



Study on selective hydrogen sulfide removal over carbon dioxide by catalytic oxidative absorption method with chelated iron as the catalyst



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ABSTRACT

H₂S is a detrimental impurity that must be removed for upgrading biogas to biomethane. H₂S removal selectivity over CO₂ employing catalytic oxidative absorption method and its influence factors were studied in this work. The desulfurization experiments were performed in a laboratory apparatus using EDTA-Fe as the catalyst and metered mixture of 60% (v/v) CH₄, 33% (v/v) CO₂ and 2000–3000 ppmv H₂S balanced by N₂ as the simulated biogas. It was found that for a given catalytic oxidative desulfurization system, it exists a critical pH, at which desulfurization selectivity achieves the highest. It was also observed that desulfurization selectivity increased along with the increase of chelated iron concentration, gas flow rate, and ratio of gas flow rate to liquid flow rate (G/L). This demonstrated that high selectivity and high efficiency for biogas desulfurization could both be achieved through optimizing these parameters. Specific to the desulfurization system of this work, when the gas flow rate was set as 1.1 L/min, after optimizing the above mentioned parameters, i.e. EDTA-Fe concentration of 0.084 mol/L, absorption solution pH of 7.8, and G/L of 55, the desulfurization selectivity factor reached 142.1 with H₂S removal efficiency attained 96.7%.

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1. Introduction

Biogas, a renewable energy source, is a competitive energy alternative in both its energy efficiency and environmental impact. It can be used for heat and electricity production as well as be upgraded to biomethane for flexible utilization [1]. In order to transform biogas into biomethane, a cleaning process to remove the harmful components is needed [2]. Among the trace harmful impurities in biogas, H₂S is extremely troublesome because it causes corrosion in piping, compressors, gas storage tanks and engines. Moreover, H₂S converts to more corrosive sulfur dioxide (SO₂) and sulfuric acid (H₂SO₄) upon combustion, which causes

severe damage in combustion equipment. Therefore H₂S removal is generally the preceding procedure of biogas purification.

Various techniques are developed for H₂S removal from biogas, including liquid absorption [3–6], solid adsorption [7–11], biological degradation [12–15], membrane separation [16], and so on. Absorption of H₂S in liquids is a kind of widely used desulfurization method for biogas, in which H₂S is chemically absorbed by different liquids such as NaOH, FeCl₃, and Fe(OH)₃ solution according to different reaction mechanisms [17,18]. Compared with other liquid absorption methods, catalytic oxidative absorption of H₂S using a chelated iron solution has distinctive advantages. It transforms H₂S into the desirable product of elemental sulfur directly, which could be recovered to bring considerable economic benefits. Also, the reaction rate is quite fast. Therefore, this desulfurization method is a prior choice in many biogas utilization projects.

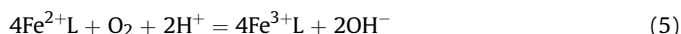
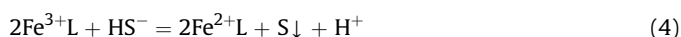
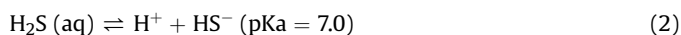
The mechanism of catalytic oxidative absorption desulfurization is described as Eqs. (1)–(5) [6]. During the process, H₂S is dissolved in an aqueous scrubbing solution which contains ferric chelate

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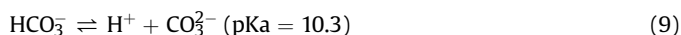
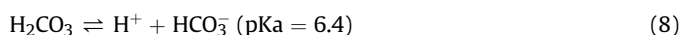
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(Fe^{3+}L) (Eq. (1)), followed by two dissociation reactions (Eqs. (2) and (3)). HS^- produced in Eq. (2) is oxidized by Fe^{3+}L in the solution to produce elemental sulfur (Eq. (4)). After separating the oxidation product of elemental sulfur, Fe^{3+}L is regenerated through the re-oxidation of ferrous chelate (Fe^{2+}L) by air in the regenerator, and then it is used for oxidizing HS^- again. The regeneration reaction is described as Eq. (5). Fe^{3+}L is the oxidizer in the desulfurization process. As it is regenerated during the circulations, it could also be considered as a catalyst of the process. In order to maintain a high H_2S absorption rate, an alkaline solution is generally used for the scrubbing to neutralize the produced hydrogen ions (H^+) in Eq. (2) and make the reactions (1) and (2) shift to the right.



(where L represents chelant such as EDTA.)

In the circulation of catalytic oxidative desulfurization, H^+ produced in Eq. (4) is balanced by OH^- produced in the regeneration reaction (Eq. (5)). Therefore, no additional alkali is needed to maintain pH of the scrubbing solution theoretically. However, biogas contains CO_2 with concentration much higher than that of H_2S , and it is also dissolved in the desulfurization solution. The dissolved CO_2 would be hydrolyzed and dissociated in the solution. Consequently additional H^+ would be produced (Eqs. (8) and (9)), which results in gradual decrease of pH in the desulfurization solution. The corresponding reactions of CO_2 absorption is illustrated in Eqs. (6)–(9) [6]. As above mentioned, high pH of the scrubbing solution is desired for maintaining a high H_2S absorption rate, while the concurrent high concentration of CO_2 in biogas would cause decreasing of pH. In order to maintain a high desulfurization rate, additional alkali should be supplemented frequently, which leads to additional operational costs.



In order to reduce the operational costs, it is of significant importance to minimize the absorption of CO_2 under the premise of ensuring the desulfurization efficiency, which can decrease the consumption of alkali. The process to increase the absorption ratio of H_2S to CO_2 as high as possible without much loss of desulfurization efficiency at the same time could be named as selective desulfurization. Desulfurization selectivity is defined as the absorption ratio of H_2S to CO_2 . Selective absorption of H_2S over CO_2 using amine solutions such as monoethanolamine, *N*-methyl-diethanolamine or more complex mixtures has been deeply studied by several researchers [19–23]. In recent years, the selective H_2S absorption using different alkaline (other than amines) scrubbing systems has also been studied [6,14,24]. To our knowledge, the selectivity for biogas desulfurization using catalytic oxidative absorption method with chelated iron as the catalyst has not been reported. As it is a widely adopted method in many biogas

utilization projects, it is necessary to understand the factors that influence H_2S removal selectivity over CO_2 . The objective of this work was to determine the desulfurization selectivity of the catalytic oxidative absorption method for biogas desulfurization. The experiments were performed on a laboratory scale set-up which consists of a gas scrubbing column and an air regenerator, and EDTA-Fe was selected as the desulfurization catalyst. Removal efficiencies for both H_2S and CO_2 were tested under different experiment conditions. The selectivity factor which represents H_2S removal selectivity in each case was calculated. Effects of the solution pH, chelated iron concentration and ratio of gas flow rate to liquid flow rate (G/L) on the desulfurization selectivity were discussed.

2. Material and methods

2.1. Experimental apparatus

The desulfurization experimental apparatus is shown in Fig. 1. A simulated biogas containing 60% (v/v) CH_4 , 33% (v/v) CO_2 , and 2000–3000 ppmv H_2S was prepared in the mixer with N_2 as the balance gas before entering the scrubbing column. Concentrations of the gas components were respectively adjusted by the mass flow controllers at outlet of the gas cylinders. The internal diameter and height of the scrubbing column were 70 mm and 280 mm, respectively. Pall rings in size of $16 \times 16 \times 1$ mm (external diameter \times height \times thickness) were packed in the column to generate a packing bed. The height of the packing bed was 200 mm. The desulfurization solution was regenerated in the regenerator equipped with an air blower.

2.2. Experimental procedure

EDTA-Fe(III) solution was used as the desulfurization solution in this work. It was prepared via mixing equimole of EDTA-2Na and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous solution through heating. The prepared desulfurization solution was verified containing no free ferric ions through potassium thiocyanate (KSCN) solution. pH of the desulfurization solution was adjusted by adding proper amount of sodium carbonate (Na_2CO_3) solution based on the indicating values of a pH meter. Three EDTA-Fe(III) solutions with concentrations of 0.084, 0.042, 0.021 mol/L were respectively used in the experiments.

The experiments were carried out at ambient pressure and temperature. The absorption and oxidation of H_2S occurred in the scrubbing column, while the solution that scrubbed H_2S and CO_2 was regenerated in the regenerator. In the scrubbing column, the absorption solution was sprayed from the top, while the simulated biogas entered from the bottom and flowed upward. H_2S and CO_2 were absorbed in the solution and the former was oxidized by EDTA-Fe(III) in the absorption solution, producing some elemental sulfur (Eq. (4)). After sedimentation of the elemental sulfur in the scrubbing column, the solution was fed into the regenerator, while the gas effluent was led into a sodium hydroxide (NaOH) solution and then discharged. In the regenerator, air was bubbled into the solution to regenerate the desulfurization solution (Eq. (5)), and if needed, proper amount of Na_2CO_3 solution was added to adjust pH of the solution to the desired value. The regenerated desulfurization solution was then recycled into the scrubbing column for absorption again.

Flow rates of the simulated biogas and absorption solution were respectively controlled in the range of 1.0–1.5 L/min and 10–60 mL/min during the experiments. Concentrations of H_2S and CO_2 in the fed and effluent gas were measured respectively by a H_2S detector (PN2000- H_2S , Shenzhen Yiyuntian electronics technology Co. Ltd., China) and a CO_2 detector (PN1000- CO_2 , Shenzhen Yiyuntian electronics technology Co. Ltd., China). pH of the solution was

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