HYDROGEN SULFIDE REMOVAL FROM INDUSTRIAL GASES USING ADVANCED, MODIFIED CLAUS TECHNOLOGY

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Abstract

A number of commercial processes are available for removing hydrogen sulfide (H_2S) from natural gas, tail gas from the Claus Process (containing un-reactive sulfur compounds, particularly CS_2 and COS), coke-oven gas, pyrolysis gas and solution tail gas from heavy oil production. These processes are often limited by economics and technology.

In the economic range from about 0.1 to 15 tons sulfur per day, a new process effects the Claus Reaction in a single (pressure) vessel, not unlike the conventional amine acid gas absorption tower. Sulfur is removed by cooling a slipstream, in the form of large crystals, where carbon dioxide is not absorbed, and water formed is carried out in the clean gas. This paper technically discusses this new, patented, sulfur purification process that offers clear advantages over current, conventional technologies.

Introduction

Research and development work on technologies for removing hydrogen sulfide (H_2S) from industrial gases began at the University of Toronto under the direction of Dr. James Smith almost 40 years ago. In 1988, a proprietary gas-liquid contacting system in which H_2S is absorbed in a solution, which is then regenerated by air. The elemental sulfur formed during the regeneration process is separated by flotation and filtered to produce a high sulfur cake. The process was successfully commercialized on a digester gas in the Virginia Beach, Virginia (USA) wastewater treatment plant. Subsequently, the technology was used in Australia on digester gas from biological material separated from garbage. The gas–liquid contacting technology has also been applied to stripping H_2S from liquid sulfur in plants in Alberta, Canada.

During the 1990s, interest in using biogas declined due to very low natural gas prices and failure to appreciate the environmental benefits of using renewable energy for energy production, economically reducing CO_2 emissions to combat global warming. Recognizing the complete reversal of this situation, the technology has been recognized as the latest in innovative technology[1] and successfully marketed for a range of applications including:

[1] Eco-Tec has been awarded the Canadian Innovation Award for Biogas Purification Technology, 2007.

- Digester biogas from corn-ethanol production
- Digester biogas from food processing plants
- Landfill biogas
- Removing H_2S from sweep air managing emission from a liquid sulfur handling facility

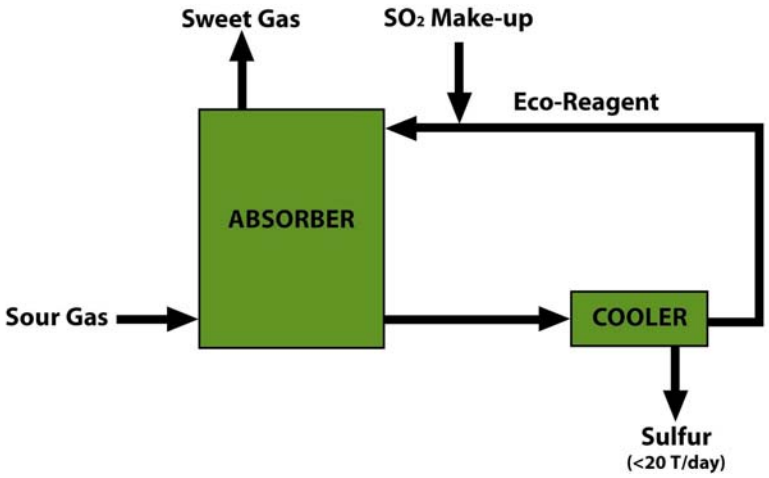
Managing High Sulfur Loading and Gas Flow Rates

The biogas purification process becomes economically prohibitive at high sulfur loadings and gas flow rates. Moreover, it presents challenges when applied at high gas temperatures and pressures. Consequently, the research team at the University began to look for alternative processes to address these challenges. In 1996, the team developed the hypothesis that certain organic reagents could catalyze the reaction between sulfur dioxide and H_2S in liquid sulfur, and development work began on finding candidate materials. Suitable reagent mixture were found in 1997, and evaluated on a bench-scale, demonstrating outstanding control of SO_2, H_2S, carbonyl sulfide (COS), and carbon disulfide (CS_2) according to the Claus reaction:

$$\mathbf{SO_2 + 2H_2S \rightarrow 3S + 2H_2O}$$

The removal of carbonyl sulfide (COS) and carbon disulfide (CS_2) to elemental sulfur and carbon dioxide ($C0_2$) is effected by hydrolysis with water and reaction of the H_2S produced with SO_2. The bench-scale and subsequent pilot scale development projects demonstrated outstanding performance.

A number of commercial processes are available for removing H_2S from natural gas (normally at very high pressure), tail gas from the Claus Process (containing un-reactive sulfur compounds, particularly CS_2 and COS), coke-oven gas, pyrolysis gas, synthesis gas and solution tail gas from heavy oil production containing toxic and/or high molecular weight contaminants. These processes are often limited by economics and technology. The scale of most of these projects limit the economical use of solid-state adsorption, aqueous processes are limited by fouling problems and toxicity to biological regeneration systems, and conventional Claus plants by high capital costs, which becomes uneconomical at sulfur production rates less than about 15 tons/day. The new sour gas purification process is applicable and economical in the niche market for the above gas sources at up to 20 tons/day.



The Figure shows a simplified process flow diagram for the process. The process affects the Claus Reaction at moderate temperature in a single (pressure) vessel, not unlike the conventional amine acid gas absorption tower. A slipstream portion of the sulfur-bearing reagent is cooled in a in a crystallizer, producing elemental sulfur in the form of large crystals. Carbon dioxide is not absorbed, and water formed is carried out in the clean gas. In the economic range from about 0.1 to 20 tons Sulfur per day, the process has clear advantages:

- Capital cost is significantly lower than that of a conventional Claus plant
- Operating costs are low, involving the production of sulfur dioxide in a burner using sulfur produced in the process, and the addition (at low H_2S concentrations) and removal of heat
- The process is able to convert carbonyl sulfide and carbon disulphide to elemental sulfur and innocuous by products (carbon dioxide) by hydrolysis with water
- The reaction medium is insensitive to deactivation by high MW hydrocarbons and nitrogen compounds.
- The elemental sulfur produced is crystalline, bright yellow, and easily washed and filtered.

In summary, the new, advanced sour gas purification process fills the need for a robust and effective technology for removing reduced sulfur compounds from natural and industrial complex gases. Using this process, the complex Claus process, for the recovery and conversion of hydrogen sulfide to elemental sulfur, can be achieved in a single adsorption and reaction vessel at significantly lower capital and operating costs.