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Kinetic Study on Selective Sulfur Dioxide Reduction from Flue Gas: Higher selectivity and stability for SO_2 Reduction from Power Plants

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Abstract

The work includes an exhaustive study on the reduction of Sulfur dioxide gas via a novel selective amine based absorber in order to show the optimum process and reaction kinetics as well. Experimental studies were conducted in a pilot plant aiming to reduce SO_2 in a mixture of flue gas with the emphasis on the kinetics of the process and final released SO_2 emission by obtaining the optimal process condition. Sulfur dioxide was reduced from 4000-8000ppm to an amount of less than 10 ppm in the outlet of the pilot. During the scrubbing process, SO_2 absorption was performed in atmospheric pressure and a temperature between 52 to 73 degrees Celsius. Various flow rates were implemented to reach an effective performance of the pilot process. A highly efficient process was obtained based on experimental results in a long operational time in comparison with the commercial solvents. Finally, the reaction kinetics between SO_2 and Amine-based solution were measured over a range of temperatures from 40°C to 60 °C with the concentrations of SO_2 ranging between 2500 ppm and 8500 ppm and the results shows a first order reaction between the absorbent and SO_2 was determined.

1. Introduction

A Lot of effort have been done to reduce SO_2 emissions on human and the environment to keep SO_2 concentration below a critical concentration in power plants [1-4]. One of the main problems caused by SO_2 is known as acid rain, where SO_2 reacts with water present in rain, to form sulphuric acid (H_2SO_4). Eventually, this 'acid rain' returns to the earth and can cause corrosion structures, soil damages, and lakes resulting in damaged ecosystems [5,6]. In the past 20 years, technological absorption methods of SO_2 have tried to make a considerable progress in terms of design efficiency and reliability. Therefore invention of highly effective gas removal plants seems to be more necessary than before.

Removal of sulfur dioxide from gas emissions by selective absorption is a common method to separate and concentrate sulfur dioxide and reduce air pollution and environmental risks [3]. Nowadays SO_2 scrubbing in the wet scrubbing tower is done by absorbents which absorb SO_2 and CO_2 simultaneously. Since a few amount of SO_2 exist in flue gas in comparison with CO_2, this simultaneous absorption requires an extra volume of absorption tower, large amount of solvent and more equipment to separate these two gases [4, 5].

Regenerative methods lead to more sustainable process operational conditions. They also cause increasing efficiency and higher production rate. There are four processes that handle SO_2 capturing with an amino compound solvent: Sulphidine, ASARCO, DOW, and CANSOLV processes [6-10]. Sulphidine (1932) was the first pragmatic process that used an amine-based solvent to capture SO_2 contaminations. British Patent 371,888 was the first industrial plant used aromatic amines like aniline and its homologues in SO_2 reduction process in 1935 [11]. The process releases toxic emissions such as xylidine and toluidine and as a result became prohibited in 1955. In this method, the gas faces an electrostatic cleaning at first. It is then passed through two xylidine water absorbent packed absorbers and that's where it contacts xylidine vapors. The vapors are then washed with dilute sulfuric acid in order to get recovered from gas streams. The clean gas that enters atmosphere contains around 0.05 to 0.10% SO_2. The absorbent is saturated with SO_2 with a concentration of 130 to 180 grams per liters and then pumped to a raschig ring-packed stripping column in which SO_2 is removed by heating. A temperature of 95 to 100 degrees centigrade is reached by indirect heating of the reboiler [12, 13].

American Smelting and Refining Company (ASARCO) invented a novel flow system in 1947 [11, 14]. The new process was more influenced by flow pattern rather than the solvent. Due to steam consumption and operating labor requirements, the process had improvements over the Sulphidine process. ASARCO used dimethylaniline (DMA) as the solvent. It can absorb larger quantities of sulfur dioxide than xylidine in high concentrations of SO_2 and it does not require water to dissolve the sulfur dioxide compound formed. The use of xylidine may be advantageous and economic in low concentrations of gas. ASARCO has licensed at other locations worldwide. However, no ASARCO amine flue gas desulfurization (FGD) systems have been built since 1979; and they commenced operations in 1992 [14]. ASARCO consumed chemically pure nitrogen, N-dimethylaniline (commercial grade), as the absorbing liquid. The liquid absorbent was pumped from the storage tank. Experiments were carried out at 16 ºC where gas and liquid flow rates were 1 liter per minute [12-14].

As mentioned, many processes have been offered to remove sulfur dioxide from gas streams but few of them have obtained commercial condition. Only the limestone/lime wet Flue Gas Desulfurization systems, predominantly with spray, tray, or packed tower absorbers. Users have opted for low cost, proven systems that operate with high availability [7-10]. Selective SO_2 Regenerative process with a cheap initial cost for solvent with no need to separate absorbed SO_2 byproducts lower charge and high absorption rate, increase the performance more than that of lime/limestone, citrate, double alkali or other processes. Among the wet process is the most cheap and suitable method for flue gas desulfurization. Sodium based sorbents are most effective compared to other absorbents due to its high oxidative tendency such as CANSOLV process [11-12].

Amine absorbent used in our study covers all the characteristics mentioned which specify it from other solvents. Removal of sulfur dioxide is conducted by a selective regenerative process using an amine-based solvent which performs with a lower solvent cost, higher efficiency and selectivity. SO_2 recovered by this method can be used in refinery sulfuric acid units as a raw material, a reactant in chemical reactions, a refrigerant or a reagent and/or solvent in laboratory tests and we optimize the process conditions of SO_2 absorption [14, 16]. This paper is focused on study of reduction of sulfur dioxide gas with the novel selective amino compound solvent. Conducting the experiments on the pilot plant in the Research Center of Petroleum University of Technology, the obtained data are discussed in the article. AIT500 is more economical, regenerative and stable than its commercial opponent CANSOLV. The efficiency of the absorber is proved to be applicable and economical in the industry. Due to relative simplicity of the process and possibility of producing the exclusive absorbent in large amounts and also the type of the equipments used in construction of the pilot, the construction of the pilot plant in industrial scale is accessible with low costs. It is illustrated that the results of this research are completely practicable in all industries that use combustion heaters. The kinetics of the performing process controlled by the novel amine based solvent AIT500 was analyzed for the first time and the order of the reaction was reported. In addition, optimal process parameters are achieved using optimization method applied in our previous achievements published earlier [16,17]. The effect of working parameters such as solvent flowrate, PH and temperature on the amine based solvent are described in long term runs proving the stability of the reactive absorber.

2. Experimental Details

2.1. Kinetics of the Absorption Process:

The process is based on a unique class of amine absorbents that optimally balance the ability to absorb and regenerate sulfur dioxide. The reactions in the process are as below:

$$\mathrm{SO_2} + \mathrm{H_2O} \leftrightarrow HSO_3^- + H^+ \qquad K_1 = forward\ ,\ K_2 = reverse \qquad (1)$$

$$NR1R2R3 + HSO_3^- + H^+ \leftrightarrow NR1R2R3H^+ + HSO_3^- \qquad K_3 = forward\ , K_4 = reverse \qquad (2)$$

The output of the combustion enters the packed absorption column from the lower part and the amine based absorber solution is injected to the column from the opposite side at top. The output of the column is then sent to desorption tower.

$$R_{SO_2} = K_1 C_{SO_2} - K_2 C_{H^+} \times C_{HSO_3{}^-} \qquad (3)$$

Since H^+ is produced in the first reaction (1) and consumed in the second one (2), it is not stable and is considered as the intermediate product.

$$R_{C_{H^+}} = K_1 C_{SO_2} - (K_2 C_{H^+} \times C_{HSO_3{}^-}) - (K_3 C_{NR123} \times C_{C_{H^+}} \times C_{HSO_3{}^-}) + (K_4 C_{NR123H^+} \times C_{HSO_3{}^-}) \qquad (4)$$

The last term of above correlation is disregarded due to existence of reviving column for absorber. The outlet of the absorption column enters the desorption tower in which the absorber is revived in several reactions. As a result, reaction B is led forward to transform amine to $NR1R2R3H^+$ .NR1R2R3 is then obtained via the reviving column.

From correlation (2) it can be obtained that:

$$C_{H^+} = \frac{K_1 C_{SO_2}}{K_2 \times C_{HSO3^-} + K_3 C_{NR123} \times C_{HSO3^-}} \qquad (5)$$

Substituting (3) in (1) correlation:

$$R_{SO_2} = K_1 C_{SO_2} - \frac{K_1 K_2 C_{SO_2}}{K_2 + K_3 C_{NR123}} \rightarrow R_{SO_2} = \frac{K_1 K_3 C_{SO_2} C_{NR123}}{K_2 + K_3 C_{NR123}} \qquad (6)$$

The aqueous amine solvent used in this process is very stable and highly selective for SO_2. Correlation 4 is analyzed as follow: Based on 'A' reaction, increase of SO_2 rate would cause increment of reaction rate (R_{so2}). Increase of inlet amine concentration leads the first reaction to the right and therefore raises SO_2 consumption rate. As illustrated in correlation 4, the term $C_{NR1R2R3}$ is in the numerator and denominator; however, the effect of multiplication in the numerator is much more noticeable. K_2 illustrates the reverse direction of (A) reaction and reduces SO_2 consumption rate as a result. Located in denominator, it displays the reverse relationships with SO_2 consumption.

The absorbent used in the process is a diamine; one of the amines remains and functions in the salt form permanently in order to prevent volatilization and loss of solvent to the cleaned gas, as well as avoiding contamination of the byproduct SO_2 with the solvent. The treated gas could be gained with high purity with a minimum energy consumed to regenerate the absorber if the process is performed in optimum conditions.

2.2. Filling the Test Cylinders

The experiments were carried out following the stages bellow:

The inlet gas is confined to a 5-kilogram cylinder that is filled with gas inlets from CO_2, SO_2, and N_2high-pressure cylinders. The cylinders are filled with pressure resisting hoses in a procedure described below: First, ensuring that the test cylinder is empty, it is connected to the SO_2 cylinder and put on a digital weighing machine; with a control knob, it regulates the amount of SO_2 entering the test cylinder. This SO_2 has the least amount in comparison with other gases of the mixture and needs to be measured first with reliable precision. To measure the amount of gases in cylinders, ideal gas law was used to obtain the amount of gas experimentally.

Considering: allowable pressure of cylinder=17.5 Bars, Volume of the cylinder= 10.5 liters, and molecular weight of SO_2= 64 gr/mol, it can be achieved that:

2.3. Analyzing the Inlet Gas

The analysis of the inlet gas was carried out using gas detector TESTO 350. While injecting the gas and steam, a proportion of %20 should be looked after. As a result, an amount of 7.5 liters per minute of gas from the test cylinder enters along with 1.5 liters per minute of steam.

These inlets are mixed in the collector and then sent to the absorption column. The mixture of gases and water steam pass through absorber solution in various flows. Eventually, the sweetened gas leaves the desorption tower through a flow meter.

2.4. Process Equipment's:

The designed pilot plant consists of two major parts: absorption and desorption columns. The absorption column has an internal diameter of 15.24 cm. It is filled with packings made of metal grids. Maximum flood would bring the column to up to 29.65.Absorption column is 1.5 meters in height. The pressure meter in the entrance of the column can measure quantities up to 0.6 Bars. Table 1 illustrates the specifications of the absorption column in detail.

Table 1: Specifications of absorption column in pilot plant

Section Diameter (m)	0.1524
Max Flooding (%)	29.56
X-Sectional Area (m2)	1.824e-002
Section Height (m)	2.286
Section Delta P (KPa)	4.675e-002
DP per Length (KPa/m)	2.502e-002
Flood Gas Velocity (m3/h-m2)	1.829e+004
Flood Gas Velocity (m/s)	5.080
HETP (m)	0.1524

The gas collector uses four gas injection inlets in order to blend the entering gases. Additionally, four high-pressure cylinders with specific amounts of SO_2, CO_2, and N_2 were provided. A 60-liter tank was placed in the right side of the desorption column. Three pumps of 0.75 KW power are placed in the plant to move the absorber solution. One of these pumps (103) is located below the tank to send the absorber solution to the absorption column. It also supplies the vaporized absorber in the stripping column through a valve and a connecting pipe. The steam outlet of desorption column is cooled via a condenser and sent back to the tank of absorber solution. The steam is controlled by a valve, which is placed above the condenser. In the lower part of the desorption tower, there is a sign that shows the fluid level in the column.

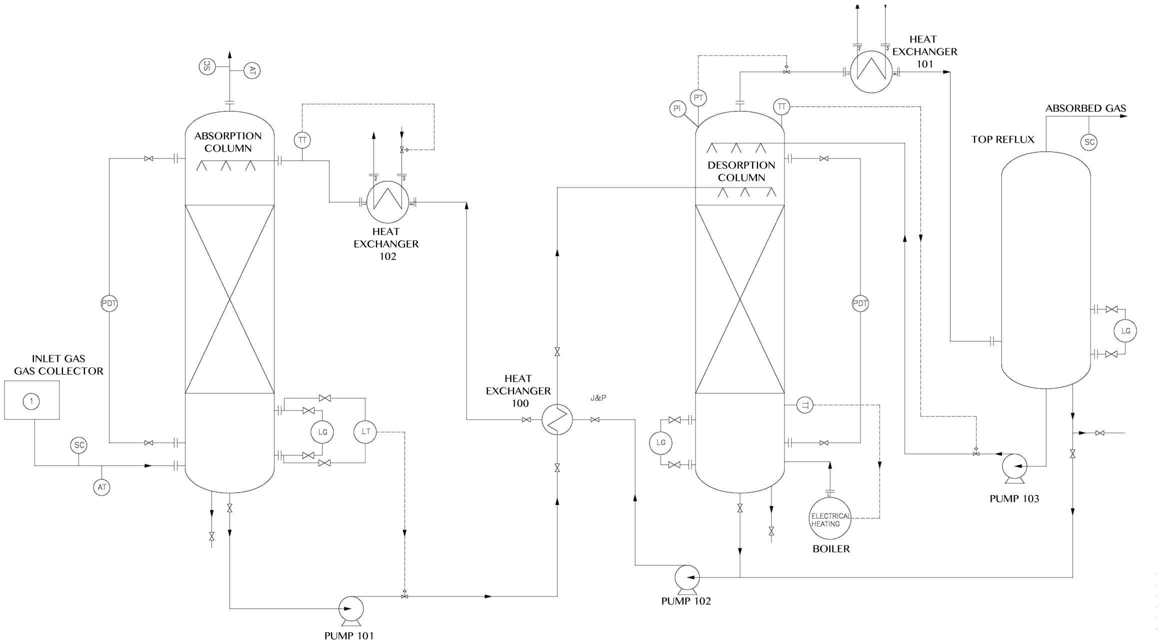

Figure 1: Schematic view of the pilot plant

Two elements of 2 KW power are placed in the desorption column to evaporate specific amounts of absorber solution while whirling. When the temperature rises in the desorption column to 120 ºC which is the operational temperature, the absorber solution is sucked from the lower portion of the column and is pumped into the absorption column. On its way, it passes a shell and tube heat exchanger (E-101) and the reciprocating absorber gets cooled to a temperature of about 60-65 ºC. If not cooled enough, the absorber passes a cooler controlled by a solenoid valve. The valve works using a signal of temperature controller. The amount of absorber flow in the inlet of the absorption column can be set from 100 to 400 milliliters per minute. After entrance of absorber and its distribution, the absorption column is filled with the fluid and the level of absorber solution is specified. It is then sent to the desorption column via a 0.75 Kilowatt pump. As mentioned earlier, the absorber flow is preheated in a shell and tube heat exchanger prior to entering the desorption tower.

The control board in the right side of the pilot contains three controllable temperature displays illustrating the temperatures of upper and lower parts of desorption column and the upper part of the absorption column. It also includes switches of pumps, solenoid valves and elements.

The four-liter-volume boiler, located in the center of the pilot, provides steam for entrance of inlet gases. As a result, a throttle valve is set between the boiler and the collector entrance to regulate the proportions of inlet steam. The temperature of the boiler is controlled with a thermo set in order to maintain its pressure. It is activated in high pressures where it would let out steam. A compressor that provides the necessary pressure behind valves is supported by solenoid valves.

3. Absorption process

The tests were done in an experimental plant in the laboratory of the research center. The plant is specially designed for the experiments and uses AIT500, an industrial amine based absorber, with an innovative formulation. In the plant, the absorption tower, with a diameter of 15cm and a height of 150cm was designed and the experiments were done using an absorber solution rate ranging from 400 to 500 ml/min.

The tests were done in 100, 200, 300, 400 ml/min levels. Examining the optimum point of absorption, the desorption temperature and pH were taken as variables; the first of which was analyzed in five levels of 105, 110, 115, 120, and 127°C, and the latter was observed in levels of 3, 4, and 6. Analysis of the output gas from the stack of catalytic cracking units of a typical refinery after passing through the designed plant illustrates that the gas contains %65 Nitrogen, %19 water steam, and %12 Carbon dioxide. The concentration of the consumed absorber was 0.85 gr/lit; noting its low concentration in proportion to the input SO_2 of the absorption tower, the efficiency is to the nearest 100 percent that is quite unique and desirable and more than what is expected from the cat-cracker unit. Consequently, the amount of SO_2 inlet to the absorption column was tested in three levels of 4800, 6800, and 8800 ppm. The results of the experiment demonstrate that the absorber -even with a low concentration- has strong absorption ability so that it can reduce the amount of 8800 ppm of SO_2 feed to 10 ppm in the outlet. Table 2 and 3 display the experimental data of final released SO_2 in comparison with the inlet concentration. Various tests were implemented choosing pH as the variable in order to find an appropriate experimental result in absorption of SO_2. As shown in the Table 1 and 2, the efficiency is more than 99% and 90% in flue gas purification processes respectively.

Table 2: Operational conditions of SO_2 absorption process.

No.	pH	SO_2 inlet concentration (ppm)	Solvent flow rate (Lit/min)	Desorption bottom Temperature (°C)	Gas flow rate (Lit/min)	Absorption tower Temperature (°C)	Absorption tower P (bar)	Desorption Top Temperature (°C)	Desorption Tower top P (bar)	Desorption Tower bottom P (bar)	Solvent concentration (gr/lit)	SO_2 outlet concentration (Ppm)
1	2	4870	100	110	8	53	0.01	100	0.35	0.4	0.85	7
2	2	4690	100	110	7	52	0.01	101	0.35	0.4	0.85	6
3	2	4700	100	110	9	52	0.01	100	0.35	0.4	0.85	6
4	2	6760	250	120	8	62	0.02	110	0.9	0.95	0.85	4
5	2	6400	250	120	8	64	0.02	109	0.9	0.95	0.85	3
6	2	6600	250	120	10	62	0.03	111	0.9	0.95	0.85	4
7	2	8670	400	126	7	72.5	0.03	114.5	1.2	1.25	0.85	7
8	2	8800	400	126	7	71	0.03	115	1.2	1.25	0.85	8
9	2	8750	400	126	8	72	0.3	114	1.2	1.25	0.85	8
10	4.1	4700	250	126	7.5	63	0.02	116	1.25	1.3	0.85	9
11	4.1	4500	250	126	8	65	0.02	117.5	1.25	1.3	0.85	10
12	4.1	4800	250	126	8	63	0.02	116	1.25	1.3	0.85	11
13	4.1	6700	400	110	7.5	69	0.03	98	0.35	0.4	0.85	0
14	4	6450	400	110	9	70	0.03	98	0.35	0.4	0.85	1
15	4	6600	400	110	8	71	0.03	100	0.35	0.4	0.85	0
16	4	8450	100	120	8	54	0.01	109	0.9	0.95	0.85	3
17	4	8250	100	120	7	53	0.01	110	0.9	0.95	0.85	2
18	4	8500	100	120	9	52	0.01	110	0.9	0.95	0.85	3
19	6	4300	400	120	6.5	61	0.03	114	0.95	1	0.85	1
20	6	4400	400	120	10	70	0.03	110	0.9	0.95	0.85	2
21	6	4500	400	120	9	71	0.03	110	0.9	0.95	0.85	3
22	6	6864	100	126	10	50	0.02	113	1.2	1.25	0.85	5
23	6	6500	100	126	6.5	51.2	0.02	115	1.2	1.25	0.85	2
24	6	6700	100	126	7	53	0.02	114	1.2	1.25	0.85	4
25	6	8830	250	110	6	63	0.02	98	0.35	0.4	0.85	11
26	6	8550	250	110	11	66	0.02	96	0.35	0.4	0.85	9
27	6	8600	250	110	10	64	0.02	100	0.35	0.4	0.85	10

Table 3: Operational conditions of large solvent flow rates

No.	pH	SO_2 inlet concentration (ppm)	L (ml/min)	G (m^3/hour)	Solvent flow rate (Lit/min)	Desorption bottom T (° C)	Absorption tower T (° C)	Absorption tower P (bar)	Desorption Top T (° C)	Desorption Tower top P (bar)	Desorption Tower bottom P (bar)	Solvent concentration (gr/lit))	SO_2 outlet concentration (Ppm))
1	6	4700	140	4.2	500	110	60	0.07	100	0.3	0.35	54.1	223
2	6	4000	140	4.2	500	110	59	0.07	105	0.3	0.35	54.1	370
3	5.87	6000	140	3.2	375	120	52	0.03	110	0.8	0.85	54.1	987
4	6	6000	140	3.2	375	120	60	0.03	110	0.75	0.8	54.1	780
5	6	8000	140	3.6	430	100	64	0.03	76	0.2	0.2	54.1	960

4. Effect of Process Parameters

4.1. Solvent Flow Rate Effects on Absorption

As a result of solvent flow rate increment SO_2 reduction is improved. This fact was tested at pH of 4 and a flow rate of 9lit/min and a temperature of 120 ºC. The results are demonstrated in Table 4. Assuming a constant pH, the increment of solvent flow rate was investigated in the experiments. Figure 2 displays the relation between flow rate and enhancement of SO_2 capturing.

Table 4: Increment of solvent flow rate in a constant pH

pH	Inlet SO_2 concentration (ppm)	Solvent flow rate (ml/min)	Gas flow rate (lit/min)	outlet SO_2 concentration (ppm)
4	6500	100	9	5
4	6500	200	9	3
4	6500	300	9	2
4	6300	400	9	1

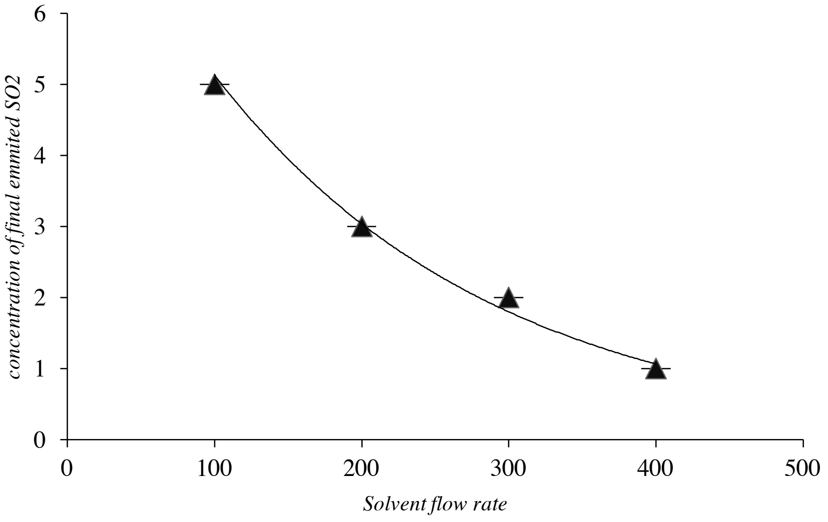

Figure 2: Solvent flow rate versus final concentration of released SO_2in a constant pH.

4.2. Effect of the SO_2 Concentration

As it can be seen from the Figure 3, desulfurization strongly depends on the concentration of SO_2 in the feed gas. By increasing the SO_2 concentration it's clear that the absorbent saturates more quickly and less SO_2 can be absorbed. As it is expected by increasing SO_2 concentration the absorbent is saturated sooner which cause the outlet concentration of SO_2 to increase quickly as shown in Figure 3.

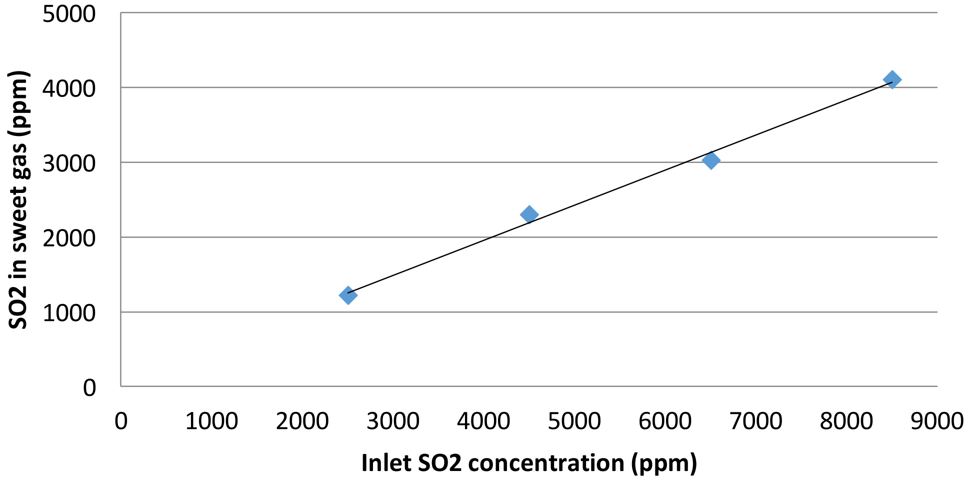

Figure 3: Absorption variation versus variation of SO_2 concentration, at 110 °C, gas flow rate of 2.5 m^3/hr and pH of 4.

4.3. Effects of the Flue Gas Flow Rate

To investigate the effect of flue gases flow rate three levels were investigated as shown in Figure 4 these three levels are 2.5 $(\frac{m^3}{hr})$, 3 $(\frac{m^3}{hr})$, and 3.5 $(\frac{m^3}{hr})$. It seems that at 2.5 $(\frac{m^3}{hr})$, the best performance is achieved. As can be seen from Figure 5 in the flue gas flow rate change scope, SO_2 absorption decreased when the flue gas flow rate increased. Increasing flue gas flow rate is equivalent to reducing the gas-liquid two phase residence time in the absorption column so the reaction rate of SO_2 absorption slowed down and it observed that with increasing flue gas flow rate, it carried spray absorbent out from the tower, led to the loss of absorbent. Therefore, when increased flue gas flow rate, the SO_2 absorption decreased.

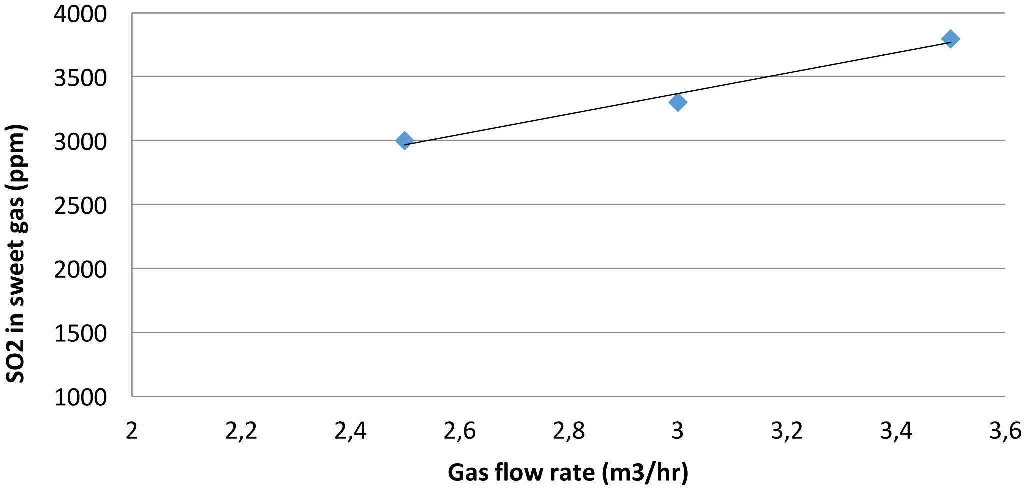

Figure 4: Absorption variation versus variation of gas flow rate in SO_2 concentration of 6500 ppm, at 110 °C and pH of 4.

4.4. Effects of the desorption temperature

Figure 5 shows the effect that temperature has on absorption. The results indicate that the desulfurization efficiency will increase when the temperature is increased from 100 °C to 110°C, and will decrease when the temperature is increased from 110°C to 120°C. Because by increasing the temperature to 110 °C better absorption capacity is reached by better absorbent stripping. also by increasing temperature to 120 °C absorption highly decrease By increasing the temperature from 100 °C to 120 °C the desorption pressure increase from 0.3 bar to 0.85 bar which don't permit the absorbent to desorb the dissolved SO_2. Thus the suitable temperature is specified as 110 °C.

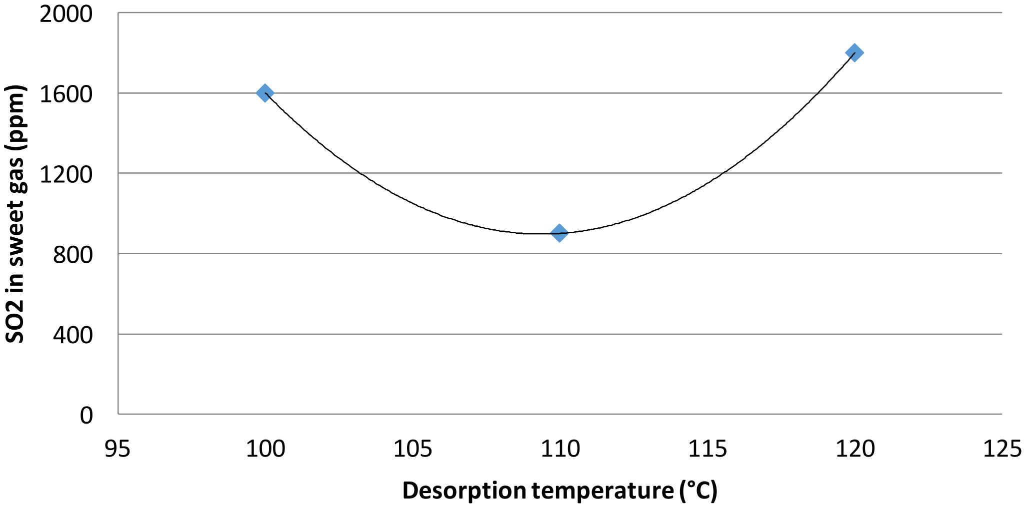

Figure 7: Absorption variation vs. temperature variation in SO_2 concentration of 6500 ppm, at gas flow rate of 2.5 m^3/hr and pH of 4.

5. Absorber Selectivity

The selective amine-based absorber used in this study chooses SO_2 contaminations and reduces it to an appropriate concentration. In about 10 experiments CO_2 and O_2 quantities of inlet, which are combined with SO_2 in the entire stream, were detected at the final gas that left the pilot. The data is shown in Table 5. Obviously, concentrations of the mentioned materials in outlet terminal were not changed. Differences are rare and restricted to one or two experiments, where a few changes are evident. Table 5 illustrates a comparison between inlet and outlet condition of flue gas compounds that determines constant value in CO_2 and O_2 quantities. As a result selectivity of absorber in the process is confirmed.

Table 5: Comparison of inlet and outlet flue gas mixtures

Inlet			**Outlet**		
SO_2	CO_2	O_2	SO_2	CO_2	O_2
4690	5.7	11.2	6	5.7	11.2
6760	5.3	11.7	4	5.3	11.7
8800	5.4	11.5	8	5.4	11.5
6700	5.3	11.6	0	5.3	11.6
6450	5.6	11.5	1	5.6	11.2
4300	3.6	13	2	7.6	13
6500	5.4	11.5	2	5.4	11.5
8600	5.5	11.3	10	5.5	11.3

A worth noting advantage to be mentioned in this process is high gas solubility of the solvent which results in the least absorber quantity requirement. The absorption rate is still so high even while a low rate of solvent is used. Owing to the fact that the solution is a salty one, the volatility and pressure of the solvent is low. In each absorption process, the outlet vapor from absorption column is saturated with solvent; the solvent waste is negligible as a result. Another specific feature of the solvent is having no corrosion on the packings and absorption column facilities that was evident in months of running the pilot plant.

The selectivity issue of our process of absorbing SO_2 nuisance gas is very delicate. To address this, one may refer to a possible competition of the absorption reaction of CO_2 gas in parallel with the reaction of the amine with SO2. As a matter of fact due to the acidic nature of CO_2 and SO_2 gases, both of them react with any basic solution such as amines, however, our amine agent may prefer to react with SO_2 at the governing operating conditions. In other words, a unique combination of solution concentration, PH, temperature and amine types in our process displays a tendency towards the absorption of SO_2 rather than any other gas in the system including CO_2. Hence the qualitative kinetics of the proposed reaction mechanism in this process is majorly based on the fact that SO_2 absorption reaction rate is much greater than that of CO_2.

6. Kinetic study

Initial rate of reaction was used throughout this study to evaluate effect of operational parameters such as temperature and initial concentration of SO_2,as well as to determine the reaction kinetic. For this purpose, a simulated flue gas containing CO_2, N_2, O_2 and SO_2 was led into the column with a flow rate of 2.5 ($\frac{m^3}{hr}$). The process was terminated when the temperature had stabilized at the desired level. The reaction rate is given by:

$$-r = \frac{\dot{m}_{in} - \dot{m}_{out}}{V} \qquad (7)$$

where $\dot{m}$ is the molar flow rate ($\frac{mol}{hr}$), r is the reaction rate ($\frac{mol}{m^3.hr}$) and V is the reactor volume (m^3) [15].

In water solution, dissolved SO_2 undergoes reversible hydration and ionization to produce bisulphite and sulphite according to the following equations. Diffusion of carbon dioxide from the gas phase into the aqueous phase:

$SO_{2(g)} \leftrightarrow SO_{2(aq)}$ (8)

$SO_{2(aq)} + H_2O_{(L)} \leftrightarrow H_2SO_{3(L)}$ (9)

$H_2SO_{3(L)} \leftrightarrow HSO_3^- + H^+ \leftrightarrow SO_2 + 2H^+$ (10)

Adding amine, to the water increases the quantity of SO_2 dissolved[18]. According to equation (8-10), the buffer drives the above equilibrium to the right by reacting with the hydrogen ions to form ammonium salts. The overall reaction indicates that as the concentration of SO_2 in the feed gas increases, the equilibrium moves to the right, i.e. the quantity of SO_2 dissolved in the rich solvent increases. Thus, the scrubbing of more concentrated gas streams requires a less than proportional increase in solvent circulation rate. Since the gas volume, and therefore the gas side equipment, remains constant, a relatively small total cost increase is caused by an increase in feed SO_2 concentration.

$NR_1R_2R_3NR_4R_5 + H^+ \longleftrightarrow NR_1R_2R_3NR_4R_5H^+$ (11)

The SO_2-amine-H_2O is a reactive system [15-19]. The chemistry of the system is very complex. The system gives rise to a large number of possible chemical reactions and formed species. Finally, after simplifying, the reaction rate for this mechanism is

$$r = k\,[SO_2]^n \qquad (12)$$

or

$$\text{Ln r} = \text{Ln K} + \text{n Ln}\,[SO_2]$$

The operational conditions used for kinetic experiments in this study are summarized in Table 6.

Table 1: Kinetic experimental setup.

Parameter	Range
SO_2 concentration in feed gas (ppm)	2500-8500
Temperature (K)	313-333
Gas flow rate ($\frac{m^3}{hr}$)	2.5
PH of absorbent	4

Results for concentration of SO_2 in sweet gas are shown in Table 7 when the PH of absorbant and gas flow rate are held constant.

Table 2: Outlet concentration of SO_2 in various inlet concentration of SO_2 and constant PH and gas flow rate.

Temperature (K)	Outlet concentration of SO_2 (ppm)			
	2500ppm SO_2	4500ppm SO_2	6500ppm SO_2	8500ppm SO_2
313	1220	2300	3023	4100
323	960	1500	2035	3500
333	930	1400	1950	3100

Molar flow rate is extracted from ideal gas law (PV=nRT) and then initial rate of reaction is calculated according to equation 5. 5. as given in Table 8.

Table 3: Initial rate of reaction in various inlet concentration of SO_2 and constant PH and gas flow rate.

Temperature (K)	Initial rate of reaction ($\frac{mol}{m^3.hr}$)			
	2500ppm SO_2	4500ppm SO_2	6500ppm SO_2	8500ppm SO_2
313	4.34	7.46	11.79	14.92
323	5.38	10.48	15.6	17.47
333	5.66	11.18	16.41	19.48

As shown by figure 8, 9 and 10, a first-order reaction with respect to the SO_2 concentration was obtained.

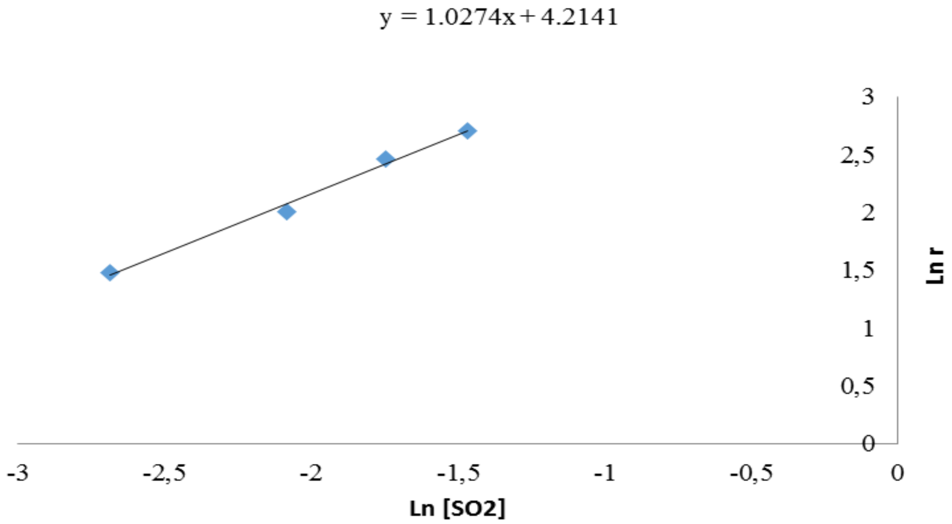

Figure 8: Ln r vs. Ln [SO_2] at 40 °C, gas flow rate of 2.5 m^3/hr and pH of 4.

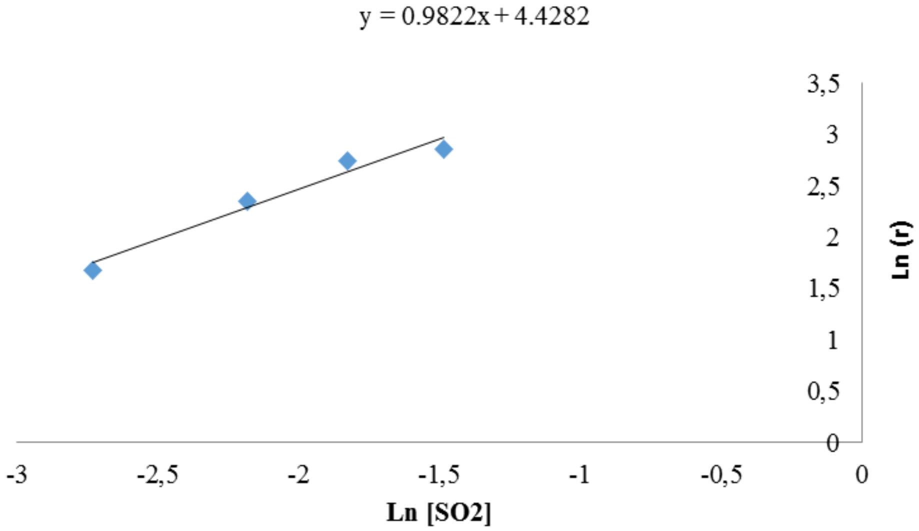

Figure 9: Ln r vs. Ln [SO_2] at 50 °C, gas flow rate of 2.5 m^3/hr and PH of 4.

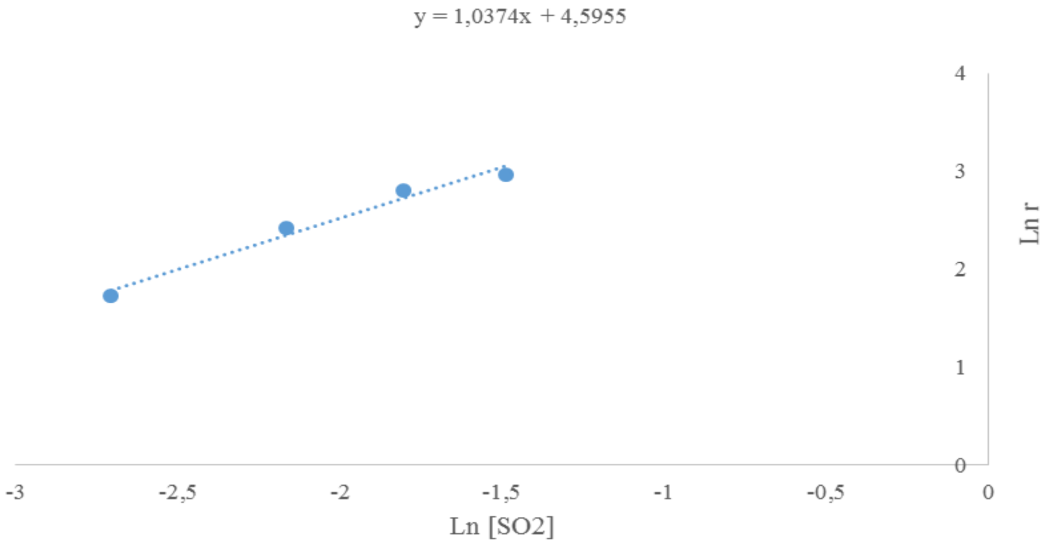

Figure 10: Ln r vs. Ln [SO_2] at 50 °C, gas flow rate of 2.5 m^3/hr and PH of 4.

In general, temperature is an important parameter influencing reaction kinetics. For SO_2 absorption kinetics, the reaction rate constant normally is based on the Arrhenius expression:

$$Ln\ K = -\frac{Ea}{RT} + Ln\ K0 \qquad (13)$$

Where K is chemical reaction rate, K_0 pre-exponential constant and E_a = activation energy (J/mol).

Parameters of the kinetic model such as k_0 and E_a is extracted by taking the best-fit straight line between ln K and 1/T. Values estimated for activation energy and pre-exponential constant are respectively 17.32 KJ and 5.1×10^4. From the figure 7, an Arrhenius expression is defined as follows

$$K = 5.1 \times 10^4 \exp\left(\frac{-2084}{T}\right) \qquad (14)$$

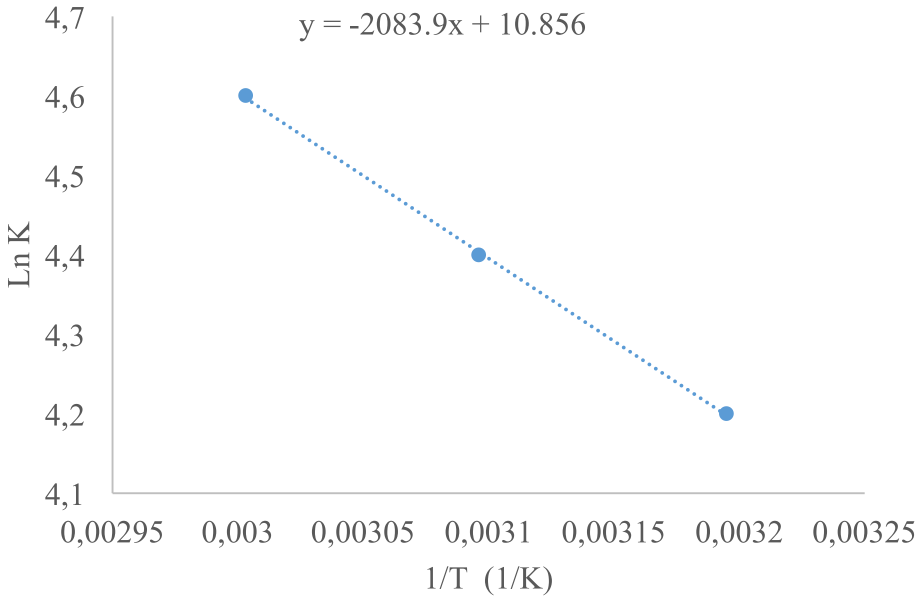

Figure 11: Relationship between Ln K and 1/T

Conclusion

In this study, the experimental conditions to increase the absorption efficiency for absorbing SO_2 using an amine-based absorber to above 90% were studied. Investigations were done to obtain the optimal conditions of the process that yield the least SO_2 concentration in the outlet stream of the pilot. To achieve this purpose four parameters including, absorption temperature, desorption temperature, liquid ratio and inlet SO_2 concentration were also evaluated.

The consumed absorber is long lasting and can be revived entirely at a temperature of 120°C. Setup of the pilot plant was quite cheap and economical in industry. Besides, the process is economical due to low costs of providing the absorber. Also by adding H_2SO_4 to the absorber solution the pH can be regulated without resulting noticeable changes in efficiency. No precipitation was made from the absorber during the whole absorption process and consequently the pilot was not damaged corroded. Analysis of the outlet gas from the pilot plant illustrates that it contains %65 Nitrogen, % 19 water steams and %12 Carbon Dioxide while the concentration of consumed absorber was 0.78 gr/lit. Noting its low concentration in proportion to the input SO_2 of the absorption tower, the efficiency is to the nearest 100 percent that is quite unique and desirable and more than what is expected from the stack of a typical catalytic cracking unit. In this paper, the amount of SO_2 inlet to the absorption column was tested in three level of 4800, 6800 and 8800 ppm. In addition, the first-order rate constant for the reaction between the absorbent and SO_2 was determined. Under the experimental conditions, the SO_2 reaction rate increases when the SO_2 concentration increases from $2500\,ppm$ to $8500\,ppm$ and the temperature increases from 40 °C to 60 °C. The results of the experiment demonstrate the absorber- even with a low concentration- has strong absorption ability so that it can reduce the amount of 8800 ppm of SO_2 feed to nearly 10 ppm in the outlet.

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