

Калбеков А., Талантбек кызы Ж., Гүлтекин С.

**АРАЛЫК МУЗДАТУУ-ЭТАПТУУ, КЫЙМЫЛСЫЗ
КЕРЕБЕТ РЕАКТОРУНДА SO_2 НИН SO_3 КӨ ӨТҮҮ РЕАКЦИЯСЫНЫН
КИНЕТИКАСЫНЫН СИМУЛЯЦИЯСЫ**

Калбеков А., Талантбек кызы Ж., Гюльтекин С.

**СИМУЛЯЦИЯ КИНЕТИКИ РЕАКЦИИ SO_2 К SO_3 В РЕАКТОРЕ С НЕПОДВИЖНЫМ
СЛОЕМ С ПРОМЕЖУТОЧНЫМ ОХЛАЖДЕНИЕМ**

A. Kalbekov, Talantbek kyzy Zh., S. Gültekin

**SIMULATION OF KINETICS OF SO_2 TO SO_3 REACTION IN A FIXED-BED
REACTOR WITH INTER-COOLING-STAGE**

УДК: 660

Күкүрт кислотасы (H_2SO_3), ар кандай химиялык каражаттар жана продукталардын өтдүрүшүндө жана башка учурларда колдонулуучу өтө маанилүү кислота болуп саналат. Күкүрт диоксидинин (SO_2), күкүрт триоксидине (SO_3) кычкылданып өтүү реакциясы, H_2SO_3 өндүрүшүндө эң маанилүү этаптардын бири болуп саналат. Бул изилдөөдө, адиабатикалык шарттарда иштеген, реакторлор арасында продукталарды муздатуу этабына ээ, кыймылсыз керебет реакторунда SO_2 нин SO_3 кө өтүү реакциясынын кинетикасы изилденди жана ар бир реактордун симуляциясы, кыскача МАТЛАБ атында белгилүү болгон көп парадигмалуу, сандык эсептөө проприетардык программалоо тилини колдонуу аркылуу жасалды. Изилдөө жыйынтыгында, жалпы басымды жана SO_2 нин баштапкы концентрациясын арттыруунун оң таасири бар экендиги белгиленди. Алынган жыйынтыктар баардык термодинамикалык эрежелерге жана мыйзамдарга туура келет.

Негизги сөздөр: кычкылдануу реакциясы, реакция кинетикасы, күкүрттүн диоксиди, күкүрт кислотасы, симуляциялоо, кыймылсыз керебет реактору, матрикалык лаборатория (МАТЛАБ).

Серная кислота (H_2SO_3) является чрезвычайно важной кислотой, которая используется при производстве различных видов химических продуктов и в других случаях. Одним из наиболее важных этапов в производстве H_2SO_3 является реакция окисления диоксида серы (SO_2) к триоксида серы (SO_3). В этом исследовании изучалась кинетика окислительной реакции SO_2 к SO_3 в реакторе с неподвижным слоем, который работает в адиабатических условиях, и с промежуточной стадией охлаждения и симуляция в каждом реакторе выполнялось с помощью много-парадигменного вычислительного и проприетарного языка программирования, так называемого MATLAB. Согласно результатам, увеличение общего давления и начальной концентрации SO_2 оказывает положительное влияние на кинетику реакции окисления SO_2 . Эти результаты согласуются с термодинамическими правилами и законами.

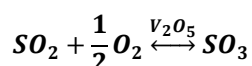
Ключевые слова: реакция окисления, кинетика реакции, диоксид серы, серная кислота, симуляция, реактор с неподвижным слоем, матричная лаборатория (МАТЛАБ).

The sulphuric acid (H_2SO_3) is extremely important acid, which is used in the production of various kinds of chemical products and in other cases. One of the most important stages in the production of H_2SO_3 is the oxidation reaction of sulphur dioxide (SO_2) to sulphur trioxide (SO_3). In this study, the kinetics of SO_2 to SO_3 reaction in a fixed-bed reactor, which is operating under adiabatic conditions, with inter-cooling-stage was investigated and the simulation in each reactor was done by a multi-paradigm numerical computing environment and proprietary programming language so called MATLAB. According to the results, increasing in total pressure and in feed concentration of SO_2 has positive effects on the kinetics of the oxidation reaction of SO_2 . These results are consistent with thermodynamical rules and laws.

Key words: oxidation reaction, reaction kinetics, sulphur dioxide, sulphuric acid, simulation, fixed-bed reactor, matrix laboratory (MATLAB).

1. Introduction.

Sulfuric acid (H_2SO_3) is highly demanded product of the present industrial world. It is used in the production of fertilizer, refining petroleum, leaching metallic ores and in other chemically important processes [1]. Due to the fact that oxidation process of SO_2 to SO_3 ,



in the production of H_2SO_3 is highly exothermic and the most significant reaction, the simulation of the process is very important to predict reaction kinetics and effects of influences of components' concentrations and total pressure. It is

heterogeneous reaction and V_2O_5 is used as a catalyst [2]. For higher conversion, the oxidation process is carried out in an inter-cooling-stage system [3]

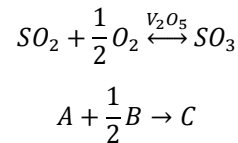
Kinetics of the oxidation reaction depends on various variables such as temperature, total pressure and reactants' concentrations.

2. Materials and Methods.

For this study, two adiabatic operating fixed-bed reactors with inter-cooling-stages were taken and the simulation of kinetics of the reaction in each reactor was done by MATLAB package program [4].

3. Results and Discussions.

For the reaction



In a real production, the following concentrations of feed components to the first reactor are used (Fogler, 2016): 79 % N_2 , 10 % SO_2 , % 11 O_2

The kinetics of this reaction was studied by Eklund and others [5], and for the conversion above 5%, the following reaction rate and reaction rate constant were found,

$$-r'_{SO_2} = k \sqrt{\frac{P_{SO_2}}{P_{SO_3}}} \left[P_{O_2} - \left(\frac{P_{SO_3}}{K_p P_{SO_2}} \right)^2 \right] \quad (lb \text{ } SO_2 / lb \text{ cat. } * s) \quad (1)$$

$$k = \exp \left[-\frac{176008}{T} - (110.1 \ln T) + 912.8 \right] \quad (lb \text{ } SO_2 / lb \text{ cat. } * s * atm) \quad (2)$$

From recent JANAF values, the equilibrium constant can be found as follow [6],

$$K_p = \exp \left(\frac{42311}{RT} - 11.24 \right) \quad (atm^{1/2}) \quad (3)$$

The partial pressure of any component is [7],

$$P_i = P_{A_0} \frac{(\theta_i + v_i X) P}{(1 + \epsilon X) P_0} \quad (4)$$

When we put all variable into total mole balance equation, then we will get,

$$\frac{dX}{dW} = -\frac{r'_A}{F_{A_0}} = \frac{k}{F_{A_0}} \sqrt{\frac{1-X}{\theta_{SO_3} + X}} \left[\frac{P}{P_0} P_{A_0} \frac{\theta_{O_2} - \frac{1}{2}X}{1 + \epsilon X} - \left(\frac{\theta_{SO_3} - X}{1 + X} \right)^2 \frac{1}{K_p} \right] \quad (5)$$

where: $\theta_{SO_3} = 0.0$, $\theta_{O_2} = 1.1$, $\epsilon = -0.055$ and

P_i = partial pressure of component i , atm

X = conversion of SO_2 ,

F_{A_0} = initial molar rate of A , $lbmol/h$

T = temperature of the reaction, R

Using JANAF thermodynamical values of feed (SO_2 , SO_3 , N_2 and O_2) [8] and from total energy balance [9],

$$\text{Energy rate by inlet mass flow} + \text{Energy rate by outlet mass flow} + \text{Energy rate from the surroundings to the system} + \text{Energy rate by work done by the system} = \text{Energy accumulation rate in the system}$$

$$E_{in}F_{in} - F_{out}E_{out} + Q - W = \frac{dE_{sys}}{dt} \quad (6)$$

for the feed temperature 1206 R (670 K) and a steady-state system (no energy accumulation in the reactor), we have found the relationship between conversion and temperature as follow,

$$T = \frac{86065+38383X}{71.36-3.2X} \quad (7)$$

We have done our simulation based on these equations for our condition, which is the feed temperature is 1200 R (670 K) and the total pressure is 2 atm (2 bar), and the results are shown below. In our previous work, we have found that at a feed temperature of 670 K and a total pressure of 2 bar (2 atm), the maximum conversion in the first reactor can achieve only 76.5 % [10]. When we plot Levenspiel plot (Figure 1), the area under the curve will be the amount of catalyst to achieve that conversion [11].

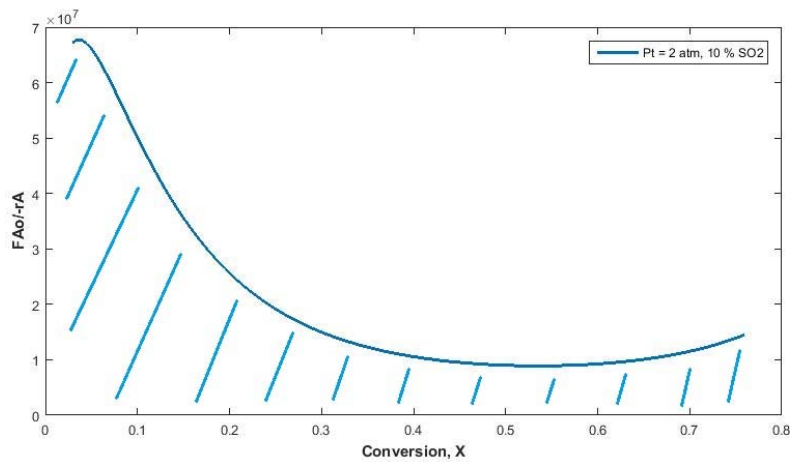


Figure 1. Levenspiel plot for adiabatic fixed-bed reactor.

And the reaction rate changes along the reactor were as follow,

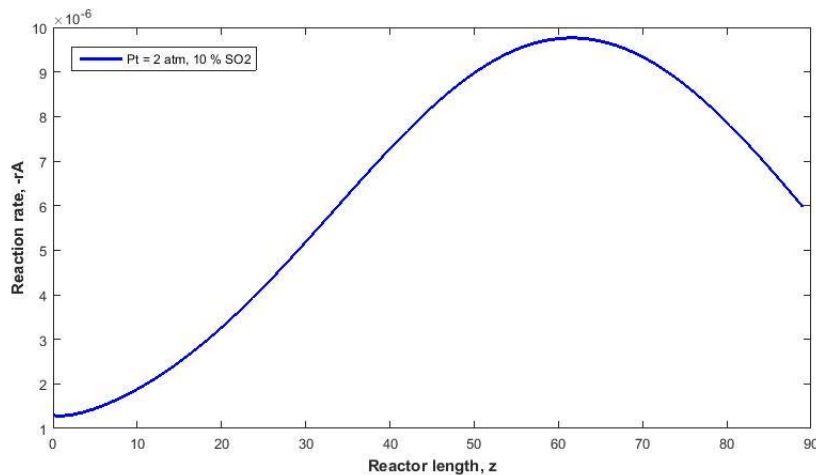


Figure 2. Reaction rate changes along the reactor.

The reaction rate has increased in the beginning and has decreased later. Because the reaction is exothermic and operates in adiabatic conditions, the temperature will increase gradually along the reactor (Figure 3). And the reaction rate is increasing by increasing the temperature and decreasing later according to the Le Chatelier's principle because it is a reversible reaction [12].

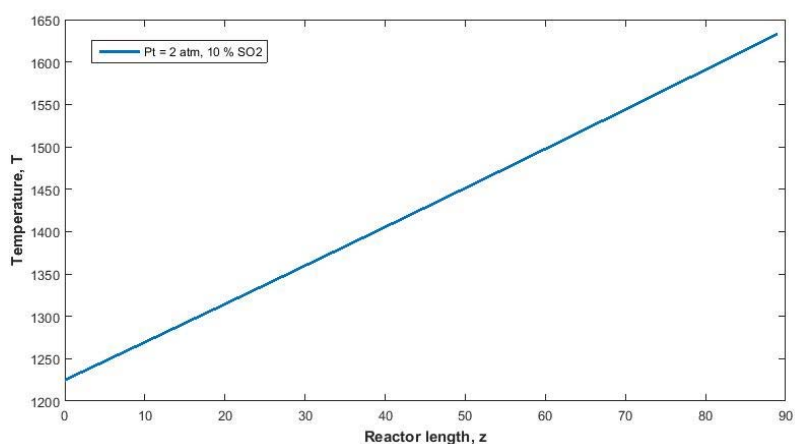


Figure 3. Temperature changes along the reactor.

When we increased total pressure in the reactor, it has affected positively and increased the reaction rate (Figure 4).

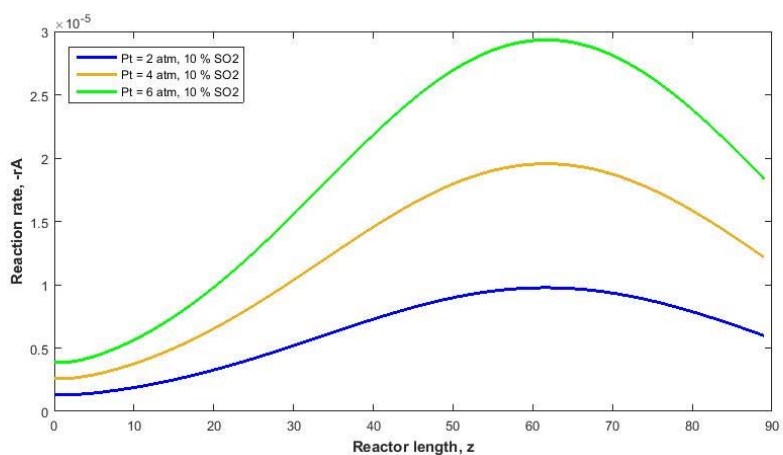


Figure 4. Effect of total pressure on the reaction rate.

It has shifted the curve (conversion curve) on the Levenspiel plot down which means we need smaller amount of catalyst for the same conversion (Figure 5).

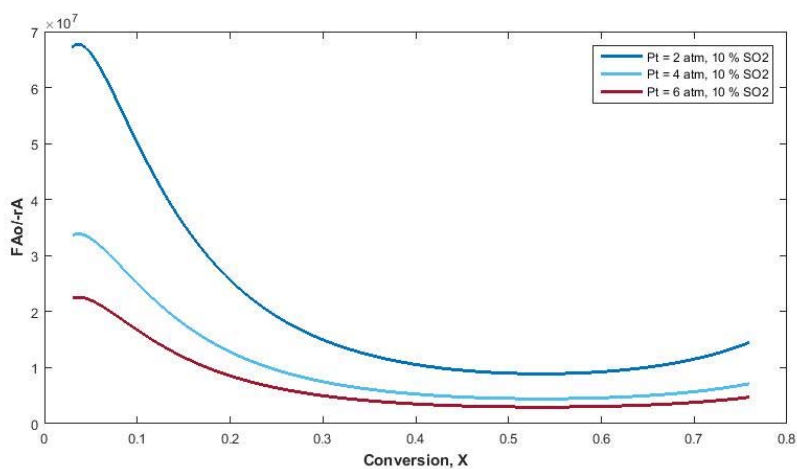


Figure 5. Effect of total pressure on the Levenspiel plot.

Increasing total pressure means increasing concentrations of every component in the feed. But we kept total pressure constant and increased only the concentration of SO_2 , which means decreasing the concentration of O_2 . The inert gas (N_2) has no effect on the reaction but when we change the concentration of it, it will affect the temperature in the reactor. That is why the concentration of inert gas (N_2) should stay constant.

Keeping total constant but increasing the concentration of SO_2 has also showed positive effect on reaction rate (Figure 6).

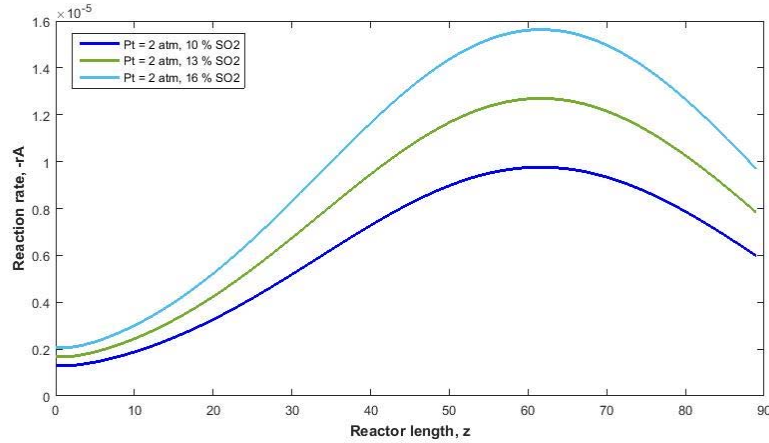


Figure 6. Effect of SO_2 initial concentration on the reaction rate.

And as we had expected, when we increased the concentration of SO_2 , it has shifted the curve on the Levenspiel plot down, so less amount of the catalyst is required to achieve the same conversion in the reactor (Figure 7).

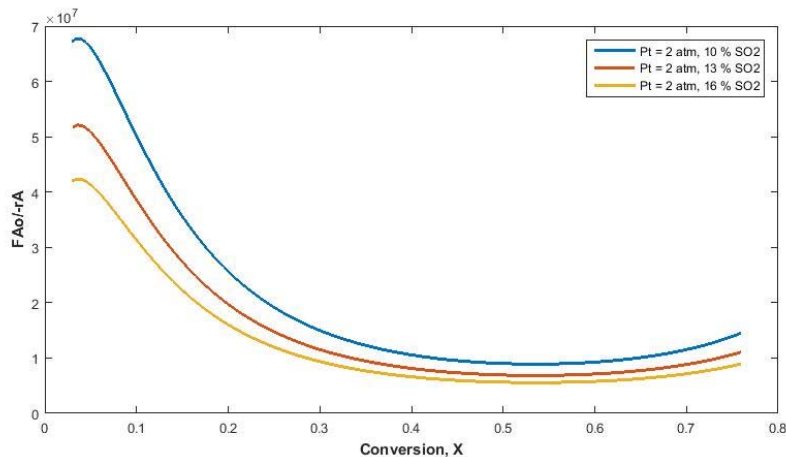


Figure 7. Effect of SO_2 initial concentration on the Lepenspiel plot.

As we mentioned earlier, the conversion in the first reactor cannot reach above 76%. To get higher conversion we need cool down the reactor outlet and feed to the second reactor. The feed to the second reactor contains less amount of SO_2 . That is why to recover it, the inlet temperature to the second reactor will be kept a bit higher. In our previous work, we took the feed temperature to the second reactor as 700 K (1260 R). In this case, we have less SO_2 (%2.9) and some SO_3 (%7.6) in the feed gas. Consequently, the reaction rate equation will change and the equation (7), which shows the relationship between conversion and temperature, will be slightly different.

$$T = \frac{86199+38383X}{71.83-3.2X} \quad (8)$$

In our previous work, we have also found that in the second reactor with total pressure of 2 atm and feed temperature of 700 K, the conversion can achieve almost 96 %. We have calculated the reaction rate and the conversion curve according to it. It can be seen in Figure 8, the reaction rate has decreased because of less amount of SO_2 .

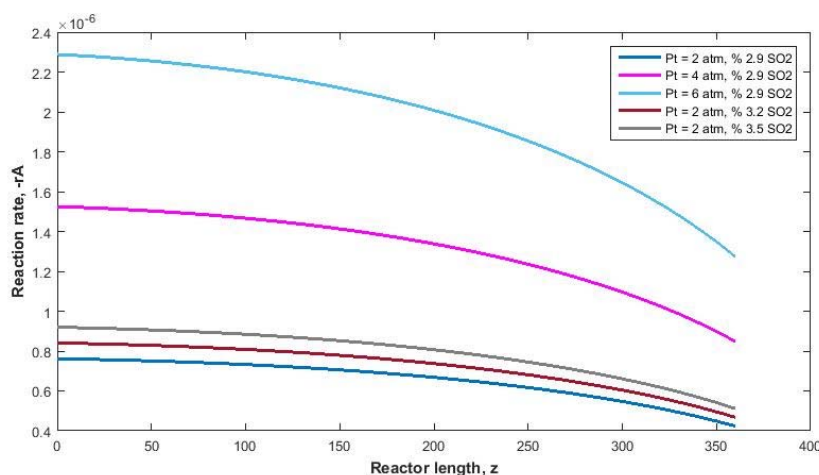


Figure 8. Reaction rate changes in the second reactor.

The effects of changing in total pressure and feed concentration of SO_2 are the same as in the first reactor. Both of them affect positively the reaction rate as well as the curve on the Lepenspiel plot (Figure 8 and Figure 9).

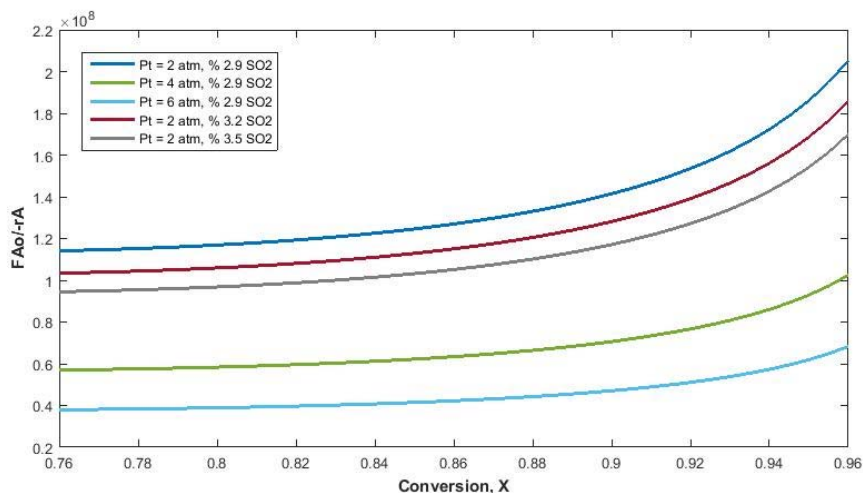


Figure 9. Conversion changes in the second reactor.

4. Conclusion.

- 1) Increasing total pressure increases reaction rate in each reactor,
- 2) Increasing concentration of SO_2 also increases reaction rate in each reactor,
- 3) By increasing the total pressure, we need less amount of catalyst for the same conversion,
- 4) By increasing the concentration of SO_2 , we need less amount of catalyst for the same conversion.

The results are consistent with thermodynamic considerations.

References:

1. Matthew J. K., Michael M., Davenport W.G., Sulfuric Acid Manufacture: Analysis, Control and Optimization, Elsevier Ltd., 2006
2. Friedman F., Chem. Eng. Prog., 78(2), 51, 1982.
3. European Sulphuric Acid Association (ESA) and European Fertilizer Manufacturers' Association (EFMA), Production of Sulphuric Acid, Brussel, 2000.
4. Luyben W. L., Process Modeling Simulation and Control for Chemical Engineers, 2E. McGraw-Hill Book Company, 1999.
5. Eklund R. B., Dissertation, Royal Institute of Technology, Stockholm, as quoted by J. R. Donovan. In: *The Manufacture of Sulfuric Acid*, ACS Monograph Series 144, Duecker W. W. and West J. R. 1959. New York, Reinhold (eds), 1956.
6. Stull D. R. and Prophet H., Project Directors, *JANAF Thermochemical Tables*, 2 Ed., NSRDS-NBS 37, Washington, D.C.: U.S. Government Printing Office, 1971.
7. Fogler H. S., Essentials of Chemical Reaction Engineering, 2 Ed., Pearson Education, Inc., New York, 2018.

8. Chase, M. W., NIST-JANAF Thermochemical Tables, 4 Ed., American Chemical Society and American Institute of Physics, Woodbury, New York, 1998. Available at: <https://janaf.nist.gov>.
9. Fogler H. S., Elements of Chemical Reaction Engineering, 4 Ed., Pearson Education, Inc., New-York, 2016.
10. Gültekin S., Kalbekov A., Simulation of the Effect of Total Pressure and Initial Temperature on the Conversion of SO₂ to SO₃ in an Adiabatic Fixed-Bed Reactor, was accepted to International Eurasian Conference on Science, Engineering and Technology (EURASIANSCIENTECH 2018), 22-23 November, Ankara, 2018.
11. Levenspiel O., Chemical Reaction Engineering, 3 Ed., John Wiley & Sons. Inc., New-York, 1999.
12. Harrer T. S., Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Vol. 19. Wiley-Interscience, New York, 1969.

Рецензент: к.т.н., доцент Боркеев Б.
