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**FACULTY OF CHEMISTRY AND  
CHEMICAL ENGINEERING**

**Doctoral School of Chemistry**

**Conversion of sulfuric acid to sulf dioxide**  
**PhD Thesis Abstract**

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**Keywords:** conversion of sulfuric acid, sulfur dioxide, reduction, catalyst, thermodynamic, kinetic, activation parameters, reactor sizing

## INTRODUCTION

Sulfuric acid is a major by-product in chemical industry, becoming a potential chemical waste if it is not recycled. A particular chemical process, in which the  $\text{H}_2\text{SO}_4$  is obtained as by-product, is  $^{15}\text{N}$  separation by isotope exchange in  $(\text{NO}, \text{NO}_2)_{(\text{g})} - \text{HNO}_{3(\text{s})}$  system. For this process,  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  is important, because the conversion of nitric acid to nitrogen oxides take place with sulfur dioxide [1]. Therefore, recycling of  $\text{SO}_2$  into isotope separation plant leads to reduction cost for  $^{15}\text{N}$  production. Sulfuric acid conversion to sulfur dioxide can be achieved by different methods: thermo-catalytic, termoelectrolytic, and by a reducing agent, but in this PhD thesis the first method is studied.

The general objective of this PhD thesis is the study of thermo-catalytic conversion of sulfuric acid to sulfur dioxide in order to recycle it in  $^{15}\text{N}$  separation plant by isotope exchange in  $(\text{NO}, \text{NO}_2)_{(\text{g})} - \text{HNO}_{3(\text{s})}$  system.

This thesis is structured in two chapters. The first chapter includes literature data that highlights the current state of knowledge regarding thermo-catalytic conversion of sulfuric acid to sulfur dioxide. The second one includes original contribution in this field. The thesis ends with conclusions and references.

## CHAPTER I

**Thermo-catalytic conversion of sulfuric acid to sulfur dioxide. Literature study**

The conversion process of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2$  can be characterized by the following chemical reaction:



but, qualitatively, it is a process that take place in two consecutive steps. In first step, non-catalytic thermal decomposition (dissociation) of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_3$  and water vapor take place at temperatures between 350 and 400°C [8]:



In second step, reduction of  $\text{SO}_3$  to  $\text{SO}_2$  and  $\text{O}_2$  take place, at temperature above 750°C [10], in presence of a catalyst:



Decomposition reaction of  $\text{H}_2\text{SO}_4$  into  $\text{SO}_3$  and  $\text{H}_2\text{O}$  vapor, (2), take place with higher rate than reduction of  $\text{SO}_3$  to  $\text{SO}_2$  and  $\text{O}_2$ , (3). It is considered that above 700°C, sulfuric acid dissociation is completed [30], and in reduction zone, enter an equimolar mixture of  $\text{SO}_3$  and water vapor [33]. Therefore, the overall rate of the process (1) is determined by rate of  $\text{SO}_3$  reduction to  $\text{SO}_2$ , (3) [34]. Taking into account that the rate determining step of  $\text{H}_2\text{SO}_4$  conversion is the reduction reaction of  $\text{SO}_3$  to  $\text{SO}_2$ , which has to proceed at higher rate and efficiency as possible, the major role is played by the catalyst. The catalyst has to fulfill two essential conditions [11]: *sufficient activity to catalyze  $\text{SO}_3$  reduction to  $\text{SO}_2$  and the capacity to maintain conversion for a long period of time, provided only by a stable structure.*

The researches focused on identification of the catalysts to fulfill the above major conditions have started sine 70's and continues today, being tested both commercial and new synthesized catalysts. Materials such as: metal oxides, for example:  $\text{Fe}_2\text{O}_3$  [10], metal on support, e.g.:  $\text{Pt}/\text{Al}_2\text{O}_3$  [35], metal oxides on support, e.g.:  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  [52], mixed metal oxides, e.g.:  $\text{CuFe}_2\text{O}_4$  [61].

Temperature is another important factor because it has a major influence on the reduction kinetics of  $\text{SO}_3$  to  $\text{SO}_2$  [66]. Both the reaction rate and thermodynamic equilibrium are influenced by temperature [55]. The reduction of  $\text{SO}_3$  to  $\text{SO}_2$  is influenced also by pressure – high conversions are achieved at low values of pressure [71]. High conversions of  $\text{SO}_3$  to  $\text{SO}_2$  are achived at low pressures and high temperatures [72].

Space velocity is an important parameter that influences the conversion degree of  $\text{SO}_3$  to  $\text{SO}_2$  and intervenes in the calculations for reactor sizing. Generally there are three types of space velocity: LHSV (Liquid Hourly Space Velocity) [11]; GHSV (Gas Hourly Space Velocity) [43]; WHSV (Weight Hourly Space Velocity) [32]. In most studies concerning the influence of space velocity on  $\text{SO}_3$  reduction to  $\text{SO}_2$ , it is expressed as WHSV, defined as the ratio between the mass flow rate of the

sulfuric acid solution fed into reactor, (g / h) and the mass of catalyst loaded into reactor (g).

Thermal decomposition of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_3$  and water vapor is an endothermic process, with  $\Delta H_{298}^0 = 97,54 \text{ kJ/mol}$  [80]. Equilibrium constant of this reaction can be calculated from thermodynamic data of pure components, for example at  $37^\circ\text{C}$ ,  $K_p = 2,9 \cdot 10^{-9}$  [81]. At  $400^\circ\text{C}$ , the equilibrium constant is above 1 and increases rapidly [66].

Reduction of  $\text{SO}_3$  to  $\text{SO}_2$  and  $\text{O}_2$  (3) is also an endothermic process, with  $\Delta H_{298}^0 = 98,92 \text{ kJ/mol}$  [80] which, even take place at high temperature, proceeds very slowly, therefore in order to increase the reaction rate a catalyst is used [50]. Equilibrium constant for this reaction is more than 1 at temperatures above  $777^\circ\text{C}$  [66].

Study of the reduction process of  $\text{SO}_3$  to  $\text{SO}_2$  it was approached in general at laboratory level, reaction being performed in a tubular quartz reactor, heated by an electric furnace. In order to shift to industrial scale, modeling and design of other types of reactors are studied, which have to be made from materials resistant to high temperatures and corrosive environment given by reaction (unreacted  $\text{SO}_3$ ,  $\text{SO}_2$ , water vapor). Most studied materials are: *special alloy*, such as Hastelloy C-276 [28], Incolloy 800H [93]; *ceramic materials*, such as SiC, SiSiC,  $\text{Si}_3\text{N}_4$  [95]; different ceramic materials supported on the special alloy, such as: SiC/Hastelloy X [98], SiC/Inconel 800H, SiC/Inconel 690 [97].

Literature study of  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  shows that is an up-to-date issue, intense investigated to be applied in S-I cycles for hydrogen production.

For us, research of this process is important, because applied for recycling of  $\text{SO}_2$   $^{15}\text{N}$  separation plant would lead to a reduction of production cost, more than that would represent an innovation regarding production of this isotope.

## CAPITOLUL II

### Original contributions

#### 2.1. Aspects regarding working method

##### 2.1.1. Materials. Catalysts

For  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  the following commercial catalysts were tested: 5 wt. % Pd /  $\text{Al}_2\text{O}_3$  (industrial catalyst produced in Rusia), 0.5 wt. % Pd /  $\text{Al}_2\text{O}_3$  (Sigma – Aldrich), 0.1 wt.% Pt /  $\text{Al}_2\text{O}_3$  (Alfa Aesar), 2 wt. % Pt /  $\text{TiO}_2$  (Johnson Mathey),  $\alpha\text{-Fe}_2\text{O}_3$  (Alfa Aesar) and iron trioxide.

In this PhD thesis, I also tried preparation of a catalyst by wet impregnation method namely iron trioxide impregnated on silica gel: 3 wt. %  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$ , 5 wt. %  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$ , 10 wt. %  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$ .

##### 2.1.2. Description of work

The conversion of the  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2$  was tested in the laboratory plant shown schematically in Figure 14. Using a peristaltic pump, concentrated  $\text{H}_2\text{SO}_4$  is fed from a graduated cylinder, in the tubular quartz reactor, placed in an electric furnace. Once inside the heated zone,  $\text{H}_2\text{SO}_4$  decomposed into sulfur trioxide and water vapor, which pass over the catalyst bed, where  $\text{SO}_3$  is reduced to  $\text{SO}_2$ . The catalyst is fixed into the reactor between two beds of quartz beads immobilized with quartz wool. Gaseous mixture ( $\text{SO}_2$ ,  $\text{O}_2$ , unreacted  $\text{SO}_3$ , water vapor, He), leaving the reactor, pass through a glass condenser cooled with water, where unreacted  $\text{SO}_3$  recombined with water forming diluted  $\text{H}_2\text{SO}_4$ , which is collected into a glass trap.  $\text{SO}_2$ ,  $\text{O}_2$  and He mixture was bubbled in 0,1N NaOH solution for  $\text{SO}_2$  absorption and determining the amount formed in the reaction. Collected  $\text{H}_2\text{SO}_4$  is analysed by titration with 0.1 N NaOH.

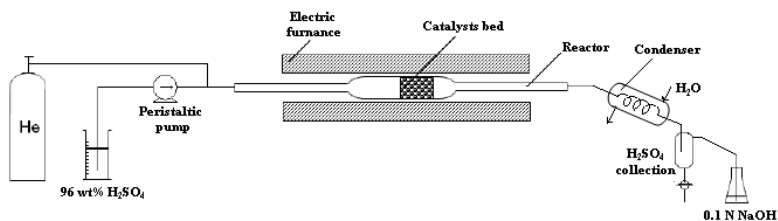


Figure 14. Experimental plant

The catalytic bed is placed in the middle of the reactor between two beds of quartz beads. Since we do not use another reactor for the decomposition of liquid  $\text{H}_2\text{SO}_4$  into  $\text{SO}_3$  and  $\text{H}_2\text{O}$  vapor, another important role of the quartz beads in front of catalyst, is that it represent the decomposition zone of  $\text{H}_2\text{SO}_4$  fed into reactor, ensuring a homogeneous evaporation and thus a steady flow of the gaseous mixture through the catalyst bed.

**2.2. Catalysts activity. The influence of different experimatal parameters on sulfuric acid conversion to sulfur dioxide**

The catalyst activity is expressed as the conversion degree of H<sub>2</sub>SO<sub>4</sub> to SO<sub>2</sub> determined by the following equation:

$$x = \frac{F_{SO_2}}{F_{H_2SO_4}^0} \cdot 100 \tag{12}$$

where:  $x$  is the conversion degree of H<sub>2</sub>SO<sub>4</sub> to SO<sub>2</sub> (%), further „conversion“;  $F_{SO_2}$  is the molar flow rate of SO<sub>2</sub> (mol/h);  $F_{H_2SO_4}^0$  is the molar flow rate of pure concentrated H<sub>2</sub>SO<sub>4</sub> fed into reactor (mol/h).

The molar flow rate of the SO<sub>2</sub> formed in reaction, was determined from the amount of sulfur dioxide absorbed in a known volume of 0.1 N NaOH solution, within a certain period of time; also in this solution few drops of phenolphthaleine are place, the solution gets pink color and a few drops of 30 % H<sub>2</sub>O<sub>2</sub>. The gases leaving the conversion plant is bubbled through this solution and measure the time in which the change in color from pink to colorless take place. Thus, molar flow rate of SO<sub>2</sub> can be calculated with the following relationship:

$$F_{SO_2} = \frac{N_{NaOH} \cdot 3600}{t_{viraj}} \tag{13}$$

where:  $N_{NaOH}$  is the number of moles that correspond to the volume of 25 ml NaOH (mol);  $t_{viraj}$  is the change time of NaOH solution from pink to colorless (s).

**2.2.1. Catalytic activity of 5 wt. % Pd /Al<sub>2</sub>O<sub>3</sub>**

*Influence of wheight horly space velocity (WHSV) on sulfuric acid conversiei to sulfur dioxide.* 5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub> catalyst, granules of 0.4 ÷ 0.8 mm, was tested H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub>, using three different flow rates of 96 wt. % sulfuric acid, at temperature of 850°C and atmospheric pressure and the amount of catalyst loaded into the reactor remained constant: 1 g. There is a decrease in conversion with increase in WHSV and H<sub>2</sub>SO<sub>4</sub> flow rate, respectively, because increasing the velocity of the gaseous mixture through the catalyst bed, the contact time gas - catalyst decreases.

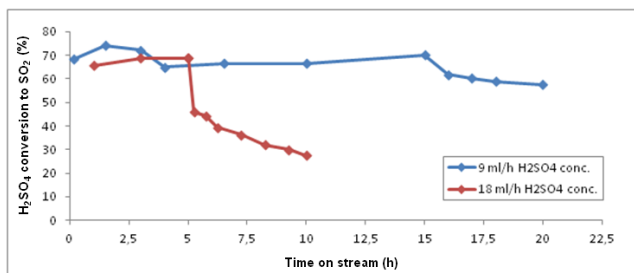
*The influence of temperature on conversion.* The temperature has a major influence over conversion degree of H<sub>2</sub>SO<sub>4</sub> to SO<sub>2</sub>, which increases with increasing of reaction temperature.

**Table 5.** H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub> depending on temperature in the presence of 5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub>

H <sub>2</sub> SO <sub>4</sub> flow rate(ml/h) Conversion (%)	Temperature (°C)					
	750	800	825	850	875	900
9	-	72.00 ± 6.6	-	79.37 ± 1.8	-	81.08 ± 6
28	31.27 ± 3.2	51.34 ± 1.0	57.63 ± 1.0	63.93 ± 1.7	68.25 ± 2.3	72.78 ± 1.7

*Maintaining catalytic activity over time.* The good results obtained in the initial determinations of activity for this catalyst motivated us to determine the capacity to maintain catalytic activity over time in reaction environment. At a feed flow rate of 9 ml / h conc. H<sub>2</sub>SO<sub>4</sub>, the catalyst maintains a

conversion approx. unchanged (68.91%) within 15 hours, then the conversion decreases gradually, reaching a value of 57.64% after 20 h (Figure 16). At a feed flow rate of 18 ml / h conc.  $H_2SO_4$ , the conversion has a sharp decline within 10 hours, thus in the first 5 hours was obtained an average conversion of 63.52%, and then it drops sharply, reaching a value of 26.96% (Figure 16).



**Figure 16.** The variation of  $H_2SO_4$  conversion over time in the presence of 5 % Pd /  $Al_2O_3$

These results are not very promising for the use of this catalyst in a pilot plant for  $H_2SO_4$  conversion to  $SO_2$ , given that for such an application is required a more efficient catalyst, stable in highly corrosive reaction environment for a long period of time, which provides a yield as high as possible at a single pass of reactant through the catalytic bed. Also, should be mentioned that this catalyst is expensive given that this a noble metal (Pd) on support.

### 2.2.2. Catalytic activity of 0.5 wt. % Pd / $Al_2O_3$

Using a feed rate of 9 ml / h conc.  $H_2SO_4$ , the activity of this catalyst at three reaction temperatures: 800°C, 850°C and 900°C have been tested, obtaining the following conversion:  $61.35 \pm 4.5\%$ ,  $64.1 \pm 1.6\%$  and  $81.14 \pm 3.5\%$  respectively.

We have chosen Pd supported on alumina catalysts to test it for  $H_2SO_4$  conversion to  $SO_2$  because in literature are not too many information about the catalytic activity, except two bibliographic sources [6, 88]. Ginosar *et al.* [6] suggests that the Pd on alumina based catalysts should be stable, especially when they work at high temperatures, but of course investigations are needed to confirm this fact. Petropavlovskii *et al.* [88] presents a kinetic study of the  $H_2SO_4$  conversion to  $SO_2$  in the presence of Pd /  $Al_2O_3$ , granules sizes between 0.25 and 0.4 mm, but does not specify the amount of metal deposited on the support. This study was performed in a high pressure range from 0.1 MPa to 3 MPa, achieving conversions below 20 %, which is normal because operation at high pressures lead to low conversion.

### 2.2.3. Catalytic activity of 0.1 wt. % Pt / $Al_2O_3$

0.1wt. % Pt /  $Al_2O_3$  catalyst was used in several experiments to determine the effect of WHSV, and feed flow rate of conc.  $H_2SO_4$  over conversion. The results are shown in Table 6.

Platinum supported on alumina catalyst, with various mass percentage of Pt, is indicated [6] as promising catalyst for the  $H_2SO_4$  conversion to  $SO_2$ , and in many studies is given as reference catalyst.



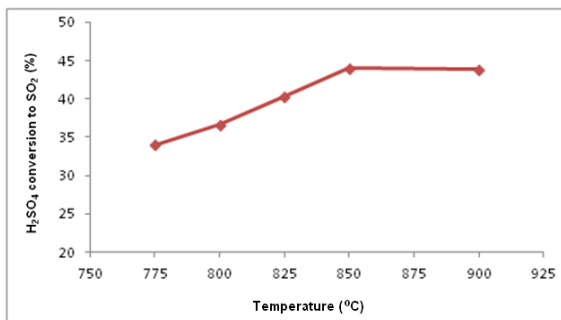
Compared with literature data, our conversions obtained using this catalyst are higher. Ginosar *et al.* [6] tested this catalyst at a flow rate of 52 g / h H<sub>2</sub>SO<sub>4</sub>, which means approx. 28 ml / h, at 850°C, obtaining a conversion of approx. 50 %. The authors [6] also showed that the catalyst reduces its catalytic activity over time due to the oxidation of platinum by the oxygen produced in reaction.

**Table 6.** H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub> depending on WHSV in presence of 0.1 wt. % Pt / Al<sub>2</sub>O<sub>3</sub>

WHSV (h <sup>-1</sup> )	96 % H <sub>2</sub> SO <sub>4</sub> feed flow rate (ml/h)	Conversion (%)
15.9	9	66.25 ± 1.6
30.0	17	62.67 ± 2.0
58.3	33	55.78 ± 1.9

**2.2.4. Catalytic activity of 2 wt. % Pt / TiO<sub>2</sub>**

2 wt. % Pt / TiO<sub>2</sub> catalyst was tested in the H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub> at different temperatures. The conversion values obtained for each operating temperature are presented in Figure 19 and will be used for the kinetic study of the SO<sub>3</sub> reduction to SO<sub>2</sub>.



**Figure 19.** H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub> depending on temperature in the presence of 2 wt. % Pt / TiO<sub>2</sub>

Such a catalyst, but with a Pt content of 1 % was tested by Petkovic *et al.* [23] for the H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub> at 850°C and atmospheric pressure at a flow rate of 49.5 g / h conc. H<sub>2</sub>SO<sub>4</sub>. The catalyst was tested in a range of 548 h in the reaction environment, the initial conversion being 65 % and decreases slowly, reaching to approx. 35 % at the end, due to sintering and oxidation of platinum, a part of it is lost by volatilization [23].

**2.2.5. Catalytic activity of α-Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar)**

In the first 5 hours of reaction, the H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub> was about 62 %, comparable to that obtained with 0.5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub> (64.1 %) and 0.1 wt. % Pt / Al<sub>2</sub>O<sub>3</sub> (66.25 %) [115, 117], but after approx. 60 hours, the conversion decreased by approx. 10 %.

In another experiment, 0.5 g of α-Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar) powder was mixed with quartz beads (0.1 ÷

0.3 mm) determining an average conversion of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2$  of about 57 % in a period of approx. 100 hours time on stream, but a pressure drop occurs in the reactor, and the experiment was stopped.

### 2.2.6. Catalytic activity of iron trioxide

For these tests, 0.5 g of catalyst mixed with 1.5 g of quartz beads (0.1 ÷ 0.3 mm) was placed in reactor, which form a catalytic bed with a length of 2 cm. At a feed flow rate of 9 ml / h conc.  $\text{H}_2\text{SO}_4$ , at 850°C, an average conversion of approx. 54% was obtained. Although iron trioxide powder was mixed with quartz beads, a pressure drop occurs in the reactor, therefore, to overcome this inconvenience in the further tests, this catalyst was used as pellets of 1 ÷ 3 mm.

#### *Long-term tests*

The good results obtained in the experiment of 200 h showed that the catalyst is resistant in the corrosive environment of the reaction, which led us to test it for a longer period of time. Moreover, in the literature lacks data on the performance of this catalyst for more than 120 h [12] in the reaction environment.

Given that in a long-term experiment the installation remained unsupervised was necessary to replace the quartz reactor with one made of metal. I chose Incolloy 800 as material for reactor, because it is used in chemical industry for the construction of reactors, heat exchangers, etc. Take into account that the high corrosive gaseous mixture (unreduced  $\text{SO}_3$ , water vapor,  $\text{SO}_2$ ,  $\text{O}_2$ ) formed in reaction and high working temperatures (800-900°C), Incolloy 800 had to be tested for chemical and thermal resistance in reaction environment. The tests performed shown that this material corrodes in the highly corrosive environment. However, in order to carry out long-term test, the reactor had to be made from a mechanically and chemically resistant material.



**Figure 25.** Reactor for sulfuric acid conversion to sulfur dioxide

The proposed solution and tested was the inserting a quartz tube in one of Incolloy 800. The quartz tube was fixed in the metal one using two pieces made of teflon, design of this reactor is shown in Figure 25.

The variation of conversion in 1100 hours is shown in Figure 26. In the first 400 hours when the temperature was set at 850°C, an average conversion of about 51 % was obtained. Then the temperature was increased at 900°C, observing a significant increase of conversion to about 78 % which was maintained for almost 27 hours, then conversion decreased by 10 %, remaining at a value of approx. 67 % almost 173 h. After about 600 hours the experiment was interrupted for approx. 1 month and after

restart a slight increase in conversion to approx. 72% was observed, probably due to this break in operation. After the restart, the catalyst was tested another 500 hours, an average conversion of 69% being achieved.

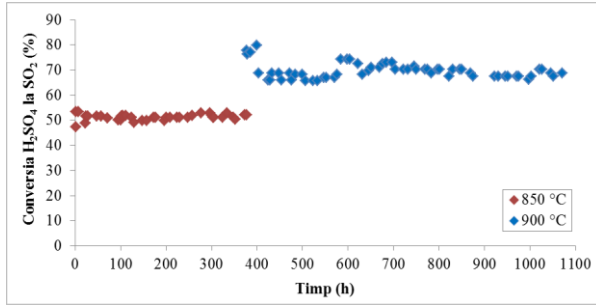


Figure 26. Long term experiments in presence of Fe<sub>2</sub>O<sub>3</sub> pellets

**2.2.7. Activity of synthesized catalysts: 3 wt. % Fe<sub>2</sub>O<sub>3</sub> / SiO<sub>2</sub>, 5 wt. % Fe<sub>2</sub>O<sub>3</sub> / SiO<sub>2</sub>, 10 wt. % Fe<sub>2</sub>O<sub>3</sub> / SiO<sub>2</sub>**

The activity of the prepared catalysts was tested in various reaction conditions: feed flow rate of conc. H<sub>2</sub>SO<sub>4</sub> was kept constant and the operating temperature was varied; the operating temperature remained constant and feed flow rate of conc. H<sub>2</sub>SO<sub>4</sub> was varied; both feed flow rate of H<sub>2</sub>SO<sub>4</sub> and temperature were kept constant and the amount of catalyst loaded into the reactor was varied. In each case there is a significant drop in conversion after two hours of reaction.

**2.3. Analysis of catalysts**

**2.3.1. BET**

The adsorption-desorption isotherms obtained for all catalysts tested are Type IV isotherms according to IUPAC classification [119], with H2 hysteresis. Type IV isotherm are characteristic for mesoporous materials which have pore sizes between 2 and 50 nm (or 20 and 500 Å). All the catalysts used in our study fits into the category of mesoporous materials (Table 10).

Table 10. The surface characteristics of commercial catalysts

Catalyst	Surface area (m <sup>2</sup> /g)		Pores volume (cm <sup>3</sup> /g)		Pores radius (Å)	
	Fresh sample	Spent sample	Fresh sample	Spent sample	Fresh sample	Spent sample
5 wt. % Pd / Al <sub>2</sub> O <sub>3</sub>	185	82.6	0.53	0.20	80-90	140-156
0.5 wt. % Pd / Al <sub>2</sub> O <sub>3</sub>	84	52	0.20	0.10	80	117-155
0.1wt. % Pt / Al <sub>2</sub> O <sub>3</sub>	290	73.7	0.35	0.13	20	88
2 wt. % Pt / TiO <sub>2</sub>	64	6.64	0.28	0.0084	80	206-226
α-Fe <sub>2</sub> O <sub>3</sub> (Alfa Aesar)	19	3.55*	0.036	0.001*	171	9-30* 50-225

\* used at 750°C

After use for  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$ , it can be seen that all catalysts undergo structural changes: the specific surface area and pore volume decrease greatly, pore size distribution increases and a less ordered pore distribution appears.

The specific surface area of granular iron trioxide was not determined, because it is under the measuring range of the apparatus, which suggests that this catalyst is a porous material.

### 2.3.2. X-Ray diffraction

Analysis by X-ray diffraction showed changes in the crystalline structure of the support for the alumina-based catalysts, due to the transformation of  $\gamma$ -alumina into  $\delta$ -alumina, at temperatures close to  $800^\circ\text{C}$ , which was also mentioned in other work [6]. This transformation explains the loss in total surface area of the alumina-based catalyst after exposure to reaction conditions [115]. Also, XRD analysis of the alumina-based catalysts shows the sulfation of alumina.

In the case of 2 wt. % Pt /  $\text{TiO}_2$ , the support is in the anatase phase, and after use in the reaction is a mixture of anatase and rutile. This phase transformation occurred after the heat treatment of the catalyst: activation in  $\text{H}_2$  flow at  $400^\circ\text{C}$ , and then increasing the temperature to the value used for the reaction. It should be noted in the case of this catalyst that the support does not sulfate.

For the  $\alpha\text{-Fe}_2\text{O}_3$  (Alfa Aesar), X-ray diffraction analysis shows that there are no phase changes, only an increase in the crystallite size: from  $444 \text{ \AA}$  in the fresh catalyst sample to  $623 \text{ \AA}$  in the spent sample [115].

X-ray diffraction analysis of the iron trioxide granules shows that it is in the hematite form ( $\alpha\text{-Fe}_2\text{O}_3$ ), and also after calcination at  $1000^\circ\text{C}$ , and after use in reaction for 1100 hours there are no phase changes. The XRD spectrum of the sample used in the reaction indicates the presence of iron sulfate, but in a very small amount compared with the alumina-based catalysts. Also, the crystallite size was calculated, obtaining the following values:  $776 \text{ \AA}$  for the powdered sample,  $892 \text{ \AA}$  for the sample calcinated at  $1000^\circ\text{C}$  and  $1024 \text{ \AA}$  for the sample used in reaction for 1100 h. The high values of the crystallite size explain the impossibility of measuring the specific surface area of this catalyst, since the large size of the crystallites is correlated with lower specific surface areas.

## 2.4. Aspects regarding thermodynamics and kinetics of sulfur trioxide reduction to sulfur dioxide

As noted, the conversion of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2$  takes place in two steps, but it is considered that  $\text{H}_2\text{SO}_4$  decomposition to  $\text{SO}_3$  and water vapor occurs faster than the catalytic reduction of  $\text{SO}_3$  to  $\text{SO}_2$  and  $\text{O}_2$ , thus the second reaction is the rate-determining step of the whole process [33, 34]. Also, it is considered that the decomposition of  $\text{H}_2\text{SO}_4$  is complete at temperatures above  $350^\circ\text{C}$  [5], so that in the catalytic bed enters an equimolar mixture of  $\text{SO}_3$  and  $\text{H}_2\text{O}$  vapor. Thus the so-called  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  is limited to the effective reduction of  $\text{SO}_3$  to  $\text{SO}_2$ , so in this chapter will be presented the thermodynamics and kinetics aspects of this reaction.

**2.4.1. Thermodynamic study of SO<sub>3</sub> reduction to SO<sub>2</sub>**

Enthalpy of reaction ( $\Delta H_{r,T}^0$ ), entropy of reaction ( $\Delta S_{r,T}^0$ ) and Gibbs free energy ( $\Delta G^0$ ) were calculated from thermochemical data tabulated for standard conditions [127], using the following equation:

$$\Delta H_{r,T}^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p^0 dT \tag{15}$$

$$\Delta S_{r,T}^0 = \Delta S_{298}^0 + \int_{298}^T \frac{\Delta C_p^0}{T} dT \tag{16}$$

$$\Delta G^0 = \Delta H_{r,T}^0 - T \cdot \Delta S_{r,T}^0 \tag{17}$$

where:  $\Delta H_{298}^0$  – standard heat of reaction (98.3 kJ/mol), calculated from standard heats of formation of SO<sub>3</sub>, SO<sub>2</sub>, O<sub>2</sub>;  $\Delta S_{298}^0$  – standard entropy of reaction (94.385 J/mol·K), calculated from absolute standard entropy of SO<sub>3</sub>, SO<sub>2</sub>, O<sub>2</sub>;  $\Delta C_p^0 = \Delta a + \Delta bT + \frac{\Delta c}{T^2}$  – heat capacity;  $T$  – temperature of reaction (K).

The values of thermodynamic data calculated in the temperature range 700-925°C are shown in Table 13.

**Table 13.** Thermodynamic data for SO<sub>3</sub> reduction to SO<sub>2</sub>

T (°C)	T (K)	$\Delta H_{r,T}^0$ (kJ/mol)	$\Delta S_{r,T}^0$ (J/mol·K)	$\Delta G$ (kJ/mol)
700	973	97.45	95.58	4.44
725	998	97.20	95.33	2.06
750	1023	96.95	95.08	-0.32
775	1048	96.69	94.83	-2.69
800	1073	96.41	94.57	-5.06
825	1098	96.13	94.31	-7.42
850	1123	95.84	94.05	-9.77
875	1148	95.54	93.78	-12.12
900	1173	95.23	93.51	-14.46
925	1198	94.91	93.24	-16.80

Thermodynamic data presented in Table 13 shows that the SO<sub>3</sub> reduction to SO<sub>2</sub> is favored by increasing of temperature.

**2.4.2. Calculation of equilibrium conversion**

Equilibrium constant (K) for the SO<sub>3</sub> reduction to SO<sub>2</sub> was determined using the relationship:

$$-RT \cdot \ln K = \Delta G \tag{18}$$

where:  $R = 8.314$  J/mol·K – universal gas constant;  $T$  – temperature, K (see the Table 13);  $\Delta G$  – Gibbs free energy, kJ/mol (see the Table 13).

Equilibrium constant expressed in molar fraction for the SO<sub>3</sub> reduction to SO<sub>2</sub> was determined with equation:

$$K_y = \frac{y_{SO_2} \cdot y_{O_2}^{1/2}}{y_{SO_3}} \tag{20}$$

where:  $y_{SO_2} = \frac{x}{1+0.5x}$  – molar fraction of SO<sub>2</sub>

$$y_{O_2} = \frac{0,5x}{1+0,5x} - \text{molar fraction of } O_2$$

$$y_{SO_3} = \frac{1-x}{1+0,5x} - \text{molar fraction of } SO_3$$

By solving the equation (20), the fractional conversion ( $x$ ) and the equilibrium composition of the gas mixture ( $SO_2$ ,  $O_2$ ,  $SO_3$ ) was determined, the results are shown in Table 14.

**Table 14.** Equilibrium data of  $SO_3$  reduction to  $SO_2$

T (°C)	T (K)	K	$x$	$y_{SO_3}$	$y_{SO_2}$	$y_{O_2}$
700	973	0.577135	0.6112	0.297794	0.468137	0.234069
725	998	0.78014	0.6421	0.270921	0.486053	0.243026
750	1023	1.038369	0.6705	0.24677	0.502153	0.251077
775	1048	1.36236	0.6966	0.225024	0.516651	0.258325
800	1073	1.7637	0.7208	0.205234	0.529844	0.264922
825	1098	2.254984	0.7428	0.187546	0.541636	0.270818
850	1123	2.849746	0.7645	0.170374	0.553084	0.276542
875	1148	3.562382	0.7809	0.157575	0.561617	0.280808
900	1173	4.408044	0.7973	0.144925	0.57005	0.285025
925	1198	5.402534	0.8123	0.133485	0.577677	0.288838

### 2.4.3. Kinetic study of $SO_3$ reduction to $SO_2$

In general kinetic studies on the catalytic reduction of  $SO_3$  to  $SO_2$  assume that this reaction is governed by a first order kinetic law [5, 83], which takes place in a tubular reactor with a fixed catalytic bed [10, 83]. This work also starts from this assumption and kinetic study of  $SO_3$  reduction to  $SO_2$  is based on the model proposed by Giaconia *et al.* [10].

*Determination of activation energy and pre-exponential factor.* Reaction rate constant,  $k$ , expressed by law Arrhenius is inserted in equation:

$$-\ln(1 - X) = \frac{k}{WHSV} \tag{28}$$

And applying the logarithm on both sides of equation, results:

$$\ln[-\ln(1 - X)] = -\ln(WHSV/A) - E_a/RT \tag{30}$$

By plotting  $\ln[-\ln(1 - X)]$  vs.  $1/T$  a straight line is obtained, and from slope the activation energy ( $E_a$ ) is calculated, and from intercept the pre-exponential factor ( $A$ ).

Both kinetic parameters,  $E_a$  and  $A$ , were determined for the  $SO_3$  reduction to  $SO_2$  in the presence of four of the catalysts studied in this work: 5 wt. % Pd /  $Al_2O_3$ , 2 wt. % Pt /  $TiO_2$ ,  $\alpha$ - $Fe_2O_3$  (Alfa Aesar) in powder form mixed with quartz beads, and iron trioxide granules. The values of this two parameters are:

- When 5 wt. % Pd /  $Al_2O_3$  is used,  $E_a = 61.6 \pm 2.3$  kJ/mol, and  $A = 3.6 \times 10^4$  h<sup>-1</sup> [128, 129]. The activation energy obtained by us is much smaller than that reported by Petropavlovskii *et al.* [88]: 154 kJ/mol, for APK-2 catalyst (palladium supported on alumina), for which is not specified the concentration of the metal deposited on the support.

- When 2 wt. % Pt /  $TiO_2$  is used,  $E_a = 44.9 \pm 3.3$  kJ/mol, iar  $A = 3.5 \times 10^3$  h<sup>-1</sup> [128]. As it was

mentioned, this type of catalyst has been tested only in terms of activity and stability for SO<sub>3</sub> reduction to SO<sub>2</sub> [38] and I have not found in literature kinetic studies regarding this reaction.

- When α-Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar) is used, E<sub>a</sub> = 109.4 ± 5.1 kJ/mol, A = 3.1×10<sup>6</sup> h<sup>-1</sup> [128], and for iron trioxide granules E<sub>a</sub> is 112.1 ± 4.9 kJ/mol, and pre-exponential factor: 1.91×10<sup>6</sup> h<sup>-1</sup>. The difference between the pre-exponential factors is given by different granulation of catalyst, this is as one of the parameters on which pre-exponential factor depends [10]. A smaller particle size of the catalyst lead to higher pre-exponential factor, because provide a larger contact surface between reactant and catalyst [10].

*Dependence of reaction rate constant on temperature.* The rate constants for SO<sub>3</sub> reduction to SO<sub>2</sub> were calculated from the Arrhenius law, with the values of E<sub>a</sub> and A previously determined. The results are presented in Table 15.

**Tabelul 15.** Dependence of reaction rate constant on temperature

Catalizator	Temperature (°C)	Rate constant (h <sup>-1</sup> )
Pd 5% / Al <sub>2</sub> O <sub>3</sub>	800	36.10
	825	42.24
	850	49.09
	875	56.67
	900	65.03
Pt 2% / TiO <sub>2</sub>	775	20.23
	800	22.81
	825	25.58
	850	28.55
α-Fe <sub>2</sub> O <sub>3</sub> (pulbere amestecat cu granule de cuarț)	750	8.04
	800	14.64
	825	19.35
	850	25.27
	875	32.62
	900	41.64
Fe <sub>2</sub> O <sub>3</sub> tehnic (granule 1÷3 mm)	750	3.61
	775	4.94
	800	6.66
	850	11.66
	900	19.45

*Determination of activation parameters:* ΔH<sup>0‡</sup>, ΔS<sup>0‡</sup> și ΔG<sup>0‡</sup>. For this proposes the linear form of Eyring-Polyani equation is used:

$$\ln \frac{k}{T} = \left( \ln \frac{\kappa}{h} + \frac{\Delta S^{0\ddagger}}{R} \right) - \frac{\Delta H^{0\ddagger}}{R} \cdot \frac{1}{T} \tag{34}$$

A plot of ln(k/T) versus (1/T) gives a straight line with slope (-ΔH<sup>0‡</sup>/R) from which the enthalpy of activation is obtained, and from the intercept (ln κ/h + ΔS<sup>0‡</sup>/R), the entropy of activation is determined, the values are presented in Table 16.

Different kinetic studies for some chemical reactions [131], both homogeneous and heterogeneous shows that in the formation of activated complex, between the activation energy, E<sub>a</sub>, and entropy of

activation,  $\Delta S^{0\#}$ , a linear dependence is established, which proves that the kinetic equation applied in order to describe the process is properly chosen and the process parameters have been well calculated. If the activation energy is plotted vs. the entropy of activation for  $\text{SO}_3$  reduction to  $\text{SO}_2$ , catalyzed by 2 wt. % Pt /  $\text{TiO}_2$ , 5 wt. % Pd /  $\text{Al}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  (Alfa Aesar), indeed a linear relationship between these parameters is obtained, so that the model chosen [10] to characterize this reaction is correct and the parameters are well calculated.

**Table 16.** Activation parameters

Catalyst	$\Delta H^{0\#}$ (kJ/mol)	$\Delta S^{0\#}$ (J/K·mol)	$E_a$ (kJ/mol)	A ( $\text{h}^{-1}$ )
2 wt. % Pt / $\text{TiO}_2$	$35.8 \pm 3.2$	$-128.0 \pm 3.0$	$44.9 \pm 3.3$	$3.5 \times 10^3$
5 wt. % Pd / $\text{Al}_2\text{O}_3$	$52.2 \pm 2.4$	$-109.0 \pm 2.1$	$61.6 \pm 2.3$	$3.6 \times 10^4$
$\alpha\text{-Fe}_2\text{O}_3$ (Alfa Aesar)	$100.2 \pm 4.9$	$-71.7 \pm 4.4$	$109.4 \pm 5.1$	$3.1 \times 10^6$

Regarding the relationship between the enthalpy and entropy of activation, Cremer [135] presents three possibilities that may appear in catalyzed reactions:

Case 1:  $\Delta H_1^\# > \Delta H_2^\# > \Delta H_3^\# \dots$ ;  $\Delta S_1^\# = \Delta S_2^\# = \Delta S_3^\# \dots$

Case 2:  $\Delta H_1^\# > \Delta H_2^\# > \Delta H_3^\# \dots$ ;  $\Delta S_1^\# < \Delta S_2^\# < \Delta S_3^\# \dots$

Case 3:  $\Delta H_1^\# > \Delta H_2^\# > \Delta H_3^\# \dots$ ;  $\Delta S_1^\# > \Delta S_2^\# > \Delta S_3^\# \dots$

As can be seen from Table 16, the results obtained for  $\text{SO}_3$  reduction to  $\text{SO}_2$  fit to case 3, such as:  $\Delta H_{\text{Fe}_2\text{O}_3}^\# > \Delta H_{\text{Pd}/\text{Al}_2\text{O}_3}^\# > \Delta H_{\text{Pt}/\text{TiO}_2}^\#$ , corresponding to  $\Delta S_{\text{Fe}_2\text{O}_3}^\# > \Delta S_{\text{Pd}/\text{Al}_2\text{O}_3}^\# > \Delta S_{\text{Pt}/\text{TiO}_2}^\#$ , therefore the adsorption of reactant is stronger on Pt catalyst than on Pd catalyst and iron oxide, respectively. Therefore, the bond formed between activated complex and catalyst breaks easily for iron trioxide than for Pd and Pt catalysts.

**2.5. Sizing of reactor for sulfur trioxide reduction to sulfur dioxide**

The calculation method chosen for sizing of the reactor to reduce  $\text{SO}_3$  to  $\text{SO}_2$  is relatively simple and can be applied for any catalyst used for this reaction, if the activation energy necessary to reduce  $\text{SO}_3$  to  $\text{SO}_2$  has been previously determined. If the activation energy and pre-exponential factor are known, the reaction rate constant is calculated with Arrhenius equation [128]. For 5 wt. % Pd /  $\text{Al}_2\text{O}_3$ , as pellets with the sizes between 0.4 and 0.8 mm, with bulk density of  $0.6369 \text{ g/cm}^3$ , for temperature of 1123 K ( $850^\circ\text{C}$ ), reaction rate constant is  $49.1 \text{ h}^{-1}$ . From equation (28):  $-\ln(1 - X) = \frac{k}{WHSV}$ , WHSV was determined for a certain fractional conversion (X). From equation (14), that defines weight hourly space velocity:  $WHSV = \frac{\dot{m}_{\text{H}_2\text{SO}_4}^0}{W}$ , the amount of catalyst loaded into reactor was determined:  $W = 1.029 \text{ g}$  for  $\text{H}_2\text{SO}_4$  mass flow rate:  $\dot{m}_{\text{H}_2\text{SO}_4}^0 = 49.46 \text{ g/h}$  (28 ml/h 96 wt. %  $\text{H}_2\text{SO}_4$ , density of  $1.84 \text{ g/cm}^3$ ).

Knowing the amount of catalyst and its bulk density the volume of the catalyst bed was calculated:  $1.61 \text{ cm}^3$ , with relation:



$$V_R = \frac{W_{cat}}{\rho_{cat}} \tag{35}$$

The total flow rate of gases that enter in the catalytic bed is 24.22 l/h ( $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$ ) + 1.8 l/h heliu = 26.02 l/h, and velocity in the free layer (9,2 cm/s) was obtained by reporting it to the section area of the reactor (0.785 cm<sup>2</sup>). From the volume of reactor (35) and section area, the length of catalytic bed was determined: 1 = 2 cm, for 5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub>, in experimental condition above presented. We proceeded in the same way for catalysts: 2 wt. % Pt / TiO<sub>2</sub> – pellets 2 ÷ 4 mm, α-Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar) – powder mixt with quartz beads, iron trioxide – pellets 1 ÷ 3 mm.

*Dependence of reactor sizes on fractional conversion.* The reactor length variation with fractional conversion when 2 wt. % Pt / TiO<sub>2</sub> is used as catalyst, is shown in Table 18, and for 5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar) – powder mixed with quartz beads [128], and iron trioxide – pellets 1÷3 mm, Tables 19 and 20.

**Tabelul 18.** The reactor length variation with fractional conversion, at temperature of 850°C, for 2 wt. % Pt / TiO<sub>2</sub>

Catalyst	X	WHSV (h <sup>-1</sup> )	V <sub>R</sub> (cm <sup>3</sup> )	W <sub>cat</sub> (g)	l (cm)	d (cm)
2 wt. % Pt / TiO <sub>2</sub>	0.45	47.79	9.48	7.87	3.42	1.88
	0.5	41.22	11.0	9.13	3.96	1.88
	0.6	31.18	14.54	12.07	5.23	1.88
	0.7	23.73	19.10	15.85	6.87	1.88
	0.8	17.75	25.54	21.20	9.18	1.88

**Tabelul 19.** The reactor length variation with fractional conversion, at temperature of 850°C, for 5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub>

Catalyst	X	WHSV (h <sup>-1</sup> )	V <sub>R</sub> (cm <sup>3</sup> )	W <sub>cat</sub> (g)	l (cm)	d (cm)
5 wt. % Pd / Al <sub>2</sub> O <sub>3</sub>	0.64	48.06	12.29	7.83	4.42	1.88
	0.70	40.78	14.49	9.33	5.21	1.88
	0.75	35.42	16.67	10.62	5.99	1.88
	0.80	30.51	19.36	12.33	6.96	1.88
	0.75	18.36	18.25	20.49	3.51	2.57
	0.80	15.81	21.20	23.80	4.08	2.57

**Tabelul 20.** The reactor length variation with fractional conversion, at temperature of 850°C, for Fe<sub>2</sub>O<sub>3</sub>

Catalyst	X	WHSV (h <sup>-1</sup> )	V <sub>R</sub> (cm <sup>3</sup> )	W <sub>cat</sub> (g)	l (cm)	d (cm)
α-Fe <sub>2</sub> O <sub>3</sub> (Alfa Aesar) powder mixed with quarts beads	0.67	22.95	14.60	16.39	2.80	2.57
	0.70	21.40	15.66	17.58	3.01	2.57
	0.75	18.36	18.25	20.49	3.51	2.57
	0.80	15.81	21.20	23.80	4.08	2.57
Iron trioxide pellets of 1÷3 mm	0.51	16.34	16.07	23.02	3.09	2.57
	0.60	12.72	20.64	29.57	3.96	2.57
	0.70	9.68	27.13	38.85	5.21	2.57
	0.75	8.41	31.23	44.74	6.00	2.57
	0.80	7.24	36.26	51.94	6.97	2.57

A comparison between catalysts studied can not be made because their surface is different due to the difference of particle size. However from the data presented we can see that there are no considerable differences between volume, respectively size of the catalytic reactor, which favors granular iron trioxide, that is the cheapest and convenient catalyst.

*Dependence of catalytic reactor length on velocity in the free layer of gaseous mixture.* In the Tables 21-22 the results obtained with the three catalysts are shown, maintaining the same inlet molar flow of  $H_2SO_4$ : 4 moles / h, a constant fractional conversion equal with that experimentally determined for each catalyst at a temperature of 850 °C and varying the velocity in the free layerb [128].

**Tabelul 21.** Dependence of reactor sizes on velocity in the free layer, for 2 wt. % Pt /  $TiO_2$ , at 850°C

Catalyst	X	$V_R$ ( $cm^3$ )	v (cm/s)	l (cm)	d (cm)
2 wt. % Pt / $TiO_2$	0.45	9.48	10	3.70	1.80
			9	3.33	1.90
			8	2.96	2.02
			7	2.59	2.16
			6	2.22	2.33

**Tabelul 22.** Dependence of reactor sizes on velocity in the free layer, for 5 wt. % Pd /  $Al_2O_3$ , at 850°C

Catalyst	X	$V_R$ ( $cm^3$ )	v (cm/s)	l (cm)	d (cm)
5 wt. % Pd / $Al_2O_3$	0.64	12.29	10	4.80	1.80
			9.2	4.42	1.88
			8.0	3.84	2.02
			7.0	3.66	2.16
			6.0	2.87	2.33

**Tabelul 23.** Dependence of reactor sizes on velocity in the free layer, for  $Fe_2O_3$ , at 850°C

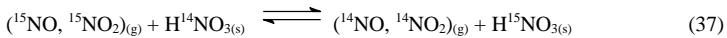
Catalyst	X	$V_R$ ( $cm^3$ )	v (cm/s)	l (cm)	d (cm)
$\alpha$ - $Fe_2O_3$ (Alfa Aesar) powder mixed with quarts beads	0.67	14.60	10	5.70	1.80
			9	5.13	1.90
			8	4.56	2.02
			7	3.13	2.16
			6	3.42	2.33
Iron trioxide pellets of 1÷3 mm	0.51	16.07	10	6.27	1.80
			9	5.65	1.90
			8	5.02	2.02
			7	4.39	2.16
			6	3.76	2.33

The reactor length for  $SO_3$  reduction to  $SO_2$  increases linearly with the velocity in the free layer of the gaseous mixture. It is observed that there are no big differences between the reactor lengths for the four catalysts, which strengthens once again the idea that, for  $SO_3$  reduction, iron trioxide can be used as catalyst in form of pellets, in order to reduce the pressure drop across the reactor.

## 2.6. Recycling of sulfur dioxide in $^{15}\text{N}$ separation plant

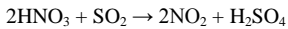
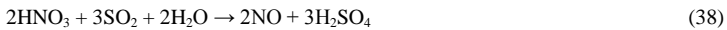
At INCDTIM Cluj-Napoca the researches for sulfuric acid reduction to sulfur dioxide were approached, in order to recycling it in  $^{15}\text{N}$  production plant.

$^{15}\text{N}$  production technology, used at INCDTIM Cluj-Napoca, is based on the isotopic exchange in Nitrox system:  $(\text{NO}, \text{NO}_2)_{(\text{g})} - \text{HNO}_{3(\text{s})}$ , in a packed separation column, where the nitric acid flows in counter-current with nitrogen oxides. Isotopic exchange reaction that takes place in the separation column:



is characterized by a single-stage separation factor,  $\alpha = 1,055$  for 10 M  $\text{HNO}_3$  solution, at temperature of  $20^\circ\text{C}$  and atmospheric pressure. According to reaction (37),  $^{15}\text{N}$  becomes concentrated in the liquid phase, in  $\text{HNO}_3$ , at the bottom of the separation column of the plant and  $^{14}\text{N}$  in the gaseous phase, in the top of the same column.

For the nitric acid conversion to nitrogen oxides, sulfur dioxide is used, and process take place in product refluxer, according to the reactions:



Sulfuric acid, waste of  $^{15}\text{N}$  production plant, is a solution of 65-70 wt. % concentration, difficult to transport and harnessed, and expensive to neutralize. On the other hand approx. 50 % of the cost of  $^{15}\text{N}$  production is due to the supplying of the plant with  $\text{SO}_2$ . Recycling of  $\text{SO}_2$  in  $^{15}\text{N}$  production plant, by  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  represents one of the important methods to increase the efficiency of isotope separation plant.

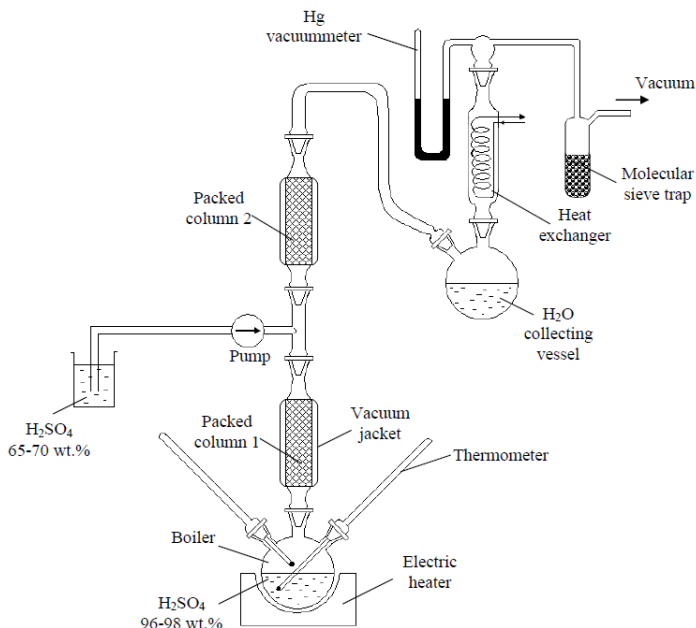
For the recycling of  $\text{SO}_2$  in  $^{15}\text{N}$  production plant have to be followed three important steps:

1. Concentration of sulfuric acid from 65 – 70 wt. % to 96 – 98 wt. %
2. Conversion of concentrated sulfuric acid to sulfur dioxide
3. Separation and collection of the sulfur dioxide from the gaseous mixture leaving the reduction reactor ( $\text{SO}_2$ ,  $\text{O}_2$  și inert gas – He sau Ar).

### *Concentration of sulfuric acid*

For the sulfuric acid concentration step have been achieved and tested a glass laboratory plant (Figure 42). The laboratory plant has two packed separation columns, first one is 35 cm length and 25 mm i.d., the second one is 30 cm length and the same i.d. Both columns are vacuum jacketed for thermal isolation and have glass Raschig packing of 5x5 mm. Using a peristaltic pump, sulfuric acid solution of 65-70 wt. % is fed through a intermediate glass part making the connection between the two columns. The boiler, from the bottom of the column 1, consists of a 3-neck round-bottom flask, with a capacity of 2 liters, and the heating is carried out by an electric heater with thermostat. The water vapors, leaving the separation column 2, enter in the collecting vessel, a 2 neck round-bottom flask with

capacity of 2 l and condense in the glass heat exchanger of 25 cm, water cooled. The distillation plant is connected to a vacuum pump, through a glass trap with 5Å molecular sieve and the vacuum is measured by a Hg vacuummeter.



**Figura 42.** Laboratory plant for concentration of sulfuric acid

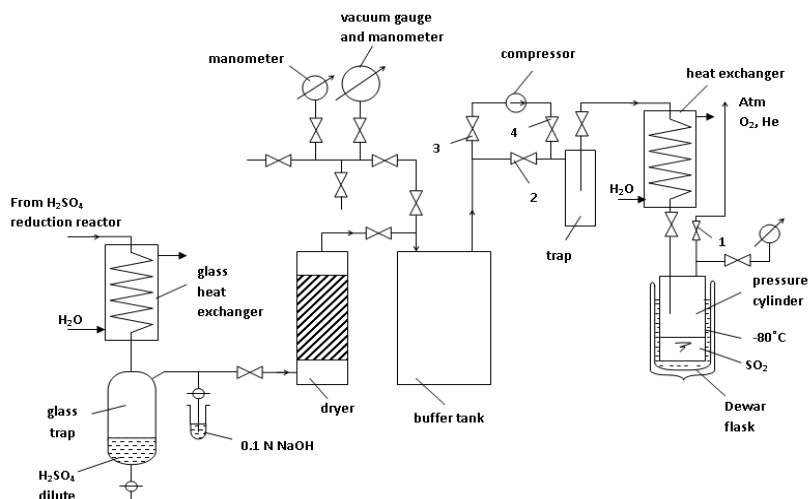
With this installation we performed a few experiments for  $\text{H}_2\text{SO}_4$  concentration, with an average duration of 5-6 hours [136]. Before the start of the distillation plant, in the boiler a  $\text{H}_2\text{SO}_4$  solution of  $96 \pm 0.5$  wt. % is introduced, this being the concentration at which the 65-70 wt. %  $\text{H}_2\text{SO}_4$  should be brought. The liquid temperature, corresponding to that  $\text{H}_2\text{SO}_4$  concentration, is  $200 \pm 5^\circ\text{C}$  under vacuum of about 5 torr. If that temperature is exceeded, the concentration of  $\text{H}_2\text{SO}_4$  solution increases, and a part of  $\text{H}_2\text{SO}_4$  will decompose into  $\text{SO}_3$  and  $\text{H}_2\text{O}$ , and sulfuric anhydride goes into distillate, increasing the acidity of the collected water. Under that temperature the concentration of the  $\text{H}_2\text{SO}_4$  solution is lower than 96 wt. %. For a feeding of 53 ml/h sulfuric acid solution 65.32 wt. % ( $d=1.557$  g/cm<sup>3</sup>) an extraction flow rate of 28.9 ml/h  $\text{H}_2\text{SO}_4$  96 % was determined, the global yield of the distillation process being 98.8 %.

This step is important in  $\text{SO}_2$  recycling process, because it increases the  $\text{SO}_2$  conversion efficiency: The more concentrated  $\text{H}_2\text{SO}_4$  is, the more higher the yield is, in a single pass through the reduction reactor.

*Separation of the sulfur dioxide from the gaseous mixture leaving the reduction reactor*

In order to recycle  $\text{SO}_2$  in the  $^{15}\text{N}$  production plant it has to be separated from the gaseous mixture leaving the reduction reactor. Thus, we achieved a laboratory plant that we managed to make this separation.

The laboratory plant, presented in Figure 43 [137], consists of: two heat exchanger, one of glass, 170 mm length and 35 mm outside diameter, and another one of steinel steel, 250 mm length and 85 mm o.d.; a stainless steel dryer, 200 mm length and 40 mm o.d.; a stainless steel buffer tank with volume of 19.15 l; a stainless steel trap, 310 mm length and 55 mm o.d.; a stainless steel pressure cylinder for  $\text{SO}_2$  collection, 250 mm length and 70 mm o.d.; the plant is also equipped with various valves, manometers and a compressor. The gaseous mixture leaving the reduction reactor contains:  $\text{SO}_2$ ,  $\text{O}_2$ , He, unreacted  $\text{SO}_3$  and water vapor. In the glass heat exchanger, cooled with water, condensation of  $\text{SO}_3$  and water vapor take place, being collected in a glass trap as diluted  $\text{H}_2\text{SO}_4$ . The remained gaseous mixture:  $\text{SO}_2$ ,  $\text{O}_2$  and He is dry in stainless steel dryer, packed with silica pellets wetted with concentrated sulfuric acid. Before  $\text{SO}_2$  collection, the gaseous mixture washes away the air from plant.



**Figure 43.** Laboratory plant for  $\text{SO}_2$  separation [137]

In order to separate  $\text{SO}_2$  from gaseous mixture two methods was used: separation at low temperature ( $-80^\circ\text{C}$ ) and separation at pressure when a mambrane gas compressor, corrosion resistant, was used.

Applying the first method,  $\text{SO}_2$  is collected in solid form into the pressure cylinder at  $-80^\circ\text{C}$ ,

temperature obtained by mixing ethanol with liquid nitrogen.

The plant was tested for separation of sulfur dioxide, by using a 96.3 wt. %  $\text{H}_2\text{SO}_4$  feeding flow rate of 14 ml/h, or 0.253 mol/h and an iron trioxide catalyst, at 850°C. After 4 hours of  $\text{SO}_2$  trapping at -80°C in the pressure cylinder, a mean amount of 34.5 g  $\text{SO}_2$ , or 8.625 g  $\text{SO}_2$ /h, has been collected. At an average  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  of 52.51 %,  $\text{SO}_2$  separation from gaseous mixture was quantitatively achieved [137].

When for  $\text{SO}_2$  separation the gas compressor is used, the pressure cylinder can be water cooled at 10-15°C only. In this case the procedure is: entire plant is washed away with gaseous mixture, the valve (1), Figure 43, being open to atmosphere. During this step the membrane gas compressor, in construction resistant to corrosion, is by-passed. Then the valve (1) is closed allowing gaseous mixture in the buffer tank to a pressure of about (1.5 absolute pressure), in order to avoid the  $\text{SO}_2$  liquefaction in the plant. Then the compressor has been started, the valve (2) is closed and the valves (3) and (4) are open.

The gaseous mixture is compressed, the liquefaction of  $\text{SO}_2$  takes place in the stainless steel heat exchanger and the liquid  $\text{SO}_2$  is collected in the pressure cylinder. The pumping continued until the buffer tank reached atmospheric pressure, when the compressor stopped and then the uncondensed gases  $\text{O}_2$  and He were evacuated from pressure cylinder to a pressure slightly higher than the pressure of the  $\text{SO}_2$  vapors at the working temperature.

The  $\text{SO}_2$  condensation takes place well, and it is separated 99 % from the gaseous mixture, if the pressure of the cylinder is around 15 atm, at the temperature of the cooling water.

## CONCLUSIONS AND FINAL REMARKS

The general objective of this work was to study the thermo-catalytic conversion of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2$  in order to recycling it in  $^{15}\text{N}$  separation plant by isotope exchange in  $(\text{NO}, \text{NO}_2)_{(g)} - \text{HNO}_3(s)$  system, technology used at INCDTIM Cluj-Napoca for production of this isotope.

The main conclusions and observations emerging from this work are:

1. *The catalytic activity was tested*, expressed as the conversion degree of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2$  for the following commercial catalysts: 5 wt. % Pd /  $\text{Al}_2\text{O}_3$ , 0.5 wt. % Pd /  $\text{Al}_2\text{O}_3$ , 0.1 wt. % Pt /  $\text{Al}_2\text{O}_3$ , 2 wt. % Pt /  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  catalyst was prepared (by wet impregnation method).

Pd 5 wt. % /  $\text{Al}_2\text{O}_3$  catalyst, pellet size between 0.4 și 0.8 mm, shows good catalytic activity, but has reduced capacity to maintain a constant conversion over a longer period of time, e.g. at a flow rate of 18 ml/h conc.  $\text{H}_2\text{SO}_4$ , conversion decrease from about 63 % to 27 %, after 10 h. These results are not promising for the use of this catalyst in a pilot plant for the  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$ . Moreover, this catalyst is expensive since this is a supported noble metal (Pd).

0.5 wt. % Pd /  $\text{Al}_2\text{O}_3$ , 0.1 wt. % Pt /  $\text{Al}_2\text{O}_3$  catalysts, both as spherical pellets with a diameter between 2 and 4 mm, lead to conversion of about 64 % for the first one, and 66 %, for the second. This conversion was obtained in 5 h time on stream, at  $850^\circ\text{C}$  and a flow rate of 9 ml/h conc.  $\text{H}_2\text{SO}_4$ , being with 15 % lower than that obtained with 5 wt. % Pd /  $\text{Al}_2\text{O}_3$  catalyst in the same experimental conditions.

Catalytic activity of 2 wt. % Pt /  $\text{TiO}_2$  at different temperature, at a flow rate of 28 ml/h conc.  $\text{H}_2\text{SO}_4$ , but conversions are relatively small and increase very slow with increasing of temperature: from 34 % at  $775^\circ\text{C}$  until just 44 % at  $850^\circ\text{C}$ , equal to value obtained at  $900^\circ\text{C}$ .

$\alpha\text{-Fe}_2\text{O}_3$  (Alfa Aesar) powder mixed with quartz beads (0.1 ÷ 0.3 mm) was tested for about 100 h, obtaining a conversion of approx. 57 %, but a pressure drop occurs in reactor.

The pressure drop was avoided when iron trioxide was granulated, thus it was possible to test  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  over 1000 h, that is a *novelty*, considering that in the literature there are no data concerning the performance of this catalyst for more than 120 h time on stream.

It was tested as material for reactor Incolloy 800, but it corrodes in the highly corrosive environment of this reaction, although in the literature it is presented as a resistant material in corrosive media and high temperature. The proposed and tested solution was the insertion of a quartz tube in one of Incolloy 800, making possible the experiment in over 1000 hours.

The catalysts prepared have not the ability to maintain the conversion, this decreasing in 2 hours more than 50% of the initial value.

2. *The catalysts were analyzed*, before and after use in process by BET method and X-ray diffraction.

All tested catalysts are mesoporous materials, except iron trioxide which failed to determine the specific surface area, which indicates that this is a non-porous material.

After use in the reduction process, catalysts are undergoing to structural changes: the specific surface area and pore volume decrease very much and pore size increases, a less ordered distribution appear.

XRD analysis shows changes in crystalline structure for alumina based catalysts, and also for the  $\text{TiO}_2$ , due to the phase transformation: from  $\gamma$ -alumina and  $\delta$ -alumina in case of  $\text{Al}_2\text{O}_3$  and from anatase to rutile for  $\text{TiO}_2$ . This phase transformation leads to the decrease of the surface area of the catalysts after use in the reaction.

Also, XRD analysis shows the transformation of alumina in aluminium sulfate after use in process, which leads to a decrease of conversion in time for alumina based catalysts.

In the case of iron trioxide there are no phase changes, but crystallite sizes increases after use in process. XRD analysis indicated the formation of iron sulfate but in very small quantities which do not influence the catalytic activity considering that the conversion is maintained constant above 1000 h.

3. *Studies on the thermodynamics and kinetics of  $\text{SO}_3$  reduction to  $\text{SO}_2$  have been performed*, considering that the decomposition of  $\text{H}_2\text{SO}_4$  into  $\text{SO}_3$  and water vapor is total at temperatures above  $350^\circ\text{C}$ , thus in the catalytic bed enters an equimolar mixture of  $\text{SO}_3$  and water vapor.

Thermodynamic data of  $\text{SO}_3$  reduction to  $\text{SO}_2$  in the temperature range of  $700\text{--}925^\circ\text{C}$  were calculated, which shows that the reaction is favored by increasing the temperature.

Kinetic study of  $\text{SO}_3$  reduction to  $\text{SO}_2$  is based on the model proposed by Giaconia *et al.* The kinetic parameters: energy of activation ( $E_a$ ) and pre-exponential factor ( $A$ ) were determined for  $\text{SO}_3$  reduction to  $\text{SO}_2$  in presence of the catalysts: 2 wt. % Pt /  $\text{TiO}_2$  ( $E_a = 44.9 \pm 3.3$  kJ/mol,  $A = 3.5 \times 10^3$ ), 5 wt. % Pd /  $\text{Al}_2\text{O}_3$  ( $E_a = 61.6 \pm 2.3$  kJ/mol,  $A = 3.6 \times 10^4$ ),  $\text{Fe}_2\text{O}_3$  (Alfa Aesar) powder mixed with quartz beads ( $E_a = 109.4 \pm 5.1$  kJ/mol,  $A = 3.1 \times 10^6$ ) and  $\text{Fe}_2\text{O}_3$  pellets ( $E_a = 112.1 \pm 4.9$  kJ/mol,  $A = 1.9 \times 10^6$ ).

The enthalpy and entropy of activation for formation of the activated complex were calculated. Between entropy and energy of activation a linear dependence exists, which proves that the model chosen for kinetic study is correct, and the parameters are correctly calculated.

4. *A simple method for sizing the catalytic reactor* for  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  at temperature of  $850^\circ\text{C}$  was presented, based on the activation energy and pre-exponential factor experimentally determined. Thus it was possible to determine the mass of the catalyst, the reactor volume and length. It is difficult to make a comparison between the catalysts included in the study due to their different structure, but are not considerable differences between volume respectively size of the reactor, therefore *iron trioxide is favored since it is the cheapest and convenient catalyst*. Also it is preferred in form of pellets in order to avoid pressure drop in the reactor.

5. For  $\text{SO}_2$  recycling in  $^{15}\text{N}$  production plant along with  $\text{H}_2\text{SO}_4$  conversion to  $\text{SO}_2$  step, there are necessary another two steps:  $\text{H}_2\text{SO}_4$  concentration from 65-70 wt. % to 96-98 wt. % and  $\text{SO}_2$  separation and storage from the gas mixture leaving the reduction installation. Thus in this paper was designed and tested two laboratory plant to carry out this two stages: overall efficiency of  $\text{H}_2\text{SO}_4$  concentration



process by vacuum distillation was 98 % and SO<sub>2</sub> separation and collection from the gas mixture leaving reduction reactor was quantitative.

Finally we are highlighting the most important original contributions of this work:

- thermo-catalytic conversion of H<sub>2</sub>SO<sub>4</sub> to SO<sub>2</sub> for its recycling in <sup>15</sup>N production plant is a novelty at national level;

- iron trioxide pellets is the catalyst indicated for H<sub>2</sub>SO<sub>4</sub> conversion to SO<sub>2</sub> without the need to depositing it on an inert support, take into account that structural changes occurs in highly corrosive environment of the reaction and the temperature at which the reaction proceeds, which leads to decreased catalyst performance.

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## Research papers related to PhD thesis

## (a) published article

1. **Ancuța Balla**, C. Marcu, D. Axente, G. Borodi, D. Lazăr, Catalytic reduction of sulfuric acid to sulfur dioxide, *Central European Journal of Chemistry*, **2012**, *10*, 1817-1823.
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## (b) patent

D. Axente, **Ancuța Balla**, C. Marcu, Ș. Gergely, Metodă și instalație pentru reciclarea dioxidului de sulf și oxigenului într-o instalație pentru producerea izotopului  $^{15}\text{N}$  prin schimb izotopic ( $\text{NO}$ ,  $\text{NO}_2$ )<sub>(g)</sub> -  $\text{HNO}_3$ <sub>(s)</sub>, *trimis spre brevetare*, Nr. Înregistrare OSIM București: A/00114/17 Februarie 2015.

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