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Simulation of Two Series Packed-Bed Reactors for SO_2 Oxidation Reaction

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Abstract: *Simulation of the oxidation reaction is being carried out for two adiabatic packed-bed reactors using MATLAB. This reaction is an important industrial catalytic reaction for the production of H_2SO_4 in the chemical industry. The catalyst is V_2O_5 and it is a heterogeneous system. The reaction rate is complex for this non-elementary exothermic reaction. It is highly important to simulate the performance of the packed-bed reactors where two beds are operated adiabatically with an inter-stage-cooling. In this study, the effects of inlet compositions of reactants, initial pressure, feeding temperature, total inlet flow rate, reactor diameter, and catalyst particle diameter on conversion and pressure drop in both packed-bed reactors were investigated.*

Keywords: SO_2; Packed-Bed Reactors; Oxidation; Sulfuric Acid; MATLAB.

1. INTRODUCTION

Presently, simulations play a crucial role in the preliminary stages of various industrial processes [1-3]. Particularly, for hazardous reactions involving significant heat release, like the production of sulfuric acid (H_2SO_4), simulations are of paramount importance. Sulfuric acid is a highly valuable product extensively used in the contemporary industrial world. Its applications include fertilizer production, petroleum refining, metallic ore leaching, and other chemically significant processes [4]. Production of H_2SO_3 is highly exothermic and the most significant reaction in the production process is the oxidation process of SO_2 to SO_3 (1),

$$SO_2 + \frac{1}{2}O_2 \overset{V_2O_5}{\longleftrightarrow} SO_3 \qquad \Delta H < 0 \qquad (1)$$

The simulation of this heterogeneous process holds significant importance as it allows the prediction of reaction kinetics and the assessment of various factors that influence the process. The process is heterogeneous and V_2O_5 serves as the catalyst in this context [5]. To achieve higher conversion rates, it is desirable to mitigate excess heat generated during the reaction. Hence, the oxidation process is performed using an inter-cooling-stage system [6]. The reaction kinetics are notably sluggish at low temperatures, necessitating an operating temperature range of *630-900* K for this catalytic reaction [7]. Thus, maintaining the temperature within this range becomes crucial for achieving optimum reaction conditions.

The sulfur dioxide converter is operated at high pressure to enhance the conversion of reactants, leveraging Le Chatelier's principle. Given these factors, it becomes essential to conduct simulation studies before proceeding with the actual design and manufacturing process. The primary objective of this work is to simulate the reaction, with the hope of utilizing the findings in the future construction of a sulfuric acid manufacturing plant in Kyrgyzstan, a developing country.

This paper serves as a continuation of previous research efforts [8,9], where the authors introduced two series packed-bed reactors with an inter-cooling stage (Figure 1) and presented the final conversion results for various initial temperature and pressure conditions (Table 3). In the current paper, the focus lies in a more comprehensive analysis of the effects of different operating conditions on the performance of these reactors.

2. MATERIALS AND METHOD

In this research study, the investigation involved the utilization of two series packed-bed reactors equipped with an inter-cooling stage to facilitate the oxidation reaction (as depicted in Figure 1). Both reactors were operated under adiabatic conditions. To conduct the simulations, the MATLAB (R2015a (MATLAB 8.5)) programming language was employed as the primary tool for analysis [10].

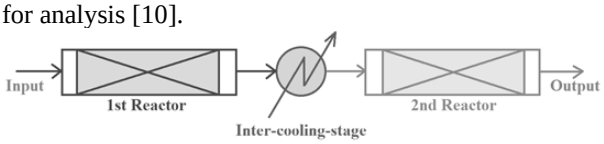

Figure 1. Two adiabatic reactors with an inter-cooling-stage.

The feed composition considered for the simulation is as follows: 79% N_2, 10% SO_2 and 11% O_2. The reaction rate expression utilized in this study was adopted from the works of Eklund 1956 [11] and given bellow,

$$-r'_{SO_2} = k\sqrt{\frac{P_{SO_2}}{P_{SO_3}}}\left[P_{O_2} - \left(\frac{P_{SO_3}}{K_p P_{SO_2}}\right)^2\right] \qquad (2)$$

The equilibrium constant (K_P) is,

$$K_P = \frac{P_{SO_3}}{P_{SO_2} * (P_{O_2})^{\frac{1}{2}}} \qquad (3)$$

k – reaction constant
P_i – partial pressure of *i*, *atm*
Ergun equation was used for the pressure drop effects [12],

$$\frac{dP}{dz} = \frac{-G}{\rho_0 g_c D_p}\left(\frac{1-\varphi}{\varphi^3}\right)\left[\frac{150(1-\varphi)\mu}{D_p} + 1.75G\right]\frac{P_0}{P}\frac{T}{T_0}(1+\varepsilon X) \qquad (4)$$

dP – pressure change, kPa
dz – reactor length, m
G – mass flow rate, $kg/m^2\text{-}s$
ρ – density, kg/m^3
g_c – conversion factor, force-to-weight ratio (1 for SI units)

μ – kinematic viscosity of gas, *kg/m-s*
The rest of the variables are given below in the tables and/or can be found throughout the paper.
The equations relating the conversion (X) and temperature (T) for the first reactor with the feed temperature of 670 K (5) and for the second reactor with the feed temperature of 700 K (6) were derived from the general energy balance and is given as follows:

$$T = \frac{86065+38383X}{71.36-3.2X} \quad (5) \text{ and } \quad T = \frac{86199+38383X}{71.83-3.2X} \quad (6)$$

Some thermochemical values were taken from JANAF sources [13].
Table 1 and Table 2 show the basic parameters values used for the simulation of the performance of two packed-bed reactors respectively.

Table 1. Basic inlet values to the first reactor.

Parameters	**Initial values**
Inlet compositions of reactants	%10 SO_2, %11 O_2, %79 N_2
Initial pressure, *Po*	2 *atm*
Feeding temperature, *To*	670 *K*
Total inlet flow rate, F_{To}	90.72 *kmol/h*
Inlet flow rate of SO_2 (A)	9.07 *kmol/h*
Reactor diameter, D	10 *m*
Catalyst particles diameter, D_p	0.46 *cm*
Void fraction, φ	0.45

Table 2. Basic inlet values to the first reactor.

Parameters	**Initial values**
Inlet compositions of reactants	%2.4 SO_2, %8.0 SO_3, %7.4 O_2, %82.2 N_2
Initial pressure, *Po*	2 *atm* (≈ 2 *bar*)
Feeding temperature, *To*	700 *K* (≈ 1260 *R*)
Total inlet flow rate, F_{To}	87.20 *kmol/h*
Inlet flow rate of SO_2 (A)	2.09 *kmol/h*
Reactor diameter, D	10 *m*
Catalyst particles diameter, D_p	0.46 *cm*
Void fraction, φ	0.45

Since the reaction under consideration is catalytic in nature, the length of the reactor is expressed in terms of catalyst weight. In the case of the second reactor, the conversion commences from 76.54%. This initial conversion value was determined based on the final conversion achieved in the first reactor, considering the fundamental inlet conditions as established in our earlier study.

3. RESULTS AND DISCUSSIONS

Figure 2 illustrates the simulation results of conversion for the first (a) and second (b) reactors. In our prior publication [10], we already elucidated the evolution of the reaction rate along both reactors. As described in that study, the reaction rate initially rises due to the favorable initial conditions, but subsequently declines as more heat is generated in both reactors. In contrast, when observing the conversion profiles, it becomes evident that the conversion increases initially and eventually stabilizes at a certain point. This plateau is attributed to the limitation imposed by the inlet gas compositions in both reactors. Additionally, the presence of friction within the reactor results in noticeable pressure drops, as depicted in Figure 2 (c,d) for both reactors.

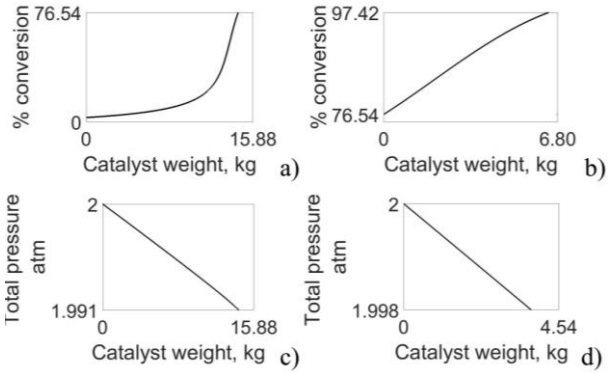

Figure 2. Conversion in the first (a) and second (b) reactor.

Considering space constraints, the presentation of figures will be limited to the first reactor, as the primary objective of this study is to examine the influence of various parameters on reactor performance. It is worth noting that similar trends are observed in the second reactor as well. The comprehensive results for both reactors can be found in Tables 3, 4, 5, and 6, providing a detailed summary of the findings.
As observed in Figure 3, augmenting the initial pressure has resulted in higher conversion rates for both reactors. Consequently, this enhancement in conversion allows for the utilization of a smaller quantity of catalyst to attain the desired level of conversion, as evident from the data presented in Table 3. However, it is noteworthy that excessively increasing the initial pressure does not have a significant impact on the conversion. Therefore, it becomes essential to identify and determine the most suitable initial pressure value to optimize the reactor's performance effectively.

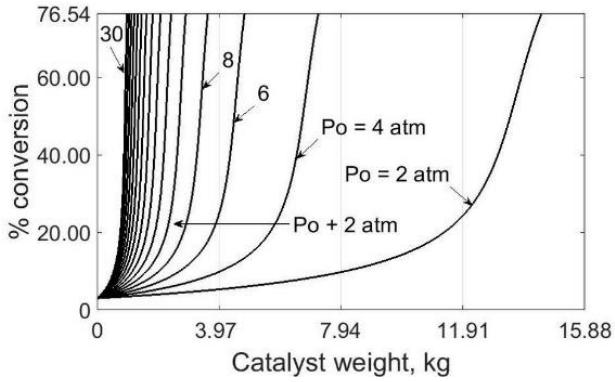

Figure 3. Effect of initial pressure in the first reactor.

The temperature has a substantial influence on the reaction rate as general. As the temperature increases, the rate of the reaction also rises, leading to higher conversion in both reactors, as illustrated in Figure 4. However, due to the exothermic nature of the reaction, increasing the temperature will lead to a decrease in the equilibrium conversion. This phenomenon was demonstrated in our earlier publication [8] and can be

seen in Figure 4 as well. Increasing from 620K to 650K will affect conversion significantly while from 700K to 730K does not have much effect due to the exothermic nature of the reaction described above. Therefore, maintaining an optimum temperature is crucial for managing such reactions effectively, striking a balance between achieving higher conversion rates while also considering the impact on the equilibrium conversion.

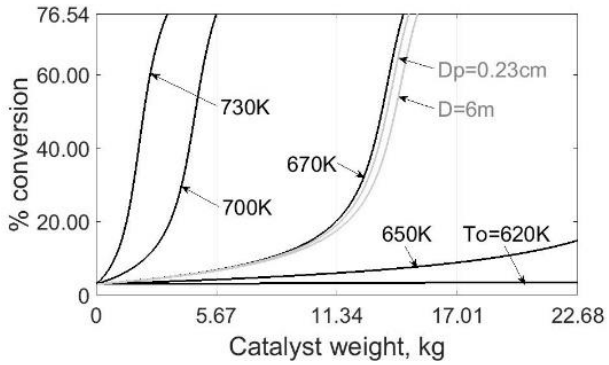

Figure 4. Initial temperature effect on the conversion in the first reactor.

Increasing the temperature results in only a minor pressure drop in both reactors (Figure 5). This can be attributed to the higher kinetic energy of molecules, leading to increased movement and collisions with the reactor's surface and among themselves, which contributes to the pressure drop. Another plausible explanation is that the reaction involves a transition from a state with more molecules (and greater volume) to a state with fewer molecules (and reduced volume). This is evident from Figure 5, where the pressure drop remains relatively constant in all temperature cases in the beginning until a certain level of conversion is achieved.

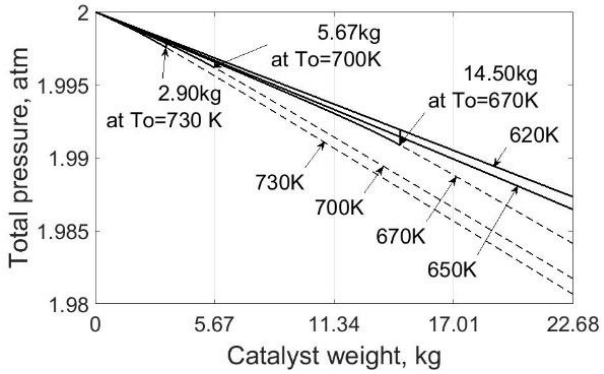

Figure 5. Temperature effect on pressure drop in the first reactor.

Assuming the volume of the reactors remains constant while decreasing their diameter, the resulting increase in surface area leads to higher frictional effects. As a consequence, the pressure drop experienced in both reactors becomes significantly higher (Figure 6). The increased surface area generates more resistance to the flow of reactants and products within the reactor, resulting in a pronounced rise in the pressure drop.

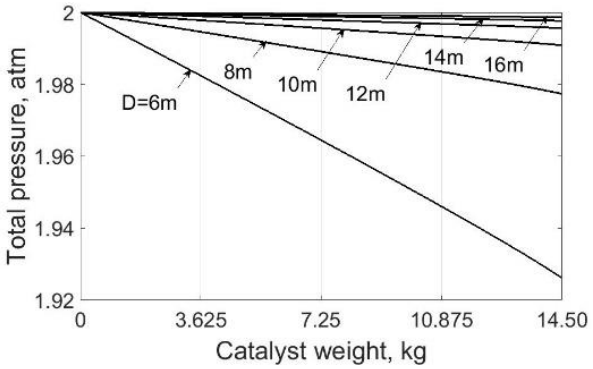

Figure 6. Effect of reactor diameter on pressure drop in the first reactor.

The calculation of conversion using the total mole balance solely takes into account the total volume of the reactor, represented by the total weight of the catalyst in this study. Consequently, altering the reactor diameter while maintaining a constant volume does not directly impact the conversion. However, changing the reactor diameter does have an effect on the pressure drop experienced within the reactors, as evident from the results shown in Figure 6. This pressure drop, in turn, slightly influences the conversion, as illustrated in Figure 7, As we can see from Figure 4 as well, changing the base reactor diameter (D) from 10 to 4 show only minor changes in conversion. The influence of the pressure drop on the conversion in the second reactor is negligible.

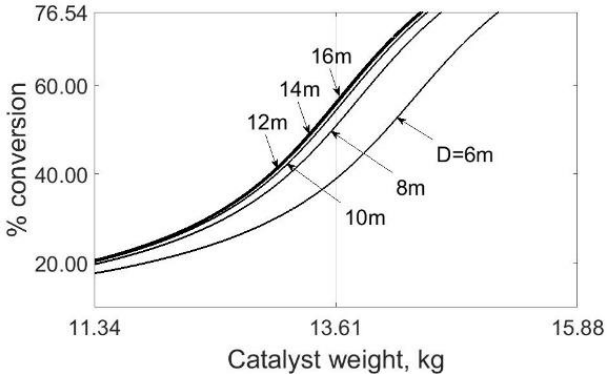

Figure 7. Effect of reactor diameter on conversion in the first reactor.

Changing the diameter of catalyst particles, similar to modifying the reactor diameter, can have significant effects on the reactor's performance. When reducing the diameter of catalyst particles, a larger surface area is created for the same amount of catalyst material. This increase in surface area results in more friction within the reactor, leading to higher pressure drop in both reactors (Figure 8). The increased friction caused by the smaller catalyst particle size contributes to the overall pressure drop, influencing the reactor's behavior and performance.

Undoubtedly, reducing the size of catalyst particles will augment their specific surface areas, leading to a consequential impact on the conversion process [14]. Nevertheless, our current investigation has not accounted for the influence of catalyst particle surface area on the conversion rate, necessitating further in-depth explorations. Our focus has been solely on the effect of catalyst particle diameter on pressure drop, which

subsequently influences the conversion process, as depicted in Figure 9. For comparative purposes, the corresponding data can also be observed in Figure 4.

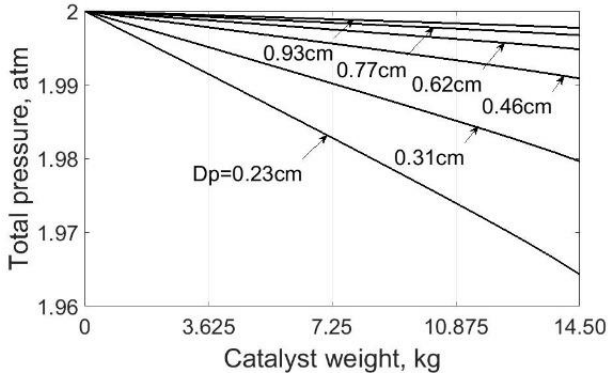

Figure 8. Effect of catalyst particles diameter on pressure drop in the first reactor.

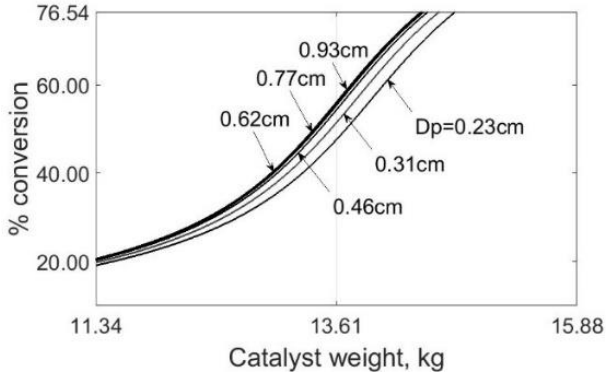

Figure 9. Effect of catalyst particles diameter on conversion in the first reactor.

When reducing the inert gas content in the feed (from %79 to %58 N_2) while maintaining a constant SO_2 to O_2 ratio, an initial increase in conversion (Figure 10). However, achieving 100% conversion becomes challenging. This difficulty arises because introducing a feed with higher concentrations of SO_2 and O_2 into the reactor results in a rapid reaction due to the elevated reactant concentrations, leading to an immediate increase in reactor temperature and subsequent energy production. With a lower amount of inert gas, the reactor is unable to absorb as much energy, causing the temperature to rise even more rapidly. As previously mentioned, elevated temperatures enhance the reaction kinetics, leading to a faster attainment of equilibrium conversion. Consequently, the reaction cannot proceed further, resulting in lower overall conversion within a single reactor, as depicted in Figure 10. This phenomenon is also supported by findings from a previous study [15], which illustrated that increasing oxygen concentration eventually renders the reaction rate independent of further increases, indicating a limiting factor in achieving higher conversions.

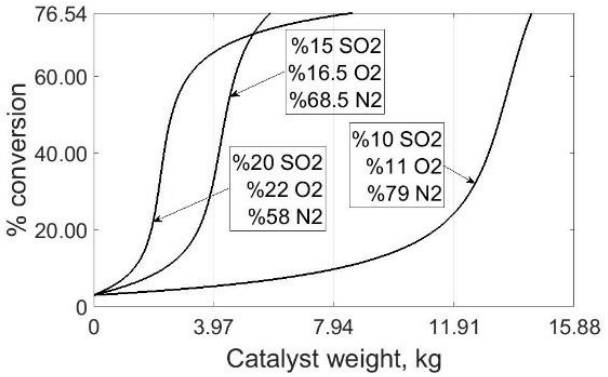

Figure 10. Effect of change of compositions of reactants on conversion in the first reactor.

Upon reducing the amount of inert gas (from %79 to %58 N_2) in the feed, the increased presence of reactants initially leads to higher conversion rates. However, this augmentation in conversion corresponds to a rise in pressure drop due to changes in the number of moles in the system. Subsequently, as the reaction progresses, the pressure drop persists due to a combination of frictional effects and ongoing reactions, as illustrated in Figure 11.

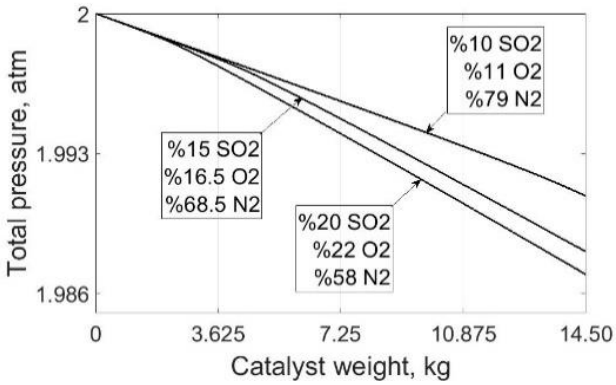

Figure 11. Effect of change of compositions of reactants on pressure drop.

The simulation results for changes in pressure and temperature at the outlet are presented below for both the first (Table 3, Table 4) and second (Table 5, Table 6) reactors.

Observations reveal that operating the reactor at higher pressure and elevated inlet temperatures results in improved conversion rates and reduces the required catalyst amount. However, it is noteworthy that higher inlet temperatures lead to lower final conversion levels in each reactor. Hence, a careful evaluation of the optimal conditions concerning the inlet temperature and catalyst quantity is essential.

Moreover, doubling the pressure decreases the necessary catalyst amount by approximately two-fold (as shown in Table 3). On the other hand, higher operating pressures correspond to reduced pressure drop within the system. However, it is essential to consider that elevated inlet pressures also entail increased financial expenditures. Therefore, a comprehensive analysis considering both performance and cost factors is vital to determine the most suitable operating conditions for the given system.

Table 3. Simulation results for the first reactor

Inlet temperature, $T_0(K)$	Outlet temperature, $T\ (K)$	Final conversion in the first reactor, $\%X_{SO_2}$	Required catalyst amount for the final conversion in the first reactor, *kg*	Final pressure in the first reactor, *atm*
Inlet total pressure to the first reactor, $P_{To} = 2\ atm$				
670	898	76.54	14.5	1.991
730	931	67.54	2.9	1.998
Inlet total pressure to the first reactor, $P_{To} = 4\ atm$				
670	908	79.93	7.3	3.998
730	941	71.00	1.5	3.9995

Table 4. Outlet component compositions from the first reactor

Total inlet flow rate to the first reactor, $F_{To} = 90.72\ kmol/h$			
Inlet total pressure to the first reactor, $P_{To} = 2\ atm$			
Feed temperature, $T_0(K)$	**Component**	**Mole number, *kmol***	**Per cent, %**
670	SO_2	2.1	2.4
	SO_3	6.9	8.0
	O_2	6.5	7.4
	N_2	71.7	82.2
730	SO_2	2.9	3.4
	SO_3	6.1	6.9
	O_2	6.9	7.9
	N_2	71.7	81.8
Inlet total pressure to the first reactor, $P_{To} = 4\ atm$			
Feed temperature, $T_0(K)$	**Component**	**Mole number, *kmol***	**Per cent, %**
670	SO_2	1.8	2.1
	SO_3	7.3	8.3
	O_2	6.3	7.3
	N_2	71.7	82.3
730	SO_2	2.6	3.0
	SO_3	6.4	7.4
	O_2	6.8	7.7
	N_2	71.7	81.9

In the second reactor, similar trends are observed as in the first reactor. The conversion rate in the second reactor increases from approximately 70% to close to 98% under high inlet temperatures. However, it is noteworthy that the required amount of catalyst in the second reactor, particularly when the feed temperature is high, is considerably higher (as indicated in Table 5). This phenomenon can be attributed to the reduced number of reactant molecules present in the feed stream to the second reactor. Consequently, a larger quantity of catalyst is necessary to facilitate a sufficient encounter of reactant molecules within the reactor and enhance the conversion process.

Table 5. Simulation results for the second reactor.

Inlet temperature to the first reactor, $T_{1,o}(K)$	Inlet temperature to the second reactor, $T_{2,o}(K)$	Outlet temperature from the second reactor, $T_2(K)$	Final conversion in the second reactor, $\%X_{SO_2}$	Required catalyst amount for the final conversion in the second reactor, *kg*	Final pressure in the second reactor, *atm*
Inlet total pressure to the second reactor, $P_{To} = 2\ atm$					
670	700	762	97.42	3.80	1.9980
730	705	783	95.47	2.72	1.9980
Inlet total pressure to the second reactor, $P_{To} = 4\ atm$					
670	700	755	98.44	2.13	3.9990
730	705	781	96.85	1.59	3.9995

Table 6. Outlet component compositions from the second reactor

Total flow rate to the second reactor, $F_{To} = 87.20\ kmol/h$					
Inlet total pressure to the second reactor, $P_{To} = 2\ atm$					
Feed temperature to the first reactor, $T_{1,o}(K)$	**Feed temperature to the second reactor, $T_{2,o}(K)$**	**Outlet temperature from the second reactor, $T_2(K)$**	**Component**	**Mole number, *kmol***	**Percent, %**
670	700	762	SO_2 SO_3 O_2 N_2	0.22 8.85 5.49 71.67	0.25 10.26 6.37 83.12
730	705	783	SO_2 SO_3 O_2 N_2	0.48 8.50 5.64 71.67	0.55 9.85 6.54 83.06
Inlet total pressure to the second reactor, $P_{To} = 4\ atm$					
670	700	755	SO_2 SO_3 O_2 N_2	0.14 8.90 5.51 71.67	0.16 10.33 6.39 83.12
730	705	781	SO_2 SO_3 O_2 N_2	0.29 8.76 5.55 71.67	0.34 10.16 6.43 83.07

4. CONCLUSION

* Pressure: For the investigated system, implementing inter-stage cooling is crucial to achieve high conversion rates in multi-bed setups involving reversible exothermic reactions. Additionally, operating at high total pressures can lead to increased overall conversion in a series of reactors. However, it is important to consider the financial implications since higher pressures require additional funding. Thus, the economic aspect should be taken into account while designing such a system. For systems similar to the investigated system, an initial pressure of between 4 and 6 *atm* is recommended after the considerations.
* Temperature: Maintaining optimum temperatures in the reactors is vital, as it not only impacts the final conversion but also influences the size of the reactors, including the number of required catalysts. For similar systems, the initial temperature of the first reactor around 730 *K* is recommended.
* Catalyst particle size and reactor size: This study focused solely on the effect of catalyst particle size and reactor diameter on total pressure changes, omitting the surface effect on reaction kinetics. Surface effects play a significant role in reaction kinetics [16-18]. Therefore, for more rigorous studies, it is crucial to consider surface effects as well.
* Initial components ratio: Adding the appropriate amount of inert gas is necessary since it influences overall conversion and reaction kinetics. The optimal amount of inert gas should be such that it can absorb excess heat, while also ensuring that it does not excessively reduce the number of reactants available for the reaction. Striking this balance is crucial for achieving efficient reaction rates. For similar systems, an initial ratio of 15% SO_2, 16.5% O_2 and 68.5% N_2 is recommended.

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