, a better understanding of the effect of diffusional resistances on reactor performance was possible.

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1. Introduction

The manufacture of sulfuric acid from sulfur involves three important steps: (1) the formation of sulfur dioxide (SO₂), (2) its

catalytic oxidation to sulfur trioxide, SO₃ (a reversible and highly exothermic reaction – ca. 96,000 kJ/kmol of SO₃ formed) and (3) the reaction of sulfur trioxide with H₂O in absorption towers. Sulfuric acid is recognized as very important commodity chemical. Only in 2012, its world production was about 220 million tonnes. Most of it is used for the production of phosphatate fertilizers, calcium dihydrogen phosphate, and ammonium phosphates [1].

In order to start the catalytic oxidation reaction, the temperature of the feeding gas to the converter reactor must be high

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Nomenclature

Latin letters

C_{pi}	specific heat capacity of component i , kJ/(kmol K)
C_i	molar concentration of component i , kmol/m ³
$D_{ij,ef}$	effective molecular diffusivity of component i binary with j , m ² /h
$\bar{D}_{ij,ef}$	Maxwell–Stefan diffusivity, m ² /h
$D_{i,Kn,ef}$	Knudsen diffusivity for component i , m ² /h
D_p	diameter of particle in the bed, m
G_o	superficial mass velocity, kg/(m ² h)
J_i	diffusion flux of species i relative to the molar average reference velocity, kmol/(m ² h)
k_i	reaction rate constant
K_p	equilibrium constant
L	reactor length, m
M_i	molecular mass of component i , kg/mol
N_i	molar flux of species i in a stationary coordinate frame of reference, kmol/(m ² h)
N_t	total molar flux, kmol/(m ² h)
P	total pressure, bar
p_i	partial pressure of component i , bar
R	universal gas constant, J/(mol K)

r_{SO_2}	intrinsic SO ₂ rate of reaction, kmol SO ₂ /(kg cat h)
r_{js}	rate of reaction of component j at the catalytic surface, kmol/(kg h)
T	temperature of the reactor, K
X_{SO_2}	conversion of SO ₂ , dimensionless
x_i	mole fraction of component i , dimensionless
z_p	half-thickness of the catalyst particle, m

Greek letters

∇	gradient
η	effectiveness factor
ΔH_{Rxn}	heat of reaction, kJ/kmol
ε	porosity, m ³ (gas)/m ³ (cat)
ε_B	bed voidage fraction, dimensionless
Γ	thermodynamic correction factor matrix
μ_G	viscosity of the gas mixture, kg/(m h)
ρ_G	density of the gas mixture, kg/m ³
ρ_B	bulk density of the catalyst bed, kg/m ³
τ	tortuosity, dimensionless

enough to activate the catalyst (e.g., 688–700 K for vanadium pentoxide based catalyst) and next to guarantee a high reaction rate. As the gas passes through the reactor, the exothermic reaction proceeds and the gas temperature increases. The reaction rate is dependent on catalyst activity and approach to equilibrium. The reaction extent depends on the reaction rate and the residence time of the gas in contact with the catalyst in the reactor. Several papers on modeling and simulation of SO₃ oxidation have been published in the open literature. Some relevant characteristics related to both catalyst pellet and reactor modeling can be summarized as follows:

- **Catalytic pellet:** In an early attempt, Olson et al. [2] have studied experimentally the importance of diffusion in the catalytic oxidation process. Later, Livbjerg and Villadsen [3] analyzed the kinetics and effectiveness factor for the industrial vanadium catalyst. They restricted their study to a very narrow range of experimental data (727–757 K) and to an intraparticle effective diffusivity model. Some inadequacy of this model was pointed out by Davis et al. [4]. They improved the analysis using the dusty-gas model and a single value for the tortuosity factor. In fact, other authors also discourage the use of the Fickian type models because they do not represent qualitatively the diffusion process in multicomponent systems [5]. However, effective diffusion coefficient approach, though it fails in the mechanistic sense, is nevertheless adequate in several situations and could be safely used for reactor simulation studies in such cases. Nevertheless, the basic problem is how to identify these *a priori*. In the present work, it was done using the procedure of Reddy and Murty [6].
- **Packed-bed oxidation reactors modeling:** Young and Finlayson [7] and Rosendall and Finlayson [8] proposed a model including radial and axial dispersion, heterogeneity, and density variations. Some criteria were developed to predict *a priori* which effects should be included. More recently, Nodehi and Mousavian [9] used a model for the simulation and optimization of a multi-bed adiabatic reactor, including a heterogeneous plug flow model (expressing the mass transfer by Fick's law with an effective diffusivity coefficient). A dynamic model was also proposed by Kiss et al. [1]. They include the catalytic reactor

(five pass converter), heat exchangers, mixers, splitters and reactive absorption columns. The kinetic parameters were fitted to the real plant data.

In this work, a rigorous heterogeneous model for the simulation of an industrial adiabatic multi-bed catalytic reactor for sulfur dioxide oxidation is developed. The reactor comprises one cylindrical vessel which acts as a fixed bed reactor with four separate beds of catalyst. For a satisfactory yield of sulfur trioxide (above 99.5% conversion is needed), the applied temperature is as low as economically possible. Thus, the heat is removed and recovered from the gas leaving each bed using heat exchangers. The produced sulfur trioxide is removed from the reactor between its third and fourth bed and passed to the next stage, where the sulfur trioxide is converted into sulfuric acid. However, a low amount of sulfur dioxide remains without conversion and is returned to the reactor through the fourth bed of catalyst and then the resulting gases, mainly sulfur trioxide, flow to the next stage of the process. In the view of the state of the art of previously proposed models, the following advances of this work can be pointed out: (i) the suitable model for diffusion and reaction in the catalyst pellet (vanadium (V) oxide supported on silica) was justified basing on the methodology proposed by Reddy and Murty [6] and confirmed by a comparison of the results obtained using the dusty-gas, the Maxwell–Stefan, and the effective diffusivity (Fick) models; (ii) the catalyst effectiveness factor was calculated and evaluated for each catalytic bed; (iii) model validation was done comparing the simulation results with plant data.

2. Mathematical model

2.1. Reaction and rate expression

The exothermic, gas phase, reversible reaction under study can be expressed as follows:



The following factors can increase the formation of SO₃: high pressure (this is not economical due to the high energy cost to compress the gas and the high capital cost to build vessels strong

enough to safely resist the pressure); low temperatures (cooling the gas between each pass provides the optimum temperature for conversion); high O₂ concentration (addition of atmospheric air to the process increases the oxygen content, favoring the SO₃ formation); and low SO₃ content (adding double absorption with an interpass tower completely removes SO₃ ahead of the final reaction pass).

Some industrial rates laws, reported in the literature, are suitable for a precise reactor, working at specific operational conditions. In this work, the SO₂ rate equation of Collina et al. [10], Eq. (2), was used, as suggested by Froment et al. [11]. This intrinsic reaction equation is based on the Hougen–Watson concept and on the observation that the reaction between adsorbed SO₂ and oxygen from the gas phase is the rate controlling step. Then, for particle modeling, the impact of diffusion fluxes on the catalyst-reactor performance will be included calculating the effectiveness factor.

$$-r_{\text{SO}_2} = \frac{k_1 P_{\text{O}_2} P_{\text{SO}_2} (1 - P_{\text{SO}_3} / (K_p P_{\text{SO}_2} P_{\text{O}_2}^{0.5}))}{(22.414(1 + k_2 P_{\text{SO}_2} + k_3 P_{\text{SO}_3}))^2} \text{ kmol SO}_2 / (\text{kg cat h})$$

$$k_1 = \exp(12.160 - 5473/T)$$

$$k_2 = \exp(-9.953 + 8619/T)$$

$$k_3 = \exp(-71.745 + 52596/T)$$

$$K_p = \exp(11300/T - 10.68)$$
(2)

2.2. Balances for the catalyst pellet

The catalyst packed in the industrial adiabatic multi-bed catalytic reactor is composed of vanadium pentoxide. It is supplied as a hollow ring shape particle with the following average dimensions: external diameter = 13 mm, inner diameter = 5 mm, and height = 14 mm. The catalyst has a porosity of 0.43, a tortuosity of 3.5, and a density of 33.8 lb/ft³ (data supplied by the catalyst manufacturer). The following benefits of ring type catalyst can be mentioned: lower gas pressure drop, greater dust holding capacity, and longer periods between screenings (catalyst removal from the reactor to separate collected dust and re-installation in the reactor).

2.2.1. Intraparticle diffusion model

Numerical simulation of intraparticle resistances, for the catalytic reactor modeling, demands the use of computationally efficient models. Some of the most notable models are: the dusty-gas, the Maxwell–Stefan, and the effective diffusivity (Fick) model. These are known to present varying degrees of rigor and computational speed. Some of their features are summarized in Appendix A. In the absence of any conclusive evidence about their relative efficacy, one often tends to use complex models in situations when simpler one suffices. Reddy and Murty [6] addressed this problem and recommended the method for the *a priori* selection of a suitable intraparticle model. It is based on the calculation of flux interactions among constituent species in a system, as also suggested by Krishna [5]. The proposed methodology can be summarized considering the type of interactions between the constituent species in the reaction system, as follows [6]: (1) if these interactions are negligible, the effective diffusivity model can be safely used even when the intraparticle regime is diffusion-controlled; (2) if the estimated interactions are strong, the effective diffusivity model can be used only if the intraparticle regime is reaction-rate-controlled; (3) if there are strong interactions between the species and also if the intraparticle regime is expected to be lightly-to-highly diffusion-controlled, the Maxwell–Stefan model should be used; Finally, (4) if in

addition to what is given in (3), there is a considerable increase or decrease in the number of moles due to the reaction, the dusty-gas model is recommended. Thus, the diffusion fluxes (J) for the $M - 1$ independent components in a system can be explicitly expressed in the terms of concentration gradients of all the components, as follows:

$$J = -c[B]^{-1}[\Gamma](\nabla x) \quad (3)$$

where $[B]^{-1}$ is the inverted matrix of the Maxwell–Stefan diffusivity and $[\Gamma]$ is the thermodynamic correction factor matrix. Their calculations are minutely explained elsewhere [12,13]. Next, the analysis of these matrices will indicate how the diffusion flux of any component is influenced by the concentration gradients of several other components presented in the system and/or the effects of mixture nonideality. Thus, in a typical situation in the SO₂ oxidation converter involving a mixture of SO₂ (1), oxygen (2), SO₃ (3), and N₂ (4), at temperature of 720 K and under atmospheric pressure, with $y_1 = 0.03$, $y_2 = 0.07$, $y_3 = 0.05$, and $y_4 = 0.85$, the $[B]^{-1}$ and $[\Gamma]$ matrices present the following values:

$$\Gamma = \begin{bmatrix} 1 & 7.28 \times 10^{-9} & 2.5085 \times 10^{-8} \\ 2.6953 \times 10^{-11} & 1 & 3.4887 \times 10^{-11} \\ 3.7529 \times 10^{-8} & 1.4098 \times 10^{-8} & 1 \end{bmatrix}$$

$$\begin{aligned} \mathcal{D}_{1-2} &= 3.3386 \times 10^{-5} \text{ m}^2/\text{s}, & \mathcal{D}_{1-3} &= 2.760 \times 10^{-5} \text{ m}^2/\text{s}, \\ \mathcal{D}_{1-4} &= 3.4183 \times 10^{-5} \text{ m}^2/\text{s}, & \mathcal{D}_{2-3} &= 4.8232 \times 10^{-5} \text{ m}^2/\text{s}, \\ \mathcal{D}_{2-4} &= 5.3839 \times 10^{-5} \text{ m}^2/\text{s}, & \mathcal{D}_{3-4} &= 4.93 \times 10^{-5} \text{ m}^2/\text{s}, \end{aligned}$$

Therefore, it is possible to argue that this reactive system may be termed as interaction-free (e.g., $[\Gamma]$ matrix is close to the identity matrix and the elements of Maxwell–Stefan diffusivity are very similar between them). Consequently, the effective diffusivity model and the Maxwell–Stefan one should yield nearly identical result. However, it is very important to notice that operative conditions of the industrial adiabatic multi-bed catalytic reactor correspond to the transition region between Knudsen diffusion and bulk diffusion [4]. Thus, in this case, the Maxwell–Stefan model should be preferred and will be applied.

2.2.2. The pellet balances equations

In the development of the diffusion–reaction model equations for the catalyst pellets, the following information is considered: (i) homogeneous porous structure of the catalyst pellet, (ii) mass transfer through the pellet, which occurs by diffusion, (iii) negligible external mass and heat transfer resistances, (iv) the gases diffusing through the pellet obeying the ideal gas law, and (v) the system is in a steady state. Since in steady state condition the problem of simultaneous diffusion and reaction is independent of particle shape [14,15], an equivalent slab geometry was used for the catalyst pellet with a characteristic length (r_p) giving a surface to volume ratio of the slab equal to that of the original shape of the ring. The slab, upon which the calculation of the effectiveness factor was made, was selected to comprise the same amount of active material, therefore the same volume as the active part of the ring. This active volume equivalent particle has an external surface per unit volume to be 1.07 times that of the active part of the ring. Therefore, the effectiveness factor, calculated on the basis of the active volume equivalent to the slab, should to be divided by this factor to obtain the value for the industrial ring-shaped catalyst.

The mass balance equations for component i are expressed as follows:

$$\frac{dN_i}{dz} = \rho_c r_i \quad (4)$$

with the boundary conditions at the center of the catalyst pellet:

$$N_i = 0 \quad \text{at } z = 0 \quad (5)$$

The equations of mass balance and the Maxwell–Stefan model are given in the following way (diffusion coefficient can be calculated according to Eqs. (A.2–A.4)) in Appendix A [12,13]:

$$-\frac{dC_i}{dz} = \sum_{j=1}^n \frac{x_j N_i - x_i N_j}{D_{ij,ef}} \quad (6)$$

with the boundary conditions:

$$C_i(z_p) = C_{i_s} \quad \text{at } z = z_p \quad (7)$$

The use of the Maxwell–Stefan model requires finding fluxes and concentration profiles by solving simultaneously the material balance equations and the Maxwell–Stefan model equations.

The performance of the pellet is expressed in terms of the effectiveness factor. It was computed using the following equation:

$$\eta = \frac{1}{r_p r_{j_s}} \int_0^{r_p} r_j dz \quad (8)$$

2.2.3. Balances for the reactor

The mass balance equation is given by:

$$\frac{dX_{SO_2}}{dL} = \frac{\eta \rho_B A_B r_{SO_2}}{F_{SO_2}} \quad (9)$$

Ergun equation is used to compute the pressure profile along the length of the catalyst beds:

$$\frac{dP}{dL} = -1 \times 10^{-5} \frac{(1 - \varepsilon_B) G_0}{D_p \varepsilon_B^3 \rho_G \mathcal{G}_c} \left[\frac{150(1 - \varepsilon_B) \mu_G}{D_p} + 1.75 G_0 \right] \quad (10)$$

and the energy balance differential equation is given as follows:

$$\frac{dT}{dL} = \frac{(-\Delta H_{Rxn,SO_2}) \eta r_{SO_2} \rho_B A_B}{\sum_{i=1}^4 F_i C_{p_i}} \quad (11)$$

2.2.4. Numerical solution of the model equations & model validation

The catalyst pellet described by the Maxwell–Stefan model is a two-point boundary value problem (given by Eqs. (4) and (6)). The set of non-linear equations resulting from the discretization of the pellet differential equations were solved using a homemade MatLab® subroutine, based on the algorithm of Finlayson [7]. The reactor model (Eqs. (9–11)) was integrated using a homemade MatLab® subroutine, which uses the Gear method with automatic step size to ensure accuracy. Since the rate equation is function of the partial pressure of the components, the mole fractions and the total pressure at each increment of the catalyst bed should be known. At the same time, mole fractions in the bulk and at the collocation points of the pellet are also required for the calculation of the effectiveness factors. This implies the simultaneous solution of the whole set of equations. Thus, at each increment of integration, the molar flow rates were calculated from the conversion values, and hence all gas mixture properties such as density, heat capacity, diffusivity and viscosity were computed.

Model validation had been done by the comparison between the simulation results and plant data of a conventional adiabatic multi-bed catalytic reactor in industrial scale, placed in Colombia (South America). The specifications of the industrial reactor and the feed conditions are given in Table 1.

3. Results and discussion

The model presented in this work provides the performance summary (conversion, pressure, and temperature profiles) along

Table 1
Sulfur dioxide oxidation industrial reactor specifications and feed conditions.

Item	Symbol	Value	Dimension
Reactor diameter	D_R	10.7	m
Catalyst volumes			
First bed		15000	L
Second bed		24000	L
Third bed		16000	L
Fourth bed		27000	L
Inlet pressure	P_0	2.0265	bar
Inlet temperature	T_0	683	K
Feed composition			
SO ₂		8.36	mol%
O ₂		8.9	mol%
N ₂		82.74	mol%
Total mass flow rate	F_{T0}	5000	kg/h

the reactor (Figs. 1–3), the gas and solid concentration profiles (not shown here), and effectiveness factor for the catalyst placed in each bed (Fig. 4). One can see that the agreement between these simulations and the industrial data is excellent. In all cases, the simulation errors were lower than 3%. For comparison, some numerical results obtained with the dusty-gas model, the Maxwell–Stefan model, and the effective diffusivity (Fick) model are presented in Appendix B together with the industrial output data of SO₂ oxidation reactor. As predicted by Reddy and Murty methodology, the results obtained using Maxwell–Stefan model presented the lowest deviation from plant data, while the Fick model showed the largest deviation. The predictions obtained using dusty gas model were usually comparable with these obtained using the Maxwell–Stefan one. However, they require more complicated calculation procedures and, comparing to the other two models, tremendous computation time.

Considering the Reddy and Murty guidelines, it is possible to say about the diffusion model for the oxidation reaction under study that the convective flux became important mostly when there is a significant change (increase or decrease) in the number of mols due to the reaction. It is also influenced by the quantity of inerts present in the reaction mixture. In this case, the number of mols during the reaction decreases (–0.5) and the content of inerts is

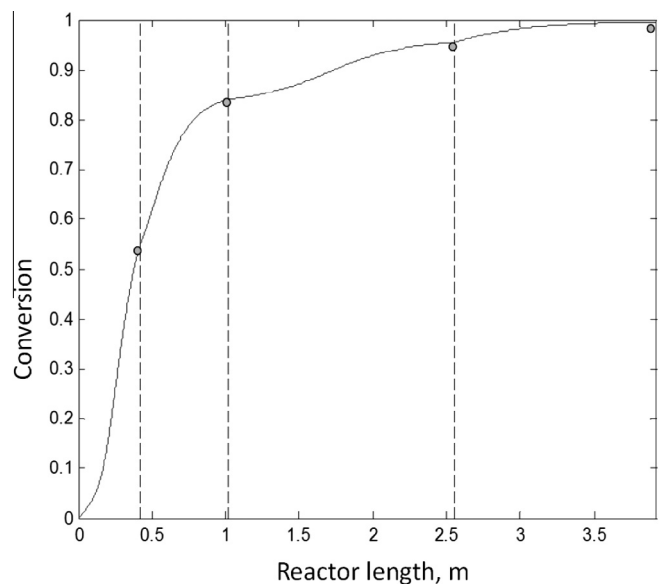


Fig. 1. Conversion profiles in the multi-bed reactor. Symbols represent plant data.

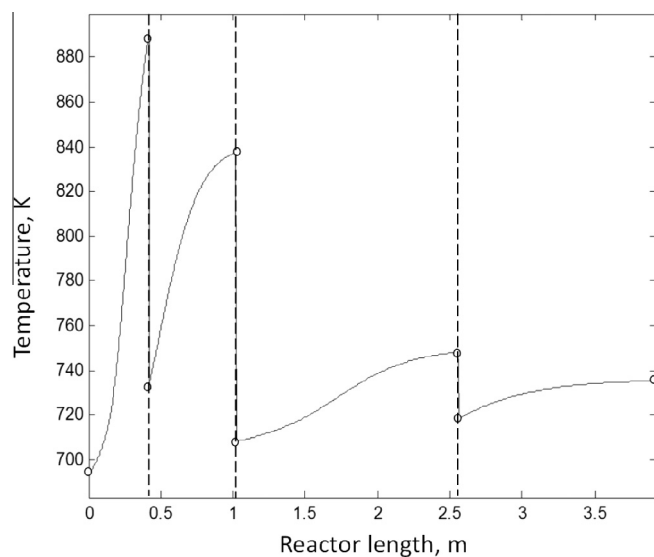


Fig. 2. Temperature profiles in the multi-bed reactor. Symbols represent plant data.

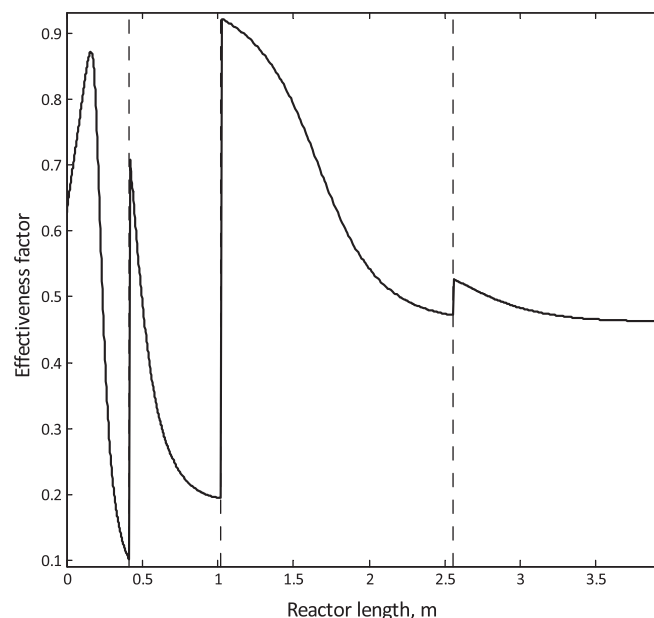


Fig. 4. Catalyst effectiveness factor in the multi-bed reactor.

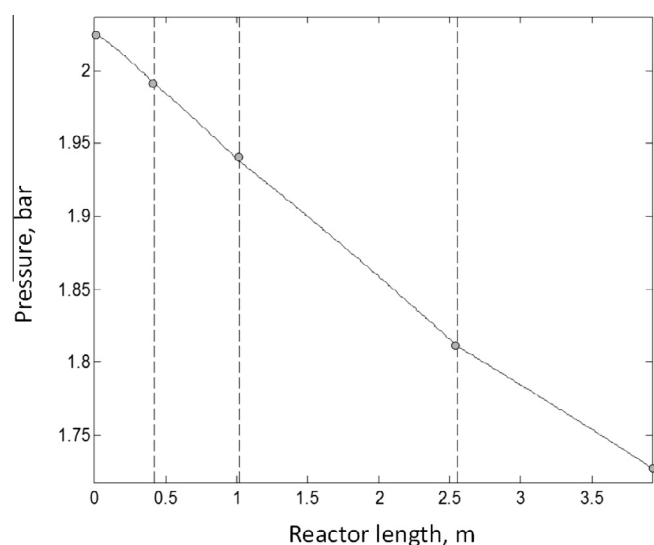


Fig. 3. Pressure drop in the multi-bed reactor. Symbols represent plant data.

quite high (typical N_2 concentration is about 80%). Thus, in this case, it could be expected that the convective flux should not be so important. Thus, Maxwell–Stefan model could be early selected.

Fig. 1 shows the conversion profile of SO_2 along each reactor bed. Under increasing temperature, the conversion rate increases from the inlet of the reactor (first bed). Fig. 2 shows the temperature profiles reaching a value of 889 K at the end of the first bed. This value is very close to the reported industrial one of 887 K, for this case. The maximum temperature difference between the calculated and the industrial data was always less than 3 K. It should be observed that the reaction mainly takes place in the first two catalytic beds (ca., 54% and 84%, respectively). Only ca. 15.5% of conversion occurs in the remaining two beds. Thus, temperature profiles became less marked in these last two

sections. Fig. 3 presents the pressure drop in the multibed catalytic reactor. For the entire system, an almost constant pressure gradient was estimated. The results are in agreement with plant data.

The effectiveness factor profiles for the four beds are shown in Fig. 4. Deviation from unity was all along the multi-bed reactor. This behavior is due to the significant internal mass transfer resistance at high reaction rates. Even in the fourth bed, although the SO_2 concentration is very low, the high temperature leads to high reaction rates and diffusion becomes the controlling factor. For the last three beds, the profiles start below unity and the effectiveness factors monotonically decreases. Effectiveness factor profiles are different for each catalytic bed. In the first one, it starts at ca. 0.63, passes through a maximum of ca. 0.87 (near to the half-length of the bed) and finally decreases sharply to 0.1 at the end of the bed. Such reduction in the effectiveness factor could be related to the decrease in reaction rate due to the temperature increase in the reactor (characteristic behavior of exothermic reversible reactions). In fact, as other authors had also reported, the temperature difference between catalyst center and surface becomes higher as the temperature of bulk phase increases [18]. For the other three beds, it decreases continuously along each bed, as the rates of this reversible reaction decreases.

4. Conclusions

A rigorous heterogeneous model was developed, and implemented in MatLab®, for steady state simulations of an industrial adiabatic multi-bed catalytic reactor for SO_2 oxidation. It allows evaluating truthfully the behavior of each catalytic bed (e.g., conversion, pressure and temperature profiles) and the effectiveness factor variation along the reactor. The Maxwell–Stefan model was properly justified as appropriate for the diffusion intraparticle model. Even if its use taxes the numerical algorithm with extra computation, the precision in plant data estimation makes the model a very useful tool. This leads to the better understanding of the effect of diffusional resistances on reactor performance. The developed model and a MatLab® interface make it suitable for operator training.

Appendix A. The most widely used intra-particle models and some of their features.

Model	Equation	Features
The dusty-gas model	$-\frac{dC_i}{dz} = \sum_{j=1}^n \frac{x_j N_i - x_i N_j}{D_{ij,ef}} + \frac{N_i}{D_{i,Kn,ef}}$	<ul style="list-style-type: none"> • It takes into account the effect of interactions among the various species on the diffusion of all the components • It presents the highest degree of complexity
The Maxwell–Stefan model	$-\frac{dC_i}{dz} = \sum_{j=1}^n \frac{x_j N_i - x_i N_j}{D_{ij,ef}}$	<ul style="list-style-type: none"> • It takes into account the effect of interactions among the various species on the diffusion of all the components • It considers that the pressure is invariant inside the pellet
The effective diffusivity model (Fick model)	$J_i = -c \sum_{k=1}^{n-1} D_{i,ef} \nabla X_k$	<ul style="list-style-type: none"> • It ignores the effect of interactions among the various species on the diffusion of all the components • It cannot represent the phenomena in a mechanistic fashion • It presents the lowest degree of complexity

* For further details, the following references are advised: Krishna [5]; Solsvik and Jakobsen [16]; Veldsink et al. [17]. For details about diffusivities parameter calculations, the Ref. [13] is suggested.

The simplest model to describe transport of components through the gas phase is the Fick model. It considers the transport as a product of a diffusion coefficient and the concentration gradient of a particular component. The diffusion process could be bounded to two asymptotic regimes: one for molecule–wall interaction (Knudsen diffusion) and molecule–molecule interactions (continuum/bulk/molecular diffusion). To evaluate the diffusion coefficient in the transition region, the Bosanquet formula can be used:

$$D_{i,Kn,ef} = \frac{4}{3} K_0 \left(\frac{8RT}{\pi M_i} \right)^{\frac{1}{2}} \quad (\text{A.3})$$

$$D_{ij,ef} = \frac{\varepsilon}{\tau} D_{ij}^0 \quad (\text{A.4})$$

For dusty-gas and Maxwell–Stefan models, the diffusion coefficients are calculated according to Eqs. (A.2–A.4).

Appendix B. Comparison between the industrial output data of SO₂ oxidation reactor and calculated results of the dusty-gas model, the Maxwell–Stefan model, and the effective diffusivity model

$$D_{i,ef} = \left(\frac{1}{D_{im,ef}} + \frac{1}{D_{i,Kn,ef}} \right)^{-1} \quad (\text{A.1})$$

Variable	Identification	Industrial reactor	Dusty-gas model	Maxwell–Stefan model	Effective diffusivity model
SO ₂ conversion, %	First pass outlet	54.3	55.0	54.8	56.1
	Second pass outlet	83.8	84.1	82.8	85.2
	Third pass outlet	91.7	92.8	91.3	93.1
	Fourth pass outlet	99.7	99.5	99.4	99.8
Temperature, K	First pass outlet	887	890	889	892
	Second pass outlet	839	843	842	844
	Third pass outlet	749	753	751	754
	Fourth pass outlet	738	740	739	744
Pressure, bar	First pass outlet	1.985	1.996	1.975	2.017
	Second pass outlet	1.943	1.951	1.949	1.969
	Third pass outlet	1.823	1.833	1.816	1.855
	Fourth pass outlet	1.728	1.734	1.726	1.763

The diffusion coefficients are effective diffusivities and can be calculated according to:

References

- [1] A.A. Kiss, C.S. Bildea, J. Grievink, Dynamic modeling and process optimization of an industrial sulfuric acid plant, *Chem. Eng. J.* 158 (2010) 241–249.
- [2] R.W. Olson, R.W. Schuler, J.M. Smith, Catalytic oxidation of sulfur dioxide. Effect of diffusion, *Chem. Eng. Prog.* (1950) 614–624.

$$D_{im,ef} = \frac{1}{(1-x_i)} \sum_{j=1, j \neq i}^n D_{ij,ef} X_j \quad (\text{A.2})$$

- [3] H. Livbjerg, J. Villadsen, Kinetics and effectiveness factor for SO₂ oxidation on an industrial vanadium catalyst, *Chem. Eng. Sci.* 27 (1972) 21–38.
- [4] M.E. Davis, G. Fairweather, J. Yamanis, Analysis of SO₂ oxidation in non-isothermal catalyst pellets using the dusty-gas model, *Chem. Eng. Sci.* 37 (1982) 447–452.
- [5] R. Krishna, Problems and pitfalls in the use of the Fick formulation for intraparticle diffusion, *Chem. Eng. Sci.* 48 (1993) 845–861.
- [6] K.V. Reddy, C.V.S. Murty, A methodology for the a priori selection of catalyst particle models, *Ind. Eng. Chem. Res.* 34 (1995) 468–473.
- [7] B.A. Finlayson, *Nonlinear Analysis in Chemical Engineering*, Ravenna Park Publishing Inc., Mansfield, Ohio, 2003.
- [8] B. Rosendal, B.A. Finlayson, Transport effects in packed-bed oxidation reactors, *Comput. Chem. Eng.* 19 (1995) 1207–1218.
- [9] A. Nodehi, M.A. Mousavian, Simulation and optimization of an adiabatic multi-bed catalytic reactor for the oxidation of SO₂, *Chem. Eng. Technol.* 29 (2006) 84–90.
- [10] A. Collina, D. Corbetta, A. Cappelli, Use of computers in the design of chemical plants, in: *Proc. Eur. Symp.*, Firenze, 1971.
- [11] G. Froment, K. Bischoff, J. De Wilde, *Chemical Reactor Analysis and Design*, third ed., Wiley, New York, 2011.
- [12] R. Taylor, R. Krishna, *Multicomponent Mass Transfer*, John Wiley and Sons, Hoboken, New Jersey, 1993.
- [13] J.A. Wesselingh, R. Krishna, *Mass Transfer in Multicomponent Mixtures*, Delft University Press, Delft, The Netherlands, 2000.
- [14] R. Aris, On shape factors for irregular particles: I. The steady state problem. Diffusion and reaction, *Chem. Eng. Sci.* 6 (1957) 262–268.
- [15] R. Aris, *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts. The Theory of the Steady State*, vol. I, Clarendon Press, Oxford, 1975.
- [16] J. Solsvik, H.A. Jakobsen, A numerical study of a two property catalyst/sorbent pellet design for the sorption-enhanced steam–methane reforming process: modeling complexity and parameter sensitivity study, *Chem. Eng. J.* 178 (2011) 407–422.
- [17] J.W. Veldsink, R.M.J. van Damme, G.F. Versteeg, W.P.M. van Swaaij, The use of the dusty-gas model for the description of mass transport with chemical reaction in porous media, *Chem. Eng. J.* 57 (1995) 115–125.
- [18] S. Hwang, R. Smith, Heterogeneous catalytic reactor design with optimum temperature profile I: Application of catalyst dilution and side-stream distribution, *Chem. Eng. Sci.* 59 (2004) 4229–4243.