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Economic assessment of Temperature Swing Adsorption systems as Claus Tail Gas Clean Up Units

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HIGHLIGHTS

- Claus Tail Gas Treatment Units (TGTU) are used to meet sulfur recovery regulations.
- We assess the economics of a Temperature Swing Adsorption (TSA) unit as a TGTU.
- The proposed TSA incur 60% lower capital investment compared to a commercial TGTU.
- The estimated operating cost is $3.0–$3.6 per tonne of sulfur.
- Operating cost compares favorably with the operating costs of a commercial TGTU.

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ABSTRACT

Current regulations of SO_x emissions require Sulfur Recovery Units (SRUs) to achieve recoveries in excess of 99.9%. Capital cost of existing commercial Claus Tail gas clean up technologies capable of achieving that benchmark can amount to 45% of the total capital cost of the SRU. Adsorption based processes hold significant potential for achieving the targeted recovery at lower costs considering their high selectivity towards removal of ppm level contaminants. This work assesses the economics of a Tail Gas Treatment Unit relying on a Temperature Swing Adsorption module for treating a typical industrial feed. An optimization problem is formulated and solved to determine the designs that minimize Net Present Worth (NPWC) of total capital investment,operating and bed replacement costs ensued during a 30 years project life. The total capital investment contribution of the optimized TGTU is around $20 M comprising ~65% of the NPWC value. Operating costs ranged between $3.0 and $3.6 per tonne of sulfur. Both figures compare favorably with commercial technologies.

1. Introduction

The growth of world gas demand coupled with dwindling reserves of sweet easy-to-access gas have forced many nations to tap into natural gas reservoirs rich in acid gases (H_2S and CO_2) (Philip and Weems, 2009). Direct combustion of raw reservoir effluents causes the release of significant quantities of SO_x species, a major cause of acid rain, material corrosion and respiratory health problems (Hasenberg and Bender, 2008; Larssen et al., 2006). Thus, removal of acid gases from raw natural gas is necessitated by environmental considerations and sales gas specifications. This is conventionally achieved via selective capture through membrane, solvent or adsorption based technologies, followed by sulfur recovery (Kohl and Nielsen, 1997). The conventional method of sulfur recovery is the Claus process, which can achieve a Sulfur Conversion (SC) up to 98%. In 2001, the European Union commission established the legislative limits of SO_x emissions for gaseous fuels at 35 mg/Nm^3 (European-Parliament, 2001). When reflected at Sulfur Recovery Units (SRUs), this policy enforced recoveries in excess of 99.9% (Koscielnuk et al., 2001). This recovery is commercially attained via addition of a Tail Gas Treatment Unit (TGTU), which supplements the conventional Claus process (Kohl and Nielsen, 1997).

TGTU technologies capable of achieving the targeted sulfur conversions can be classified in regenerative solvent based technologies, non-regenerative solvent based technologies and adsorption based technologies (Eow, 2002; Kohl and Nielsen, 1997). Regenerative based

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technologies rely on the use of a selective solvent capable of preferential absorption of sulfur species from the Claus tail-gas stream. The Lo-Cat II™ process, licensed by Merichem©, utilizes iron chelated complex in solution, which dissolves and oxidizes the H_2S directly to sulfur. The precipitation of the sulfur during the reaction shifts the equilibrium favorably to higher conversions. During that process, the iron in the active ingredient is reduced from the +3 state to the +2 state. Regeneration of the iron complex is performed via oxidation with air. (Kohl and Nielsen, 1997). In the SCOT™ and the Clintox™ processes, licensed by Shell© and Linde© respectively, the solvent is regenerated at higher temperatures to release a concentrated stream of sulfur contaminants. The stream is then recycled back to the entrance of the SRU. Non-regenerative based processes rely on the selective capture of sulfur species from Claus tail gas into an inexpensive aqueous solvent, which chemically binds to the contaminants, thus forming sulfur based metallic salts dissolved into an aqueous solution. The solution is subsequently discarded. An example commercial realization of non-regenerative based processes is the DynaWave™ technology licensed by MERCS© (Koscielnuk et al., 2001).

Economic studies on commercially implemented TGTU technologies are limited. The Gas Technology Institute published a report, which studied the operating and capital costs of 14 TGTU options including SCOT, Clintox, and Lo-CAT II for low capacity SRUs (< 100 long ton/day) (Strickland et al., 2000). Among the TGTU technologies that achieve 99.9% recovery, the operating and capital costs contribution of the TGTU to total SRU amounts to 50% approximately for an SRU processing 76 long tons/day. Another study assessed the capital and operating cost implications of the SCOT and the Dynawave technologies for a 140 metric tons/day plant (Koscielnuk et al., 2001). The capital cost contribution of both technologies to total SRU was found to range from 29% to 45% dedicated only for increasing the SC from 98% (Conventional Claus) to 99.9% (Koscielnuk et al., 2001). Furthermore, both technologies add an additional ~20$ per ton of processed sulfur to the operating cost of the SRU (Koscielnuk et al., 2001). These studies show that implementing the mentioned TGTU technologies in order to increase SC by 1.9% (from 98% to 99.9%) is 25–50 times more expensive on a cost per percent recovery basis. Clearly, this is an opportunity for alternative technologies.

Adsorption based processes are known to be better suited for the removal of low concentration contaminants (Mccabe and Harriot, 2001). Two process technologies relying on adsorption capable of achieving the SC target are described in the open literature (Buchanan et al., 1996; John and Buchanan, 2000; Kohl and Nielsen, 1997). The Extremely Low Sulfur Emission (ELSE) process developed by AMOCO relies on the use of ZnO for the selective capture of H_2S from the tail gas at temperatures in excess of 650 °C (Kohl and Nielsen, 1997). Subsequent regeneration of the sorbent is done via oxidation using a diluted stream of air. In the Mobil Off-gas Sulfur Treatment process (MOST) sulfur species are first oxidized to SO_2. Then, SO_2 is adsorbed on a proprietary sorbent ($V–Ce–Mg_2Al_2O_5$) at temperatures in excess of 700 °C (Buchanan et al., 1996). Regeneration is achieved via a reducing gas (e.g. H_2). In both processes, the regeneration gas effluent is recycled back to the Claus unit. To our knowledge, none of the aforementioned processes achieved commercial status yet, probably due to the high operating temperatures (requiring prohibitively expensive materials of construction) and limited regenerability. The challenge in developing a successful adsorption based process lies in the development of a regenerable sorbent capable of selective removal of sulfur species among a swarm of competing contaminants (for instance, H_2O, CO_2, CO, and H_2) at temperatures sufficiently low to allow for the use of carbon steel.

Several novel materials have been investigated for low temperature removal of H_2S in the past decade. Multi-walled carbon nanotubes grafted with amine functions were found to achieve H_2S adsorption saturation capacities in the range of 1.6–1.8 mmol g^{-1} at 20 °C and atmospheric pressure (Mohamadalizadeh et al., 2011). Crespo et al. studied copper exchanged faujusite (Cu(I)–Y) prepared via a vapor phase exchange method and compared it to solution exchanged (Cu(II)–Y) (Crespo et al., 2008). At room temperature, Cu(I)–Y adsorbent exhibited higher stable saturation capacities in the order of 7 mmol g^{-1}. Kumar et al. studied several metal exchanged faujasite structures including Ag, Cu, Ni, and Na obtaining saturation capacities in the following order AgY > CuX > NiX⋙NaX (Kumar et al., 2011b). At 100 °C the highest capacities attained for CuX and AgY were 1.2 and 2.1 mmol g^{-1} respectively. Higher capacities were reported for mixed metal oxides in coal gas desulfurization ranging between 2 and 8 mmol g^{-1} within a temperature range of 200–600 °C (Karayilan et al., 2005; Polychronopoulou et al., 2005a, 2005b; Yasyerli et al., 2001). For H_2S removal from Claus Tail gas, Elyassi and co-workers reported an SBA-15 supported Copper–Zinc mixed oxide sorbent with a stable regenerable capacity of ~2 mmol g^{-1} at 150 °C (Elyassi et al., 2014) While mixed metal oxides exhibit the highest capacities among all H_2S sorbents, their high prices limit their application. Among the sorbents studied in the literature, copper exchanged zeolite Y prepared via the vapor phase exchange method combines the benefits of good adsorption properties and low price (Crespo et al., 2008; Kumar et al., 2011a).

This work assesses the economics of a Tail Gas Treatment Unit (TGTU) incorporating a TSA module designed based upon the reported and the experimentally determined adsorption properties of a Copper exchanged zeolite Y sorbent (Cu(I)–Y) targeting the achievement of 99.9% recovery. Net Present Worth of Costs (NPWC) is chosen as the probing economic parameter. An optimization problem is formulated and subsequently solved using a dual step approach. Finally, the optimized solution results are analyzed and compared with the reported cost figures of the SCOT process.

2. TSA unit location, integration, and model

2.1. Approach, assumptions and TSA unit integration

We pursue the design of an optimized TGTU system for the purpose of removal of ppm level contaminants from a Claus tail gas. The process flow diagram of the proposed system is depicted in Fig. 1. Claus tail gas feed is firstly heated in a fired gas heater to 240 °C, the required temperature for hydrogenation of all sulfur species. Subsequently, the effluent gas is introduced to a typical hydrogenation reactor. The hydrogenation step targets the complete transformation of all sulfur species to H_2S in addition to significant destruction of carbon monoxide via the water gas shift reaction. The effluent of the reactor is introduced to a water-based cooler in order to reduce the temperature to 150 °C. The water cooler effluent is introduced to the vessel(s) undergoing adsorption. Once the contaminants' breakthrough point is reached, the Claus tail gas flow is switched to the stand-by vessels. During regeneration, a slipstream of the Claus unit air feed is re-routed using a centrifugal blower to a fired gas heater where it is heated to a temperature above the experimentally determined regeneration temperature. The hot air stream is routed to the beds undergoing regeneration for heating and regenerating the bed to fresh conditions. Finally, the air stream effluent of the centrifugal blower is introduced to the vessels undergoing regeneration for cooling purposes. Fig. 2 depicts the unit integration within the SRU for typical feed conditions.

2.2. TSA model development

The Net Present Worth Cost (NPWC) is chosen as the economic criterion. It is comprised of three cost elements: the total capital