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Experimental and modeling study of sulfur dioxide oxidation in packed-bed tubular reactor

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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 SO_2. This exothermic reaction needs a very good control of temperature, that's why it is led in the industry in a multistage converter with intermediate heat exchangers. Microreactors represent a good alternative for such reaction due to their intensification of mass and heat transfer and enhancement of temperature control. In this study, this reaction was conducted in a stainless steel tubular (4mm ID) packed bed reactor using particles of vanadium pentoxide as catalyst at atmospheric pressure. Experiments were performed with different inlet SO_2 concentration in 3-9% range and reaction temperature between 685-833K. We noticed that the conversion decreases with the amount of SO_2 and increases with the temperature until an optimum, above this value the conversion drop according to the shape of the equilibrium curve. Controlling rate mechanism is studied by varying temperature. Pseudohomogeneous perfect plug flow is used to describe this small tubular reactor. Numerical simulations with MATLAB were performed to validate the experimental results. Good agreement between the model predictions and the experimental results is achieved. 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. Velocity profile inside the reactor is theoretically obtained.

KEYWORDS: Sulfur dioxide, pentoxide vanadium, catalysis, kinetic model, heterogeneous reactor, hydrodynamic simulation.

1 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 SO_2 to SO_3 [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 V_2O_5, being the active component, together with alkali metals as promoters [2]. The oxidation of SO_2 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 SO_3 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, micro-structured 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 locally application of high temperature or

Corresponding Author: Hanen NOURI (hanennouri@gmail.com) 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 m^2/m^3 compared to more classic 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 / (m^2.K), far higher than classical known reactors. The energy and economic gains are significant because the high heat transfer allows using of 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 SO_3 with pure oxygen in a one pass process without stepwise cooling or quenching. The goal is to reach a sufficiently high SO_3 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 low diameter packed bed reactor with different SO_2 inlet content and reaction temperatures. Numerical simulations with MATLAB were performed to validate the experimental results and a detailed model solved by COMSOL Multiphysics to describe the fluid flow in the reactor.

2 EXPERIMENTAL

To highlight the effects of miniaturization, a simple packed bed tubular reactor was used. The reactor is a stainless steel tube of 4 mm inner diameter and 100 mm in length. The catalyst used in this study is the vanadium pentoxide commercial catalyst. The catalyst has a low total surface area determined with liquid nitrogen adsorption according to Brunauer ,Emmetand Teller(S_{BET}) about 4 m^2/g and estimated very reduced total pore volume 4.2.10^{-3}cc/g. The catalyst was crushed sieved and particles of sizes of 500µm were introduced into the reactor. Microreactor is filled with approximately 400 mg of catalyst in most runs. The reactor was positioned in controlled temperature electric furnace capable of reaching 1000 °C. Type K thermocouple was fitted in the catalyst bed to measure the catalyst temperature inside the reactor. 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 was analyzed by iodometric method.

The conversion of SO_2 was studied in the temperature range of 685-833K and the inlet gas of sulfur dioxide content was varied from 3 to 9% volumetric. The nitrogen flow rate was varied in such a way that the total flow rate at the inlet was the same in all the runs.

3 MODELLING

In order to validate the experimental results and to evaluate the performance of the micro packed bed reactor, a simple model was used assuming a pseudohomogeneous plug flow reactor with an inlet flow F_{A0} and a mass of catalyst W.The mass balance equation was solved using MATLAB.

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}} \tag{1}$$

In order to ensure plug flow conditions, absence of back mixing, and absence of channeling, certain criteria reported by Froment and Bischoff (1990)[7] were respected. These criteria are: (1) ratio of catalyst bed height to catalyst particle size (Lr/dp)≥ 50, and (2) ratio of internal diameter of the reactor to the catalyst particle size (d/dp)≥10. In this work, we used Lr/dp and d/dp of 100 and 8 respectively.

For the rate expression, we used the modified equation of Calderbank [7] based on the Langmuir-Hinshelwood concept and on the observation that the reaction between the adsorbed SO_2 and oxygen from the gas phase is the rate controlling step.

$$r = \frac{K_1 P_{O2} P_{SO2} (1 - \frac{P_{SO3}}{P_{SO2}\sqrt{P_{O2}} K_P})}{22{,}414 (1 + K_2 P_{SO2} + K_3 P_{SO3})^2} \qquad (2)$$

where : r: kmol SO_2/kg cat hr

and temperature influence on constants expressed by:

$$K_1 = \exp(12{,}160 - \frac{5473}{T})$$
$$K_2 = \exp(-9{,}953 + \frac{8619}{T})$$
$$K_3 = \exp(-71{,}745 + \frac{52596}{T})$$
$$K_P = \exp(-10{,}68 + \frac{11300}{T})$$

On the other hand, 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:

$$\nabla .\left[- \eta (\nabla u + (\nabla u)^T + PI \right] = - \rho (u.\nabla) u \Big] \qquad (3)$$

$$\nabla . u = 0 \qquad (4)$$

In the porous bed, we used the Brinkman equations:

$$\nabla .[- \frac{\eta}{\varepsilon_p} (\nabla u + (\nabla u)^T + PI] = - \frac{\eta}{\kappa} u \qquad (5)$$

$$\nabla . u = 0 \qquad (6)$$

In the above equations, η denotes the viscosity of the fluid (NS/m^2), ε_p is the bed porosity (dimensionless), u the velocity (m/s), ρ the density (kg/m^3), P the pressure (Pa), and κ the permeability (m^2).

A constant velocity profile is assumed at the inlet boundaries:

$$u = u_{in} \qquad (7)$$

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

t.u=0 (8)

p=0 (9)

where t is any tangential vector to the boundary.

4 RESULTS AND DISCUSSION

4.1 EXPERIMENTAL RESULTS

The temperature is a key operating parameter in this gas heterogeneous catalyst reactor. In this condition, kinetics are generally limited by heat and mass transfers, it is thus imperative to take into account the parameter temperature, to adjust and control it according to the studied reaction way. A series of experiments was undertaken to four inlet concentration of SO_2 :3%, 5%, 7% and 9% (v/v) and for a total volume flow rate of 20ml/s.

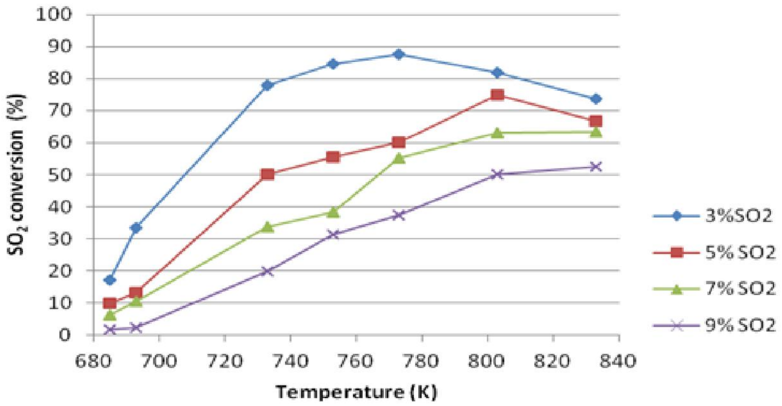

Fig. 1. Influence of temperature on conversion rate for various inlet SO_2 contents

It can be seen from figure1 that SO_2 conversion decreases with the SO_2 inlet content and that the increase in the temperature from 683 K to 773 K allows an improvement of conversion into SO_3 up to a value almost of 90% for a content of sulfur dioxide of 3%. Above this value, the effect of the temperature becomes harmful and induced a drop in conversion rate. This result is well expected since the thermodynamics of this reaction which shows that the SO_2 conversion rate is increasing up to a precise value of the temperature from which it decrease according to the shape 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.

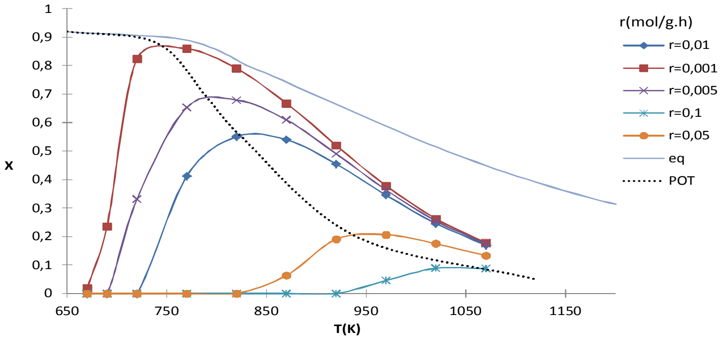

Fig. 2. Conversion of SO_2 versus temperature at various reaction rates

The variation of the observed rate versus reaction temperature for different SO_2 inlet content is reported in figure 3. The benefit effect of temperature on the reaction rate is well shown. But there is an inflexion point at a temperature of 773 K. This point divided the reaction domain in two zones. Below 773k, the inlet SO_2 content had no effect on the reaction rate and it had a significant effect above this value. To highlight this result, we represented in figure 4 the variation of logarithm of the observed rate $Ln(r_{obs})$ as function of the inverse of reaction temperature. It is very clear that the catalytic process is controlled by two different process owing temperature range: diffusional and chemical control regimes.

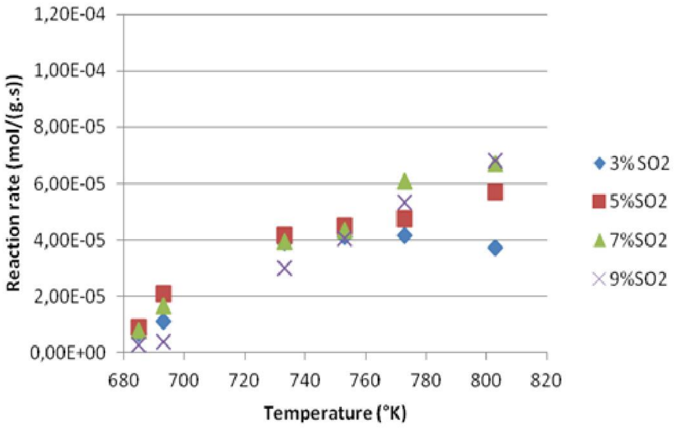

Fig. 3. Reaction rate versus temperature for different SO_2

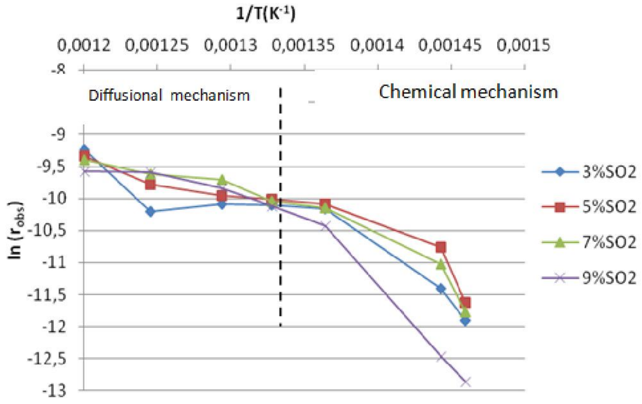

Fig. 4. Ln(r_{obs}) versus 1/T content

In order to calculate the kinetic parameters of the reaction rate, we used the domain of chemical control since in this domain the observed kinetic and intrinsic reaction parameters are the same. Table1 present the calculated activated energy and the frequency factor of the reaction determined by Arrhenius law.

Table 1. Activated Energies and kinetic Arrhenius constants for different SO_2 content

%SO_2	Ea(J/mol)	A(mol/(g.s.atm))
3	$1.14\ 10^5$	$1.34\ 10^4$
5	$1.26\ 10^5$	$7.92\ 10^4$
7	$1.45\ 10^5$	$1.68\ 10^6$
9	$2.13\ 10^5$	$8.13\ 10^{10}$

4.2 NUMERICAL STUDY

The numerical resolution of the system of the equations achieve a theoretical model which describes the conversion of sulfur dioxide in a catalytic bed with vanadium pentoxide. This model is a tool that allows simulation of the reactor performances on the same operating conditions as the experiment. The table 2 summarizes the results of the simulation at the outlet of the reactor and compares them with the experimental results. We note that there is a good agreement between the numerical and experimental results, the relative error (e %) calculated didn't exceed 20% in all experiments except for the content of 9% SO_2. This difference can be explained by the analysis method used which requires many precautions.

Table 2. Comparison between experimental and simulated results

SO2 %	3			5			7			9		
T(°K)	X_{exp}(%)	X_{th}(%)	e(%)	X_{exp}(%)	X_{th}(%)	e(%)	X_{exp}(%)	X_{th}(%)	e(%)	X_{exp}(%)	X_{th}(%)	e(%)
685	17,14	21,11	18,81	9,972	10,63	6,19	6,2	6,21	0,16	1,639	3,92	58,19
693	33,33	32,22	3,45	13,33	16,16	17,51	10,34	9,29	11,30	2,44	5,79	57,86
733	77,91	82,65	5,74	50	53,59	6,70	33,82	33,89	0,21	20	22,33	10,43
753	84,74	88,41	4,15	55,56	66,44	16,38	38,46	46,59	17,45	31,43	33,06	4,93
773	87,72	89,12	1,57	60	73,94	18,85	55,26	56,37	1,97	37,5	42,77	12,32
803	81,93	85,47	4,14	75	77,57	3,31	63	64,64	2,54	50	52,68	5,09
833	73,68	78,75	6,44	66,66	74,32	10,31	63,41	66,09	4,06	82,5	56,68	45,55

We reported in figure 5 and 6 the variation of the SO_2 conversion ratio along the catalytic bed for different reaction temperature and inlet flows. We note a good enhancement of conversion from 32% at 693K to 82% at 733K, this is explained by the activation of catalyst at this temperature. For temperature below 803K the conversion decreased according to the equilibrium curve.

In figure 6, we tested the effect of the total inlet flow. We can see that in spite of the small residence time in the reactor, the decrease of the inlet flow enhance the conversion ratio. A flow rate of 5 ml/s could achieve a conversion ratio of 90% in the first 10 mm of the packed bed.

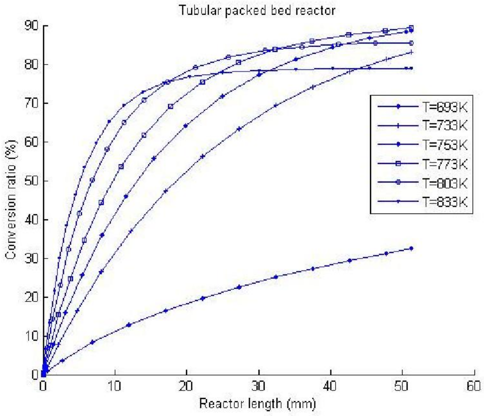

Fig. 5. ***Conversion of SO_2 along the packed bed (3%SO_2, Q=20ml/s)***

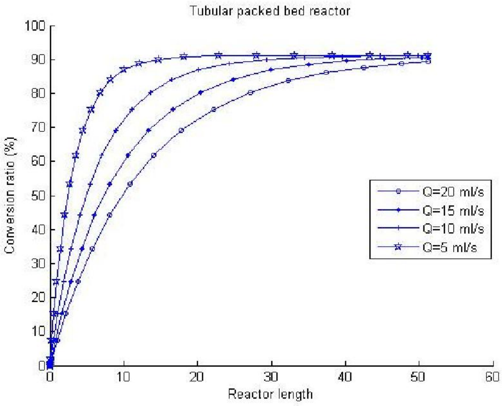

Fig. 6. ***Effect of flow rate on the conversion of SO_2 along the packed bed (3%SO_2, T=773K)***

The effect of the flow on the conversion rate of this reaction can be explained by a limitation by mass transfer. To confirm this idea we calculated criterion available in literature to determine the effects interparticle and intraparticle mass transport limitation could have on the rate of reaction.

To determine whether film mass transfer resistance has any effect on the rate of reaction, the ratio of observed rate to the rate if film resistance controls was examined. Equation (10) illustrates this criterion:

$$\frac{observed\ \ rate}{rate\ if\ film\ resist\ ance\ controls} = \frac{-r_{A,obs}}{C_{Ab}k_c}\frac{d_p}{6} \qquad (10)$$

r_{Aobs} is the observed rate of reaction, d_p is the particle diameter, C_{Ab} is the bulk concentration and k_c is the mass transfer coefficient obtained to be 0.57 m/s from the correlation of Theones Kramers [9].

The estimated value for the equation (10) was $6.966.10^{-10}$. The result indicates that the observed rate is very much less than the limiting film mass transfer rate. Thus the resistance to film mass transfer should not influence the rate of reaction [10]. Mears'criterion [9] is often considered a more rigorous criterion for determining the onset of mass transfer limitation in the film. Therefore, we decided to apply this criterion to determine if there was any mass transfer limitation during the collection of the kinetic data. This correlation is given in

$$\frac{r_{obs}\rho_b R_c n}{k_c C_a} < 0.15 \qquad (11)$$

The value of this equation is $1.3.10^{-6}$. Therefore, it can be concluded that there was no mass transport limitation in the film.

The internal pore mass transfer resistance was calculated using Weisz-Prater criterion as given by:

$$C_{wp,ipd} = \frac{-r_{A,obs}\,\rho_c R_C^2}{D_{eff}\,C_{AS}} \qquad (12)$$

Where $C_{wp,ipd}$ is the Weisz-Prater criterion for internal pore diffusion, ρ_c the pellet density, R_c catalyst radius, D_{eff} is the effective mass diffusivity obtained from Deff=($D_{AB}\varepsilon/\zeta$) [9] where D_{AB} is the bulk diffusivity of compound A in B, ε is the void fraction(=0.4), ζ is the tortuosity factor taken as 8[9] and C_{As} is the concentration at the pellet surface assumed to be equal to the bulk concentration as suggested by Levenspiel [10].

The estimated value for $C_{wp,ipd}$ was $6.26.10^{-5}$. This value is much less than 1. Thus this result indicates that the concentration on the catalyst surface is more or less the same as the concentration within its pores. So there is no internal pore diffusion limitations. We must mention that these effects were investigated at a temperature of 733 K, the low amount of SO_2 (3%) and an observed rate of $3.89.10^{-5}$ mol/(g.s).

4.3 FLOW MODELING

For the hydrodynamic study, The model presents 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.

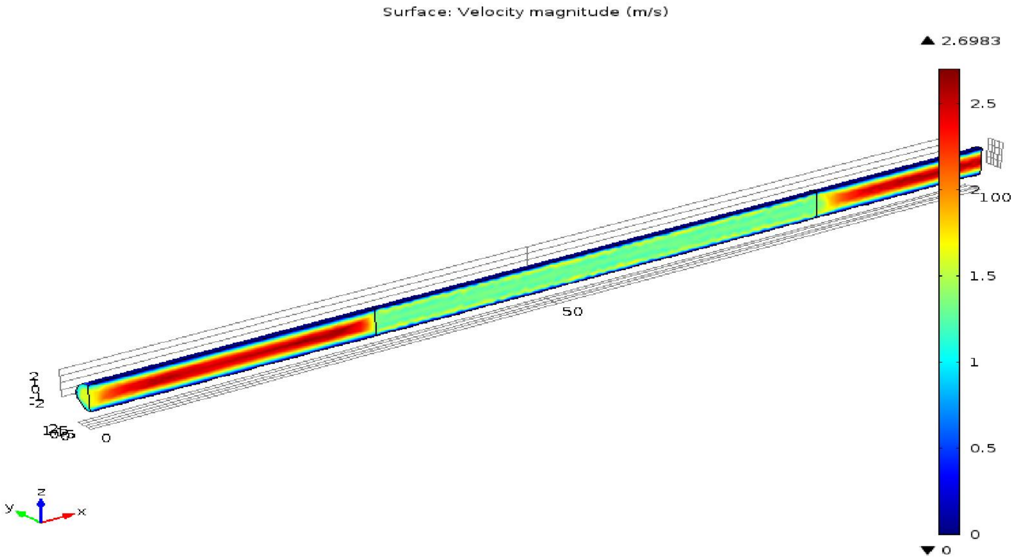

Fig. 7. Magnitude of the velocity field in the free and porous reactor domains

Figure 7 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 8 below shows the variation of the number of Reynolds Re across the tubular reactor. Re is about 7 in the catalytic bed assuring a laminar flow.

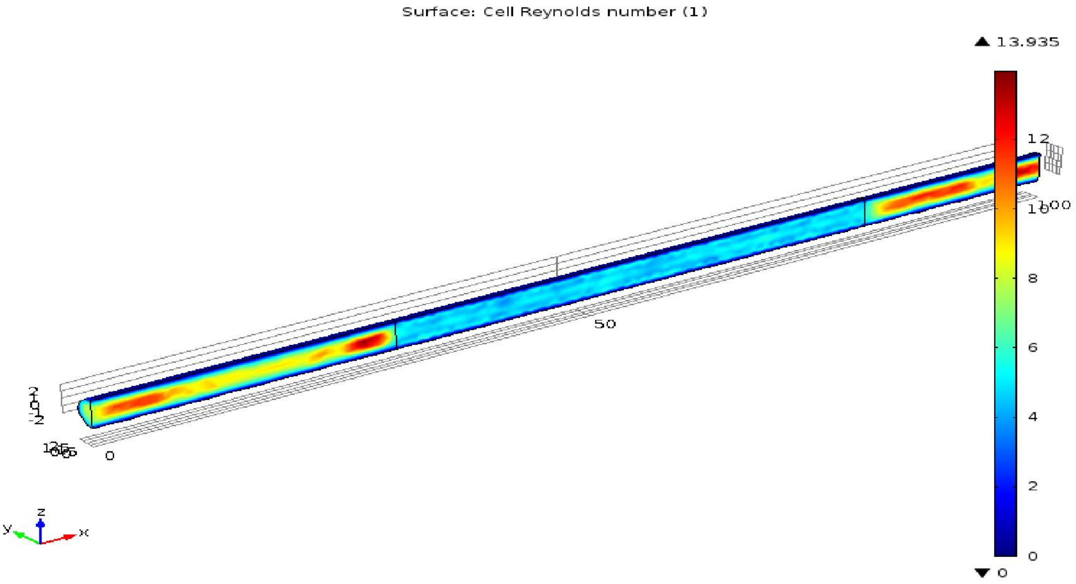

Fig. 8. The Reynolds Number across the reactor

5 CONCLUSION

This work is interested in the oxidation of sulfur dioxide in a tubular packed bed reactor. This reaction had been performed for different sulfur dioxide content and temperature reaction in the range of 685-833 K. The catalyst used was commercial vanadium pentoxide with particles's diameter of 500µm. 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 773K, above this value the conversion is limited by the equilibrium curve. Numerical simulations with MATLAB were performed to validate the experimental results and a detailed model solved by COMSOL Multiphysics to describe the fluid flow in the reactor. Good agreement between the model predictions and the experimental results is achieved.

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