Novel Methods for Sour Gas Treatment

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1. Introduction

Sour natural gas is currently treated to remove CO_2 and H_2S and the concentrated H_2S stream is sent to a Claus process to convert the H_2S to elemental sulfur. However, the per-pass H_2S conversion is only 93-96%, resulting in some "slip" of the H_2S from the catalytic reaction stage of the process [1]. This stream contains small quantities of H_2S which must be further treated. An efficient solution to this environmental separation problem would be to continuously remove and concentrate the H_2S from the tail gas, and then recycle this concentrated H_2S stream back to the Claus process. While this research project is tailored for process gas streams that contain small amounts of H_2S, the developments will also apply to streams containing high concentrations of this component.

Carbon molecular sieves

Activated carbon materials are commonly used industrially to remove H_2S from gas streams via fixed bed adsorption and high adsorption selectivities of H_2S over N_2 and H_2 have been demonstrated [2,3,4]. However, it would be more efficient if the small amount of H_2S could be removed using a continuous process such as a membrane separator, rather than a cyclic process such as adsorption. Microporous carbon membranes often exhibit *"reverse selectivity*," where more strongly adsorbed penetrants permeate faster than less strongly adsorbed species [5]. However, the strength of binding of the H_2S to the CMS membrane is likely to be too strong, resulting in pore blocking and very low surface diffusivities of the adsorbed H_2S. Consequently, in order to prepare a CMS membrane capable of removing dilute H_2S from gas streams, strategies to reduce the strength of H_2S binding with the carbon surface will be explored, including operating the membrane at elevated temperatures, surface modification of the carbon to make the carbon surface hydrophobic [7] and/or to remove surface oxygen groups such as carboxylic or phosphonic acids [3].

Solid adsorbents

Claus-process tail gas at 200°C consists of N_2, H_2O, and CO_2 and minor amounts of H_2S and SO_2 in equilibrium with gaseous S_8. Solid adsorbents remove sulfur-bearing species through either physical adsorption or chemisorption. Physical adsorption would be affected with a porous solid such as a molecular sieve or activated carbon. Prior to adsorption, the gas stream would be cooled using the Cold-Bed Adsorption Process to condense elemental sulfur. This step prevents condensed sulfur from blocking adsorbent pores in the physical adsorption process. Both SO_2 and H_2S would then be removed with the solid adsorbent to attain desired residual sulfur levels. Adsorbed sulfur compounds would be desorbed thermally yielding hydrogen sulfide and sulfur dioxide, and probably some gaseous sulfur, at concentrations suitable for conventional Claus processing.

Chemisorption has the potential to yield lower residual sulfur concentrations than physical adsorption. One especially promising technique involves SO_2 oxidation with O_2 to yield adsorbed SO_3. This process occurs readily under modest conditions on selected types of activated carbon. The SO_3 is bound very strongly to the activated carbon surface which insures effective sulfur removal. This process has been examined for sulfuric acid manufacture but has not been tested as a sulfur removal technique. We would examine this process for SO_2 and H_2S removal in the proposed research program. We further propose regenerating the activated carbon by SO_3 reduction with gaseous sulfur (S_2 or S_8), H_2S, CO or similar reducing gases. Gases from desorption would be recycled to the Claus furnace for sulfur recovery.

The purpose of the present research is to identify a suitable adsorbent system for H_2S and SO_2 in Claus process tail gas. In a proposed research extension, we would obtain data to thoroughly define the processing conditions and understand the underlying science for adsorption and desorption. Finally we would examine the proposed technique in pilot-scale and plant-scale testing.

2. Key Features

Key features of the poster will be preliminary results of the theoretical adsorbent screening activities, with equilibrium conversions shown. For reasons of confidentiality, all results will be shown in terms of relative activities, and the exact compounds screened will not be specifically identified on the poster.

3. Conclusions

Conclusions to date include theoretical screening of a number of potential solid adsorbents for chemisorption of sulfur. Thermodynamic calculations concerning equilibrium conversion of the sulfur/adsorbent reaction has allowed a suite of materials to be identified which all have promise to achieve high activity and selectivity for sulfur removal from the Claus tail-gas. Results of these calculations will be presented.

4. References and Bibliography

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