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Original Research Article

Pilot Study for Selective Hydrogen Sulfide Removal by a Jet Reactor

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Strict protocols regulate the level of hydrogen sulfide in the gas industry. Hydrogen sulfide poses serious problems during the transportation and usage of natural gas; hence its removal is of utmost importance. The works presented in this article describe the competitive alkali chemisorption of hydrogen sulfide and carbon dioxide in a jet reactor. A modeling gas mixture was used for the experiments consisting of hydrogen sulfide, carbon dioxide and nitrogen. The most important parameters during the measurements were the gas flow rate (1-2.5Nm^3/h), residence time (< 1 s and < 0.1 s), the volume flow rate of the absorbent sodium hydroxide (1-2-4-6-8cm^3/min) and its concentration (0.5-1.5-2.5m/m%). The results show that an increase in the gas flow – and hence a decrease in the residence time – results in a significant improvement in efficiency with the 0.5 m/m% alkaline solution.

Keywords: Hydrogen sulfide, Carbon dioxide, Sodium hydroxide, Competitive chemisorption, Gas purification, Jet reactor.

INTRODUCTION

Acid gases are gases which contain a significant amount of hydrogen sulfide. Hydrogen sulfide is capable of causing a number of problems in the gas industry since it produces a corrosive medium in the presence of water. This corrosive medium damages the transport pipes resulting in extra expenditures. On the other hand, hydrogen sulfide gets oxidized into sulfur dioxide, a dangerous pollutant responsible for acid rain. Besides, hydrogen sulfide is harmful for the human organism, causing headaches, fatigue and in higher concentrations death [1-5].

The removal of hydrogen sulfide is referred to as sour gas sweetening. A number of methods have been proposed for sweetening including adsorption, chemisorption, and physisorption methods, direct conversion into elemental sulfur, membrane techniques and biological solutions [4, 6-8].

The goal of this research is to provide a selective gas sweetening procedure with alkali chemisorption. Absorbents that can be used for alkali absorption are e.g. sodium hydroxide, potassium hydroxide, potassium permanganate and sodium hypochlorite [6].

Selective gas purification can be achieved with competitive chemisorption due to the kinetics of the process. Hydrogen sulfide gets absorbed in a sodium hydroxide solution by orders of magnitude faster than carbon dioxide. Because of this, one of the key parameters during the process is the residence time. A short residence time is required (< 1s) in order to achieve a good selectivity. To achieve the proper cleaning efficiency one needs to provide a high reaction surface area, intensive mixing and quick phase separation, which cannot be done with a classic packed absorber. However, these can easily be carried out with a vaporization technique (jet reactor) [1, 4, 9]. Many have experimented with vaporization techniques during alkali gas purification [1, 4, 10-11].

It is important to know that the competitive alkali chemisorption process is highly pH-dependent. The following three reactions are dominant above pH = 13:

$H_2S + OH^- = HS^- + H_2O$ *(1)*
$CO_2 + OH^- = HCO_3^-$ *(2)*
$HCO_3^- + OH^- = CO_3^{2-} + H_2O$ *(3)*

The following two reactions become significant if the pH is around 12:

$H_2S + CO_3^{2-} = HS^- + HCO_3^-$ *(4)*
$CO_2 + H_2O + CO_3^{2-} = 2\ HCO_3^-$ *(5)*

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Besides, the following two reactions are responsible for the H^+ transfer:

$H_2O = H^+ + OH^-$ (6)
$CO_3^{2-} + H^+ = HS^- + HCO_3^-$ (7)

Reactions *(2)* and *(5)* are undesirable because the carbon dioxide molecules use up too much of the absorbent. Reactions *(1)* and *(4)* are advantageous for the selective absorption of hydrogen sulfide. Equilibrium and rate characterization of these reactions has shown that reaction *(4)* has a significantly higher rate than reaction *(5)*. Optimization of the residence time around pH = 12 provides the possibility of the selective absorption of hydrogen sulfide. [10, 12-15].

It can also be mentioned that absorption into concentrated alkaline solutions is a slower process in comparison to more dilute sodium hydroxide solutions [3].

The only disadvantage of the method is that the used absorbent cannot be regenerated [3, 5]. However, the compounds formed during the process (sodium hydrogen sulfide, sodium sulfide, sodium carbonate and sodium hydrogen carbonate) are stable and not dangerous [9].

EXPERIMENTAL PROCEDURES

Chemicals and experimental conditions

The modeling gas mixture used in the experiments consisted of 90 ppm hydrogen sulfide, 23 *V*/*V*% carbon dioxide, the rest was nitrogen. The absorbents were 0.5-1.5-2.5 m/m% aqueous sodium hydroxide solutions which were introduced into the reactor at volume rates of 1-2-4-6-8 cm^3/min. The pressure inside the equipment was 30 bar, the ambient temperature 22 °C. Gas was introduced at rates of 1 and 2.5 Nm^3/h (resulting in residence times between 0.1 and 1 s; and below 0.1 s).

Experimental machinery

The experimental device is composed as follows. The gas mixture is introduced into the jet reactor from a gas cylinder with a regulator. A pump provides the appropriate volume flow of the absorbent. Both the gas and the liquid enter the reaction space (approximately 2×10^{-6} m^3 in volume) through the same nozzle at the same time. The quick separation of the liquid phase after the intensive mixing is achieved with a drop catcher. The used absorbent is collected in a separate vessel. The purified gas flow leaving the reactor is split into two: part of it is analyzed by a Dräger X-am7000 gas analysis device, the rest is bled. (The exact scheme of the device can be found in Ref 1).

Gas analysis

The Dräger X-am 7000 analyzer is fitted with an electrochemical diffusion sensor (DrägerSensor®H_2S HC – 68 09 710), which is capable of measuring the hydrogen sulfide concentration between 0 and 1000 ppm with a maximal deviation of 3%. Additionally, the device is also fitted with an infrared sensor (DrägerSensor®Smart IR CO_2HC –68 10 599) for the detection of carbon dioxide between 0 and 100%, the error is less than 3%.

The composition of the incoming gas was measured at the beginning and checked at the end of the experiments. However, the exiting concentrations were only registered after setting the parameters and getting a stable value for at least 1 minute.

OBJECTIVES

The objective of this research was to find the most effective, most selective and most economical solution for the hydrogen sulfide removal of a given gas mixture. Based on economic calculations, the concrete objective is to reach an efficiency of at least 50% by using a maximum of 10 mol NaOH / mol H_2S alkali excess.

RESULTS AND DISCUSSION

Fig.1 illustrates the efficiency of the hydrogen sulfide absorption as a function of the alkali inlet, for two different gas flow rates. The concentrations of the entering and exiting carbon dioxide were almost the same with a maximum deviation of 1%.

Based on Fig. 1 it can be stated that the efficiency can only be raised in a limited way by increasing inlet of the sodium hydroxide absorbent. For a given gas flow rate and alkali volume inlet the best efficiency can be reached with the most concentrated (2.5 *m*/*m*%) NaOH solutions, while the worst efficiency can be reached with the least concentrated (0.5 *m*/*m*%) NaOH solutions.

The results agree with the previous expectations, since by increasing the alkali rate for a given gas flow rate, the amount of inlet sodium hydroxide increases; also for a given alkali volume and concentration the amount of hydrogen sulfide with respect to the amount of sodium hydroxide increases by increasing the gas flow.

That the efficiency can only be minimally increased with the alkali inlet can be explained on the grounds that the outcome of the process does not solely depend on the amount of sodium hydroxide per time unit, but also on the quality of vaporization, mixing and time required for dissolution (which in turn depends on the concentration), on the gas flow rate (i.e. residence time). (This can be seen in Fig. 2.)

Fig. 2 illustrates the efficiency of hydrogen sulfide absorption as a function of the alkali excess. By increasing the gas flow rate for a given concentration of solvents, the efficiency of the absorption of hydrogen sulfide increases. Absorbents with a lower concentration are more efficient for a given gas flow as regards hydrogen sulfide removal if the alkali excess was measured.

The results can be explained on the grounds that by increasing the gas flow rate, the residence time decreases. Thus the carbon dioxide molecules are less readily dissolved by the NaOH solution, which makes the absorption more selective. Additionally, it is easier to diffuse into the less concentrated solutions, making once again the residence time the key of the problem.

However only at around pH = 12 can selective absorption be reached by optimizing the residence time. As for the pH values of the absorbent solutions, the pH of the 0.5 *m*/*m*% NaOH solution is approximately 12, whereas they are above 13 for the 1.5 and 2.5*m*/*m*% NaOH solutions. The efficiency of the 0.5 *m*/*m*% over the 1.5 and 2.5*m*/*m*%NaOH solutions can be explained on the grounds of the combined effect of the residence time, pH and dissolution time.

CONCLUSION

According to the data gathered, we can state that the best results were achieved with the most concentrated (2.5 *m*/*m*%) NaOH solution for a given gas and absorbent flow rate. Increasing the liquid flow rate while using a constant gas flow rate provides only an initial improvement.

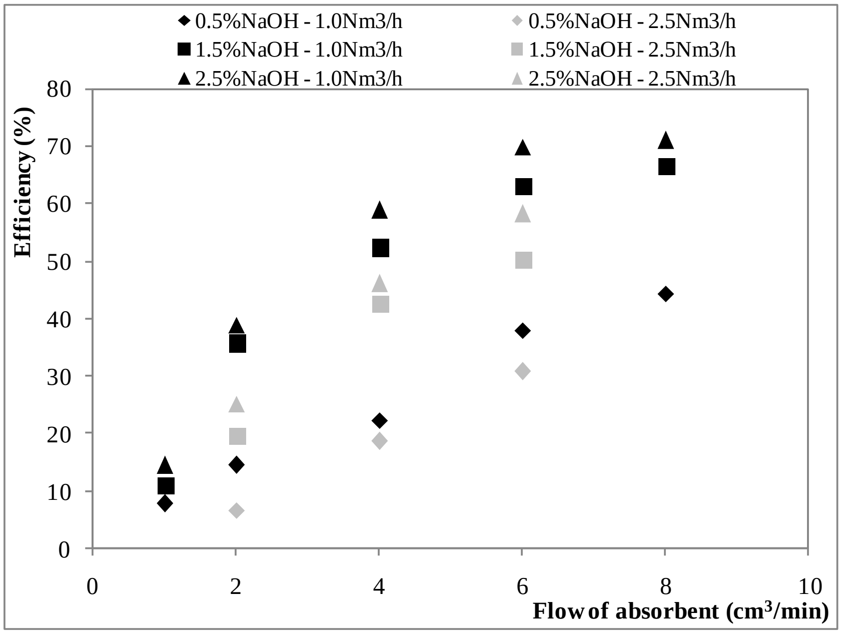

Fig.1. Examination of a modeling gas mixture consisting of 90 ppm H_2S and 23 *V*/*V*% CO_2 as the function of the absorbent inlet

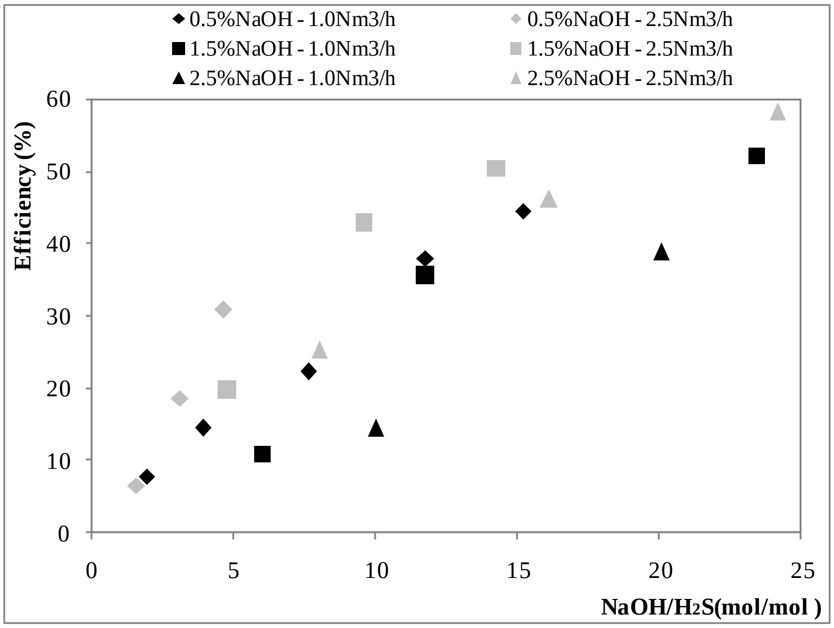

Fig.2. Examination of the H_2S absorption of a modeling gas mixture consisting of 90 ppm H_2S and 23 *V*/*V*% CO_2 as the function of the alkali excess

The efficiency vs. liquid inlet plots are approaching a maximum value (asymptotic plots). By plotting the efficiency against the alkali excess we could see that the least concentrated absorbent (0.5 *m*/*m*%) was the most effective for a given gas flow, which can be explained by both the time requirement of the dissolution and the effect of the pH. Another observation is that by increasing the gas flow rate (thus decreasing the residence time) the hydrogen sulfide absorption can be carried out more effectively and selectively when using the same absorbent concentration and alkali excess.

The concrete objective was to reach a minimum efficiency of 50% by using a maximum alkali excess of 10 mol NaOH / mol H_2S. The closest result to this was 43% with an alkali concentration of 1.5 *m*/*m*%, 4 cm^3/min liquid and 2.5 Nm^3/h gas flow rate. In order to reach the goal, the optimal alkali concentration between 0.5 and 1.5 *m*/*m*% has to be determined. Also, the gas flow has to be increased so as to decrease the residence time.

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