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SELECTIVE HYDROGEN SULPHIDE REMOVAL FROM ACID GAS BY ALKALI CHEMISORPTION IN A JET REACTOR

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Natural gas is a primary energy source that contains a number of light paraffins. It also contains several undesirable components, such as water, ammonia, hydrogen sulphide, etc. In our study, a selective hydrogen sulphide removal process was achieved by alkali chemisorption in a custom-designed jet reactor. Several model gas compositions (CO_2-H_2S-N_2) were evaluated to find parameters that enable H_2S absorption instead of CO_2. The negative effect of the presence of CO_2 in the raw gas on the efficiency of H_2S removal was observed. The beneficial effect of the low residence time (less than 1 s) on the efficiency of H_2S removal was recognized. Optimal operational parameters were defined to reach at least a 50% efficiency of H_2S removal and minimal alkali consumption.

Keywords: acid gas, H_2S selective removal, CO_2, competition with H_2S, chemisorption

1. Introduction

Natural gas is one of our primary energy sources, which contains mainly methane. However, it us comprised of several undesirable components like carbon dioxide (CO_2), hydrogen sulphide (H_2S), ammonia (NH_3), water (H_2O), etc. [1]. *Table 1* shows a typical composition of natural gas [2]; however, the content significantly depends on locality. In most cases, natural gas contains H_2S in various quantities between 10 to 20,000 ppm [1]. The gases with a measurable amount of H_2S are called sour gases. The acid gases are defined as gases containing some acidic component such as CO_2 or H_2S [3].

The H_2S containing hydrocarbon gases causes problems during the delivery, processing, and storage. H_2S is converted into SO_2 during combustion, which poses a health hazard and causes acid rain, smog. In the presence of water, acid components cause corrosion in pipelines and containers. Consequently, H_2S removal from natural gas is absolutely necessary [3].

There are several methods for reducing the H_2S content of natural gas. Membrane techniques also exist, but the adsorption and absorption processes are the most widespread. In the adsorption process, the fixed bed construction is the most common. The adsorber is usually filled with metal ions (iron, copper, zinc, cobalt, etc.) and an impregnated solid host (zeolite, activated-carbon, etc.). The disadvantage of this technique is the huge energy demand of adsorber regeneration. In the absorption process, one of the main points is the high pH value of the medium due to H_2S dissociation. There are numerous solvents for absorbing H_2S, namely alcanol-amines (MEA, DEA, DIPA, TEA, MDEA, etc.), alkali-hydroxides (KOH, NaOH), water, and ammonia. The alcanol-amines and the alkali-hydroxides are the most efficient. The alcanol-amines are widely used in H_2S removal, but their selectivity can be problematic and foaming appears during the process [4]. The use of alkali-hydroxides seems to be the most efficient process. By choosing the correct parameters, such as residence time, pH, solvent concentration, and intake, the procedure can be H_2S selective. In an alkali-hydroxide medium competitive chemisorption takes place between CO_2 and H_2S. Although CO_2 is a stronger acid than H_2S, it is a slower adsorber, thus H_2S absorption can be achieved over a short residence time. Intensive phase connection and fast phase separation afterwards are essential steps to facilitate a H_2S selective process [2]. The spray technique is a widespread method for the intensification of the reaction between the reactants. The pneumatic nozzles act as two-phase sprayers, because the gas at high speed breaks up the liquid into little droplets [5].

Table 1. A typical composition of natural gas [2].

component	concentration (%, m^3/m^3)
methane (CH_4)	97
nitrogen (N_2)	0.936
ethane (C_2H_6)	0.919
carbon dioxide (CO_2)	0.527
propane (C_3H_8)	0.363
butane (C_4H_{10})	0.162
oxygen (O_2)	0-0.800
noble gases (Ar, He, Ne)	trace
other (e.g. H_2S)	0-0.001

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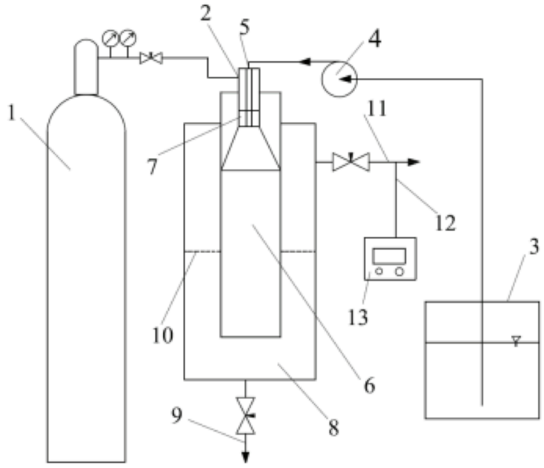

Figure 1. Experimental device equipped with a 1. gas cylinder, 2. gas inlet, 3. alkali vessel, 4. chemical feeder pump, 5. alkali inlet, 6. reactor space, 7. nozzle, 8. separation space, 9. wastewater removal, 10. drop catcher, 11. outlet of purified gas, 12. gas sampling, and 13. gas analyzer.

2. Experimental

The aim of our research is selective hydrogen sulphide removal from model gases that also contain CO_2. Our goal is to achieve the highest H_2S removal efficiency with the lowest alkali specificity as defined by the ratio of NaOH and H_2S expressed in moles. To find the parameters that support H_2S removal several experiments were carried out in a custom-designed jet reactor *(Fig.1)*. Owing to the construction of the reactor, the gas pressure, gas flow, alkali inlet flow, and alkali concentration were variable. All experiments were carried out at 30 bar total pressure. The absorbent was an aqueous NaOH solution of different concentrations, such as 0.5, 1.5, and 2.5% (g/g).

The model gas mixtures *(Table 2)* were produced in an acid-proof gas mixing bridge. For the first set of samples the H_2S content of the model gas mixtures was kept approximately constant; thus, the effect of CO_2 could be studied. For the last three samples, the CO_2 content was kept approximately constant; thus, the sensitivity of the process with regards to the variation of H_2S concentration could be investigated.

3. Results and Analysis

First, the effect of NaOH concentration, NaOH inlet flow, gas flow (residence time), and CO_2 concentration were investigated on the efficiency of H_2S removal.

3.1. Effect of Residence Time

To observe the effect of residence time on the efficiency of H_2S removal, the gas flow rate as a single parameter was varied. By increasing the gas flow rate, the residence time decreased. The gas flow rates were 3.9, 3.2, 2.4, and 1.6 N m^3 h^{-1}, which correspond to residence time rates of 0.05, 0.06, 0.09, and 0.13 s, respectively. *Fig.2* shows the effect of decreasing residence time. At a constant specific alkali value, the efficiency of H_2S removal increased as a result of a decrease in residence time. Furthermore, *Fig.2* also shows that the alkali specificity values decreased by raising the gas flow rate under a constant efficiency of H_2S removal.

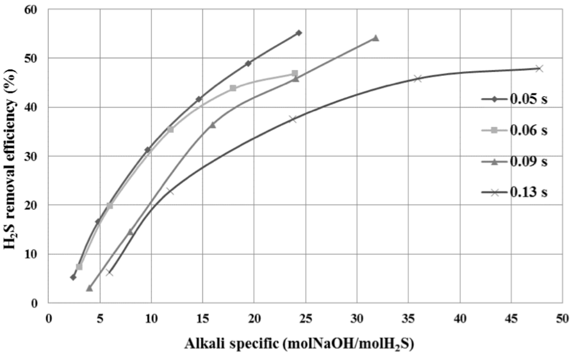

Figure 2. Effect of different residence times on the efficiency of H_2S removal (gas mixture 4, 30 bar, 2.5% (g/g) NaOH).

Table 2. Composition of the tested model gas mixture samples.

samples	CO_2 % (m^3/m^3)	H_2S ppmv	N_2 % (m^3/m^3)
1	0	100	99.999
2	23	90	76.999
3	41	80	58.999
4	60	80	39.999
5	76	85	23.999
6	72	520	27.999

3.2. Effect of NaOH Concentration

The value of alkali specificity depends on the H_2S content of the raw gas, the concentration and the flow rate of the absorbent. By increasing the concentration and the flow rate of the absorbent, the efficiency of H_2S removal is increased. However, the efficiency could not be improved after a point by the absorbent concentration or flow rate, because the efficiency reached a nearly constant value while the alkali specificity continued to increase *(Fig.3)*.

3.3. Effect of CO_2 Concentration

Model gases of different CO_2 concentrations were used to study the effect of CO_2 concentration on the efficiency of H_2S removal. The difference in H_2S concentrations of model gases is a result of non-exact gas mixing, but this does not affect the comparability of the results. *Fig.4* shows that the efficiency of H_2S removal is decreased by increasing CO_2 content. The competition between H_2S and CO_2 in alkali absorbents is documented.

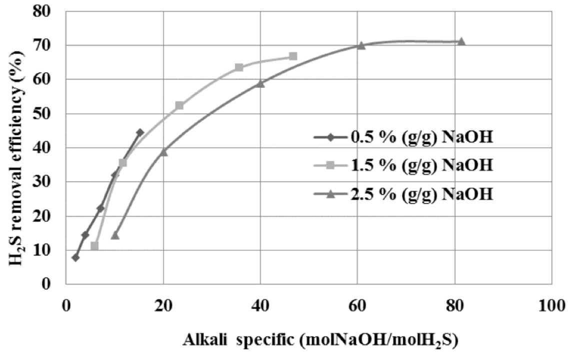

Figure 3. Effect of different NaOH concentrations on the efficiency of H_2S removal (gas mixture 2, 30 bar, 0.2 s residence time).

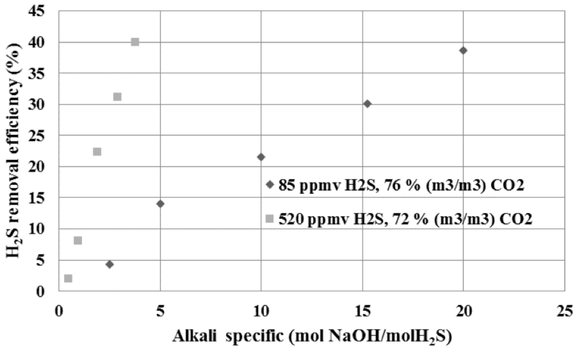

Figure 5. Effect of different H_2S concentrations on the efficiency of H_2S removal (gas mixtures 5-6, 30 bar, 0.09 s residence time, 1.5% (g/g) NaOH).

3.4. Effect of H_2S Concentration

The influence of H_2S concentration on the efficiency of H_2S removal was investigated under a nearly constant CO_2 level (76 and 72% (m^3/m^3)) and greatly differing H_2S (85 and 520 ppmv) containing model gases. When the 85 ppmv H_2S containing gas was compared to the 520 ppmv H_2S sample, the alkali specificity value measured was five times less *(Fig.5)*. On the other hand, *Fig.5* shows that the efficiency of H_2S removal does not depend on the H_2S concentration in this process. The alkali hydroxide absorbent technique shows little sensitivity to the changes in the H_2S content of the inlet gas.

3.5. Optimization of Operational Parameters

Based on the above-mentioned results, our aim was to find the optimal operational parameters for model gases of any composition in order to achieve an H_2S removal efficiency of at least 50%, while applying the minimal amount of alkali specificity. This efficiency of H_2S removal can be achieved by increasing the NaOH concentration. A low alkali specificity value can be achieved by adopting a low residence time.

As shown in *Table 3*, when the CO_2 content is below 50% (m^3/m^3), 1.5% (g/g) NaOH absorbent is enough to achieve an H_2S removal efficiency of 50% in the given type of reactor at a pressure of 30 bar. A gas flow rate of 2.5 Nm^3 h^{-1} with a 0.08 s residence time is needed.

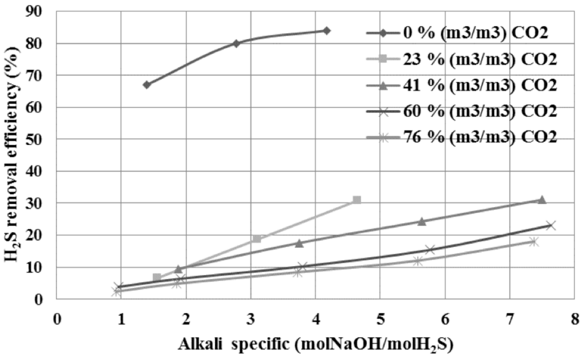

Figure 4. Effect of different CO_2 concentrations on the efficiency of H_2S removal (gas mixtures 0-5, 30 bar, 0.08 s residence time, 0.5% g/g NaOH).

When the CO_2 content is above 50% (m^3/m^3), 2.5% (g/g) NaOH is necessary to achieve a removal efficiency of 50%. The applied gas flow rate needs to be 3.8 Nm^3 h^{-1} corresponding to 0.05 s residence time in the given type of reactor at a pressure of 30 bar.

4. Discussion

In this study, model gases with different H_2S-CO_2-N_2 contents were investigated in a custom-designed jet reactor. Our aim was to achieve a H_2S removal efficiency of at least 50% with minimal alkali consumption.

The effect of the NaOH, CO_2, and H_2S concentrations, and the residence time on the efficiency of H_2S removal was studied. During our experiments CO_2 absorption was not investigated because the Dräger X-am 7000 analyser we used is only able to measure the CO_2 concentration in percent magnitude.

A positive effect of low residence time on H_2S removal was observed. By increasing the gas flow rate, the efficiency of H_2S removal was increased under constant alkali specificity. If the efficiency of H_2S removal is constant, the alkali specificity can be reduced by decreasing the residence time.

By increasing the NaOH concentration and flow rate, the efficiency of H_2S removal was improved until a point after which it nearly remained constant while the alkali specificity was still rising.

To study the effect of different CO_2 concentrations on the efficiency of H_2S removal, several CO_2 concentrations were investigated under nearly the same H_2S levels. The removal efficiency was reduced radically by increasing the CO_2 concentration.

When comparing the model gases that contain different H_2S concentrations, a reduction in the alkali specificity was observed. The alkali specificity value decreased as the H_2S content increased. The removal efficiency remained constant irrespective of the H_2S concentration of the model gases, which improves the efficiency of the alkali absorption process in terms of selective removal of H_2S.

Table 3. The best operational parameters of the tested model gases at a pressure of 30 bar.

CO_2 content, % (m^3/m^3)	NaOH concentration, % (g/g)	alkali specificity, mol NaOH (mol H_2S)$^{-1}$	H_2S removal efficiency, %	Residence time, s	Gas flow rate, $Nm^3\ h^{-1}$
23	0.5	15	44	0.20	1.0
	1.5	14	51	0.08	2.5
	2.5	19	51	0.10	2.0
41	0.5	12	44	0.20	1.0
	1.5	15	50	0.08	2.5
	2.5	20	50	0.10	2.0
60	0.5	6	27	0.06	3.0
	1.5	24	41	0.09	2.3
	2.5	24	55	0.05	3.8
76	0.5	6	20	0.07	3.0
	1.5	16	47	0.05	3.8
	2.5	22	56	0.05	3.8

We observed that when the CO_2 concentration was less than 50% (m^3/m^3), a 1.5% (g/g) NaOH concentration and 0.08 s residence time is necessary to achieve an H_2S removal efficiency of 50% at a pressure of 30 bar under the given experimental conditions. When the CO_2 concentration was above 50% (m^3/m^3), we found that this is sufficient to provide a NaOH concentration of 2.5% (g/g) over a residence time of 0.05 s at a pressure of 30 bar. Based on our experiments a high efficiency of H_2S selective removal can be achieved by NaOH absorption.

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