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Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment

Task 2.3: Sulfur Primer

Nexant Inc.
San Francisco, California

Subcontract Report
NREL/SR-510-39946
May 2006

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NREL Technical Monitor: Kelly Ibsen
Prepared under Subcontract No. ACO-5-44027

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Methodology

This deliverable is Subtask 2.3 of Task 2, Gas Cleanup Design and Cost Estimates, as part of NREL Award ACO-5-44027, “Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup and Oxygen Separation Equipment”. Subtask 2.3 builds upon the sulfur removal information first presented in Subtask 2.1, “Gas Cleanup Technologies for Biomass Gasification” by adding additional information on the commercial applications, manufacturers, environmental footprint, and technical specifications for sulfur removal technologies. The data was obtained from Nexant’s experience, input from GTI and other vendors, past and current facility data, and existing literature.

SECTION 1: INTRODUCTION

Sulfur contaminants such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), and mercaptans in syngas streams can create unacceptable levels of sulfur emissions in power applications or poison catalysts used in chemical synthesis. Sulfur contaminants are usually reduced to less than 300 ppm for power generation and considerably lower (<1 ppm) for the synthesis of methanol, ammonia, and Fischer-Tropsch (FT) liquids.

In this Subtask, previously developed technical information will be used as the basis for the technology discussion, with additional elaboration made on the drivers for technology development and rationale for technology selection. Information will be provided for each technology about the history of use, current manufacturers, industries applying each technology, and major environmental concerns.

Three major sulfur removal technologies will be detailed here, with focus on H_2S removal: chemical solvents, physical solvents, and catalytic absorbents. Chemical solvents create a chemical bond with H_2S during contact with a gas stream in an absorber column. The H_2S loaded solvent is then sent to a stripper column, where the chemical bond is broken; the solvent is reused and the H_2S sent elsewhere for sulfur recovery. Physical solvents use the high solubility of H_2S in the solvent to “dissolve” sulfur compounds. Their process layout is similar to a chemical solvent system, using absorber and stripper columns. Catalytic sorbents are usually single-use, fixed-bed solid catalysts that react with H_2S to remove it from the gas stream.

Besides information on sulfur removal technologies, information will also be provided on sulfur recovery technologies that convert H_2S into elemental sulfur. There are two main types: partial combustion followed by catalytic reaction (Claus process) and catalytic reduction-oxidation (Redox).

The technologies discussed in this Subtask have been in widespread commercial use in many applications for decades. Sulfur recovery processes have been known since the 1880s, chemical solvents used for commercial sulfur treatment since the 1920s, and physical solvents since the 1950s. Major hydrocarbon processing industries, such as natural gas and petroleum, were the first to apply these technologies. The experience developed by these industries has been applied to syngas treatment. Thousands of treatment facilities are in reliable application today, with additional research by federal agencies and private industry underway for enhancing selectivity and reducing cost.

SECTION 2: CHEMICAL SOLVENTS

The main type of chemical solvent used for sulfur removal from gas streams are amines. There are a number of different amines available for sulfur treatment; proper selection depends on the compounds to be removed, the process conditions, the level of treatment necessary, process metallurgy, and other considerations. Amines commonly used for sulfur removal include:

- MEA (Monoethanolamine) – Removes both H_2S and carbon dioxide (CO_2) from gas streams. Typically used in low-pressure systems and in operations requiring stringent sulfur removal.

- DGA (Diglycolamine) — Used when there is a need for COS and mercaptan removal in addition to H_2S.

- DEA (Diethanolamine) – Used in medium to high pressure systems (above 500 psi) and is suitable for gas streams with a high H_2S/CO_2 ratio.

- MDEA (Methyldiethanolamine) – MDEA is used when there is a low ratio of H_2S to CO_2 in the gas stream in order to concentrate H_2S in the acid gas effluent.

Technology Description and Rationale for Use

Amine processes are proven technologies for the removal of H_2S and CO_2 ("acid gases") from gas streams. Amine systems generally consist of an absorber, a stripper column, a flash separator, and heat exchangers. This is a low-temperature process in which the gas to be treated enters the absorber at approximately 110°F. In the absorber, acid gases are removed from the gas stream by chemical reactions with the amine solution. The sweet (low sulfur) gas stream exits at the top of the absorber.

Regeneration of the rich (sulfur containing) amine is accomplished through the flash separator to remove absorbed hydrocarbons, followed by a stripper column to remove the H_2S and CO_2 from the amine solution. The lean amine solution is cooled and returned to the absorber. The stripped acid gas stream is cooled to recover water and then sent to a sulfur recovery unit. A typical amine system is shown in Figure 1.

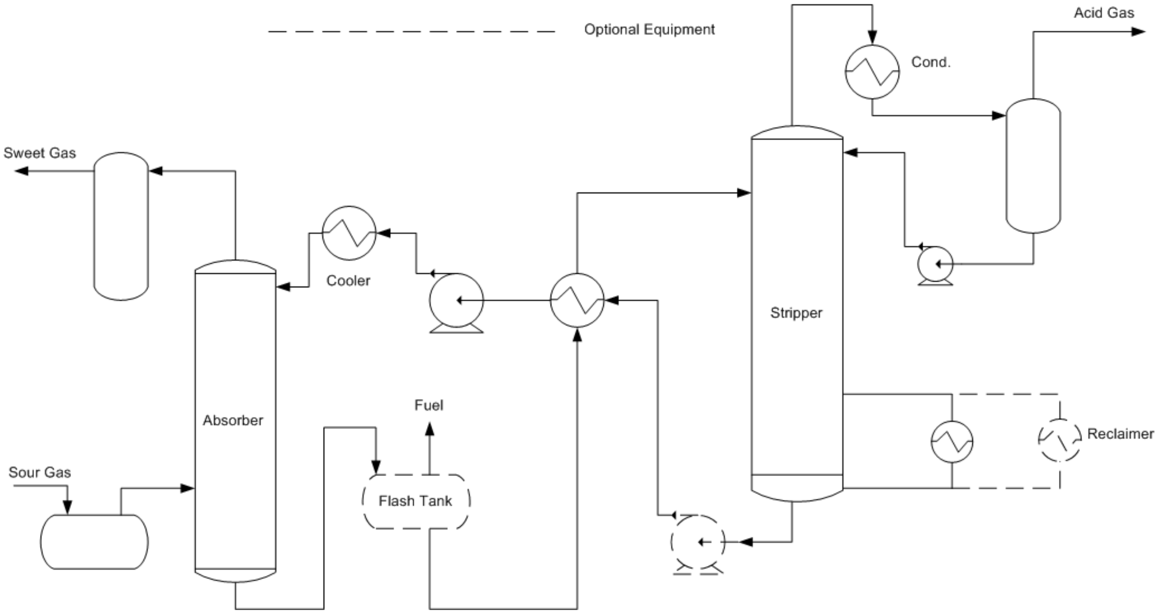

Figure 1 Typical Amine System Flow Diagram[1]

Amine systems normally operate in the low to medium pressure range of 70-360 psi, although higher pressures can be accommodated with specific types of amine solvents. However, in applications where the partial pressure of acid gases is high, the economy of an amine system declines in comparison to physical solvents. A sulfur removal level as low as 1 ppm can be achieved but at the expense of operating cost due to the large solvent circulation rate required.

In general, amine systems provide flexibility, low cost, and high reliability to industries seeking a proven sulfur removal technology. For low pressure sulfur removal applications, amines are usually the technology of choice. Their selectivity can be optimized to remove the compounds desired, while minimizing process gas losses.

Commercial Manufacturers and Applications

Design and construction of amine units is a standard practice for most major engineering firms. Selection of amine vendors tends to be more specialized, with a few firms available for packages that include process licensing and amine supply. These firms include Dow (through UOP and Union Carbide subsidiaries), BASF, Shell, Huntsman, and INEOS.

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[1] GPSA Engineering Data Book, 10th ed., "Hydrocarbon Treating," Volume II, 1987

Amine treating technologies have been the process of choice for the natural gas industry for decades, due to the limited affinity of amines for hydrocarbons. Petroleum refiners also have extensive experience with amines for similar reasons, using the technology for hydrocarbon gas sweetening and off-gas treatment. The first commercial amine applications began in the 1920's[2], with hundreds of units in active operation today. Operators of Integrated Gasification Combined Cycle (IGCC) units operating on coal, coke, and biomass also have extensive experience with amine technology. In fact, amines have been the process of choice for acid gas removal in IGCC projects, and it continues to be selected for new projects[3].

Environmental Footprint

The major direct emissions from the amine process are an acid gas stream (H_2S and CO_2, predominantly), a vent stream from the flash tank, waste water from heat exchangers, and sour water from the stripper column. Standard processes are usually integrated into a plant containing an amine unit to handle these emissions:

- Sulfur recovery units, such as a Claus or catalytic Redox unit for processing the acid gas stream. The sulfur is either sold if recovered in pure form, sent for further processing, or landfilled.
- A recycle stream to the syngas process, connection to the fuel gas system, or connection to a flare for the flash tank vent. This stream usually contains hydrocarbons or other light ends.
- Waste and sour water to appropriate water treatment facilities. These units are typically standard on any industrial hydrocarbon or syngas facility.

Besides these direct emissions, indirect emissions are generated in this process due to the need for electricity (for pumps) and steam (for reboilers and the stripper column). Since the generation of these energy sources create their own emission streams, these emission rates should be considered when determining the overall environmental footprint of the process. The amount of the footprint will vary considerably depending on the gas being treated and the depth of treatment required. In general, amine processes tend to use less electricity but more steam than units applying physical solvents.

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[2] Bullin, J., and Polasek, J, "Selective Absorption Using Amines", Bryan Research and Engineering, Bryan, TX, 2001.

[3] Korens, N., Simbeck, D., Wilhelm, D., "Process Screening Analysis of Alternative Gas Treating and Sulfur Removal for Gasification", SFA Pacific, prepared for the US Department of Energy, National Energy Technology Laboratory, December 2002.

SECTION 3: PHYSICAL SOLVENTS

This removal technology uses an organic solvent to remove acid gases from gas streams by physical absorption without chemical reaction. The driving force of this process is the high solubility of acid gases in the organic solvent. In most cases, solubility increases as the temperature decreases and the pressure increases. Thus, physical absorption is a low-temperature, high-pressure process, with high partial pressure of acid gases required for the economy and efficiency of this process. The two most common physical solvent processes are Selexol and Rectisol, which use the dimethyl ether of polyethylene glycol and chilled methanol, respectively, as the active solvents.

In general, physical solvent systems consist of an absorber, a stripper column, a series of flash separators, and heat exchangers, similar to that of a chemical solvent unit. In the absorber, acid gases in the feed stream are absorbed into the solvent solution. The sweet process stream exits the top of the absorber. Regeneration of the rich solvent stream is accomplished through a series of flash separators at reduced pressures to remove absorbed hydrocarbons followed by the stripper column to remove the acid gases from the solvent. The lean solvent solution is cooled and returned to the absorber. The stripped acid gas stream is cooled to recover water and then sent to a sulfur recovery unit. A typical physical solvent system is shown in Figure 2.

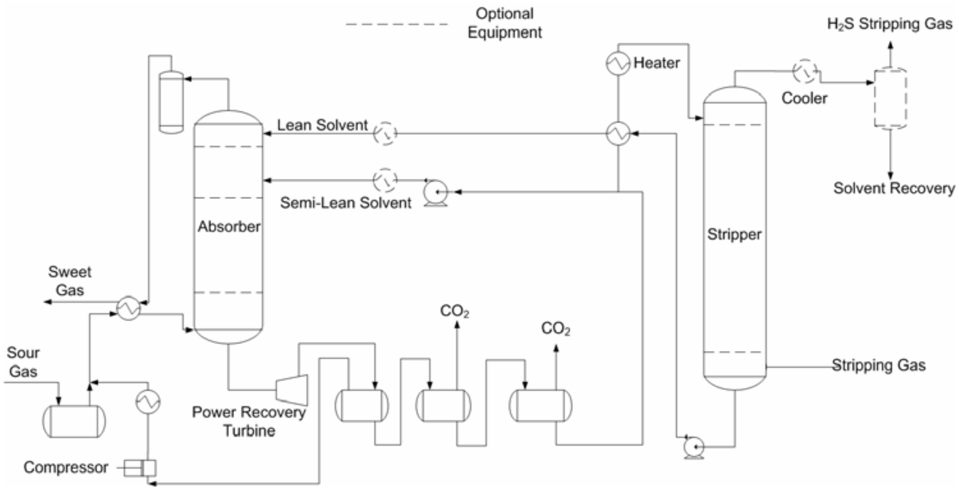

Figure 2 Typical Physical Solvent System Flow Diagram[4]

The temperature of the solvent should be as low as possible, while the temperature of the gas to be treated usually enters the absorber at about 100°F. The Selexol solvent typically operates at 20 to 80°F, while Rectisol solvents are

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[4] GPSA Engineering Data Book, 10th ed., "Hydrocarbon Treating," Volume II, 1987

kept chilled at –40 to –80°F. The minimum operating pressure for physical solvent systems is around 150 psi, but typical operation for these systems is usually much higher (500 to 1200 psi)[5].

SELEXOL

Technology Description and Rationale for Use

The solubility of sulfur compounds present in gas process streams, coupled with high solvent stability and excellent operation at high pressure, gives Selexol some advantages over other sulfur removal processes. Besides removal of H_2S and CO_2, hydrogen cyanide (HCN), mercaptans, COS, and heavy hydrocarbons can all be removed to some extent by the Selexol solvent. Process developers concerned about removal of these compounds from gas streams may find physical solvents superior to chemical ones. Depending on the level of CO_2 and H_2S removal desired, a Selexol system can be modified to meet a range of different needs.

Commercial Manufacturers and Applications

The Selexol process was first commercially used in the late 1960's. The technology is currently owned and licensed by Dow, with commercial packages available from a variety of engineering companies including UOP, Udhe, and Coastal. Roughly 60 Selexol plants are in commercial application worldwide[6].

Selexol technology is used in high pressure natural gas, IGCC, and petroleum refinery applications. At the refinery level, Selexol units can be seen upstream of reforming and partial oxidation (POX) units. This technology is currently a main competitor of amine processes for IGCC applications. Some of the key considerations for process selection for IGCC use are the gasifier technology chosen, feedstock type, and syngas end-use.

Environmental Footprint

As can be seen in Figure 2, the process configuration for a physical solvent unit is similar to that of an amine system. In general, the direct and indirect emission sources will be very similar to that of an amine unit, with differences in the relative amount of emissions and where the waste streams are emitted. Key differences of the Selexol process relative to amine units include:

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[5] Gerhard Ranke, "Advantages of the Rectisol-Wash Process in Selective H_2S Removal from Gas Mixtures," office communication, 30 January 2005.

[6] Gas Processes 2004, *Hydrocarbon Processing*, Gulf Publishing Company, 2004.

- Different acid gas and off-gas compositions. Since CO_2 has lower solubility than H_2S, the flash drum off-gas will usually contain a greater amount of CO_2. The acid gas stream will also contain a greater amount of mercaptans and heavy hydrocarbons, if these species are present in the process gas stream.
- Greater electricity use. The higher pressures and lower temperatures usually seen in a Selexol system require additional process electricity.
- Lower steam use. In general, physical solvents are easier to regenerate in the stripper column, making the steam requirements lower.

As with amine units, treatment processes for the waste streams generated are standard commercial equipment. Sulfur recovery system configurations can vary due to the different acid gas stream compositions.

RECTISOL

While many different configurations of the Rectisol process exist, the flow scheme is, in general, similar to that displayed in Figure 2. The typical difference is an additional column or process unit to aid in the regeneration of the chilled methanol. In addition, refrigeration is required to keep the methanol solvent between –40 and –80°F for process use. These additional steps add greater cost and complexity to the sulfur removal scheme.

Technology Description and Rationale for Use

The solubility of a number of sulfur compounds and other process gas contaminants is greater in the Rectisol process than in other physical solvents. This allows for very deep contaminant removal, making Rectisol a good choice in applications such as chemicals synthesis, where downstream processes are very sensitive to sulfur or other contaminants. The selectivity for H_2S over CO_2 is similar to that of the Selexol process, but the process can be configured for deep removal of both compounds if required.

Commercial Manufacturers and Applications

The German firm Lurgi GmbH first developed the Rectisol process back in the 1950's. They remain the main licenser of the technology for commercial applications. Over 50 units have been licensed and built worldwide[7]. Gasification plants with processes that are sensitive to sulfur, such as ammonia, methanol, or Fischer-Tropsch synthesis reactors, have employed Rectisol technology. While typically higher in cost than other sulfur removal technologies,

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[7] Information from Lurgi, available at www.lurgi.de.

any process looking to obtain very deep sulfur removal will usually consider applying the Rectisol process.

Environmental Footprint

The direct and indirect emissions from the Rectisol process are similar to that of Selexol, with main two differences for indirect emissions. The first is due to the use of a compressor to circulate refrigerant to keep the process cold. The addition of this unit to the Rectisol process adds greater electricity requirements to the overall process. In addition, some Rectisol process designs require multiple absorber or stripper columns for contaminant removal and solvent regeneration. This will lead to greater steam and power requirements relative to other treatment processes.

MIXED CHEMICAL AND PHYSICAL SORBENT SYSTEMS

The technologies available for sulfur removal are not limited to the ones outlined above. Two major commercially available technologies use a mix of chemical and physical sorbents to take advantage of the unique properties inherent in each type of solvent. Each process uses a proprietary hindered amine/physical solvent blend to allow selective removal of H_2S and other contaminants, such as organic sulfur compounds and CO_2.

The first is Sulfinol, developed and licensed by Shell. Since the 1960's over 200 Sulfinol units have been installed and operated worldwide[8]. Sulfinol technology has been used in natural gas and refinery applications for selective H_2S removal. The other is FLEXSORB, developed by ExxonMobil in the 1970's. Similar in nature to Sulfinol, roughly 50 commercial plants are currently in operation[9].

PHYSICAL SOLVENTS AND TAR REMOVAL

Most biomass gasification units produce some level of heavy hydrocarbons, or "tars", that must either be removed or process conditions maintained so that they do not create plugging problems. The majority of the tars are typically aromatic compounds with six carbons or more. Tar removal is currently performed by catalytic cracking of the tars just after the gasifier into lighter molecules that can be handled by the downstream process equipment. With physical solvents having an affinity for aromatic compounds, the possibility exists that they could be used in place of catalytic cracking. Aromatics are very soluble in both the Selexol and Rectisol solvents, with solubilities for benzene at ~30 times that of H_2S.

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[8] *Hydrocarbon Processing*, ibid.

[9] Fedich, R., Woerner, A., and Chitnis, G., "Selective H2S Removal", *Hydrocarbon Engineering*, Volume 9, Number 5, May 2004.

There does not appear to be any physical solvents in commercial operation for the removal of large amounts of tars, although Dow has stated that they have successfully removed "trace" amounts of aromatics from syngas streams with Selexol[10]. While aromatics are very soluble in physical solvents, aliphatic hydrocarbons have a much lower solubility—C6 compounds (hexanes) are roughly as soluble as H_2S, but this factor quickly drops off when dealing with lighter hydrocarbons. For example, methane is roughly 100 times less soluble than H_2S, and ethane is roughly 20 times less soluble.

Using physical solvents in this mode would not be a course of action that is recommended at this time. More detailed investigation could be performed, requiring vendor input and small scale testing. There are a number of concerns about using physical solvents for this application:

1. The syngas stream would need to be cooled to ~100°F or lower for feed to the physical solvent system. Cooling down the gas coming right out of the gasifier could condense oils, chlorides, ammonia, fatty acids, alkali species, and others which could create plugging problems, especially if particulates were present (due to agglomeration). Typical syngas streams from biomass gasification have a tar dew point at around ~450-500°F. One potential way to reduce the plugging risk would be to partially cool above the dew point, then have a water wash/quench to remove water soluble compounds. While this would reduce the plugging potential, the condensate would contain a considerable amount of dissolved material. This step would also likely lead to a lower process efficiency than using catalytic tar cracking.

2. Steps still need to be taken to guard against breakthrough of aliphatic hydrocarbons (~10% of the hydrocarbons in the tar). Depending on the type of aliphatic compounds present, physical solvents may or may not be very effective, especially in operations where the downstream catalyst is sensitive to residual hydrocarbons. A reformer to destroy the methane and ethane components would probably still be necessary.

3. High concentrations of tars and oils in the acid gas stream would create problems for a sulfur recovery unit, including black sulfur and VOC emissions from the incinerator. It is not clear at this time how much experimental data exists for removing a high concentration of tars from the physical solvents during the stripping step, although Lurgi has done some work in this area[11].

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[10] Jotaro Itoh, Dow Chemical Japan, "Chemical and Physical Absorption of CO2", RITE International Seminar, 14 January 2005.

[11] Dennis Leppin, Gas Technology Institute, office communication, June 2005.

4. Hydrocarbons in physical solvents have caused significant foaming and operational problems in the past, especially with Selexol. While some steps can be taken to minimize this, it can become a major operational issue.

5. It is unclear due to limited data how removing large quantities of tars and oils will impact the ability of the physical solvent to remove H_2S. As the physical solvent becomes more loaded (with preferential solubility to aromatic compounds over H_2S and CO_2), greater recycle rates and larger vessels would likely be necessary.

SECTION 4: CATALYTIC ABSORBENTS

Catalytic absorbents, such as zinc oxide (ZnO) or copper oxide (CuO), are often used as a polishing step for sulfur removal in gas streams where the incoming sulfur level is 10 to 20 ppm or lower. For hydrocarbon and IGCC applications, catalytic absorbents are usually not a primary sulfur removal process. They are typically applied downstream of either a chemical or physical solvent to assure the sulfur level entering other process equipment, such as chemical synthesis reactors, is very low. Since ZnO is the technology most commonly deployed, it will be focused upon here.

Technology Description and Rationale for Use

H_2S in a gas stream reacts with the ZnO absorbent in a fixed bed reactor, where it is converted to zinc sulfide. According to technology providers, sulfur removal down to 20 to 50 ppb is attainable with ZnO[12]. Since the sulfur specifications for alcohols and FT liquids are <1 ppm in the syngas stream, ZnO could be used to assist in achieving these requirements.

ZnO is active over a wide range of temperatures from ambient to 750°F; however, operating temperatures between 660°F and 750°F are normally used to maximize absorption efficiency. Operating pressure limits are usually not a concern for the use of ZnO absorbent.

While catalysts that could be regenerated were used for many years prior to the application of the current breed of catalysts, regulations limiting air sulfur emissions have spurred the use of hot ZnO catalysts that are disposed of after their useful lifetime. Spent catalyst usually contains a sulfur content that is low enough to enable it to be landfilled or used as an agricultural fertilizer.

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[12] Considerable information in this section provided by Ronald Huber, Sud-Chemie Technical Service Engineer, personal correspondence, 2 June 2005.

The main rationale for the use of ZnO catalysts is for systems where very low sulfur content is a key priority. For chemical synthesis, these systems can be placed downstream of amine or Selexol units to act as a secondary removal step (a "polishing" step), or downstream of a Rectisol unit (a "guard" step) to prevent sulfur breakthrough. The lifespan of the catalyst between changeouts is longer in guard operation than as a polishing step.

Commercial Manufacturers and Applications

A catalyst bed for polishing or guard sulfur removal duty is a conventional unit process that has been effectively been applied for decades. Processes for chemical synthesis from natural gas or syngas, such as ammonia, methanol, and FT liquids production, have all employed catalytic absorbents. The current hot oxide catalysts have been recently employed since the 1980's, with the current number in service estimated from the high hundreds to the low thousands. Major vendors for this technology include Sud-Chemie, BASF, Synetix, Unicat, and Haldor Topsoe.

Environmental Footprint

Catalytic absorbents are a much simpler, more environmentally benign process relative to chemical or physical solvents. This is due in large part to the lower level of sulfur removal, since absorbents act as a secondary removal step. The only environmental concern for catalytic processes is the removal of spent catalysts. As mentioned earlier, this is usually not a hazardous waste; the spent catalyst can be landfilled or, in some instances, be used as a fertilizer.

SECTION 5: SULFUR RECOVERY

Removing sulfur from a natural gas or syngas process stream is only part of the story. The residual sulfur present in an acid gas stream must then be recovered to prevent environmental and safety harms, as well as meet operator permit requirements. Two main technologies are commercially available to recover sulfur: the Claus process (partial combustion) for high levels of sulfur, and catalytic Redox processes, for relatively low levels of sulfur.

CLAUS PROCESS

Technology Description

In the Claus process, a high H_2S concentration stream is the feedstock for recovery to elemental sulfur. Roughly 1/3rd of the H_2S is burnt (partial combustion) to form sulfur dioxide (SO_2). The remaining H_2S reacts with the synthesized SO_2 over an alumina or bauxite catalyst to produce elemental sulfur. Depending on their concentrations, the unreacted components (tail gas), such as residual SO_2, CO_2, and H_2S, are either emitted, thermally oxidized, or further treated in an additional recovery process. A graphical depiction of the process can be seen in Figure 3.

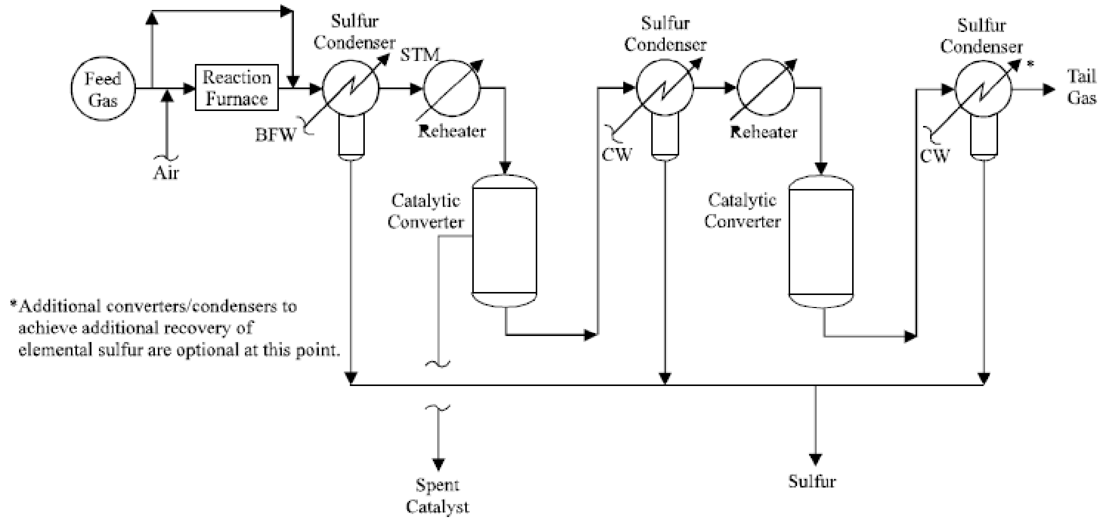

Figure 3 Typical Claus Sulfur Recovery Process[13]

The Claus process is thermodynamically limited to ~97% sulfur recovery, although additional treatment steps, such as tail gas sulfur recovery, can increase the recovery rate.

Commercial Manufacturers and Applications

The Claus process is the oldest commercial process covered in this paper, with development dating back to the late 19th century. Today, Claus processes are the main step used for elemental sulfur production worldwide—in fact, 90 to 95% of the sulfur recovered in the United States was from the Claus process. 38 companies operate 108 Claus processes in the United States, recovering nearly 9 million tons per year of sulfur[14]. The petroleum and natural gas industries are the main users of the technology, with IGCC applications making up a small but growing segment of the user population.

Since application of the Claus process is so widespread across the world, a number of major engineering firms offer licenses for the technology. These include companies such as Parsons, KBR, and Jacobs for the overall technology, and Almatis, Axens, and UOP for the process catalyst.

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[13] US Environmental Protection Agency, AP42, 5th Edition, "Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources, 1995.

[14] US Geologic Survey, Mineral Commodity Summary, Sulfur, January 2005.

In operations where the sulfur recovery is more than 20 TPD, a Claus unit is generally the most economical approach. For efficient process operation, the concentration of H_2S in the acid gas stream entering the Claus unit should be a minimum of ~40%; lower concentrations can be handled with some modifications to the process including acid gas bypass of the reaction furnace and the addition of oxygen to the air used for combustion.

Environmental Footprint

The main direct outlet streams from the Claus process are elemental sulfur, spent catalyst, tail gas, and wastewater. The sulfur is of very high purity, and can be used for industrial processes such as the production of sulfuric acid. The tail gas stream contains the major emissions from the process. Thermal oxidation of this stream could lead to emissions of SO_2, CO_2, CO, NO_x, and other pollutants. When a tailgas treatment unit is added, the emissions of sulfur oxides are reduced and overall sulfur recovery can be 99% or more. The wastewater generated from the sulfur condensers typically requires downstream treatment in a standard treatment unit.

The Claus process has a relatively small amount of indirect emissions coming predominantly from the number of reheaters used to maintain process heat. The majority of the process heat comes from the exothermic reactions involving H_2S.

CATALYTIC REDOX SULFUR RECOVERY

A catalytic sulfur recovery process is suitable for small-scale applications that require less than 20 TPD of sulfur recovery capacity, have a concentration of H_2S in the acid gas stream too low for the Claus process, or are subject to high fluctuations in acid gas rate or composition. The two main technologies for this application are marketed as LO-CAT® (by Gas Technology Products LLC (GTP), a unit of Merichem) and Sulferox (developed by Shell and Dow and currently licensed by Le Gaz Integral (LGI)). While the two technologies are relatively similar (differing in catalyst concentration and type), the LO-CAT® technology will be elaborated upon here.

Technology Description and Rationale for Use

LO-CAT® is an oxidation process that uses iron catalyst held in a chelating agent to oxidize H_2S to elemental sulfur[15]. H_2S is the only acid gas being removed in this process. A LO-CAT® process consists of 3 sections that include an absorber, an oxidizer for catalyst regeneration, and a sulfur handling unit. Figure 4 illustrates a typical LO-CAT® unit. When the gas stream comes in contact with

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[15] Information provided by GTP/Merichem, personal communications and www.gtp-merichem.com

the LO-CAT® solution in the absorber, H_2S in the gas stream is converted to elemental sulfur. The spent catalyst along with the elemental sulfur exits the absorber and then enters the oxidizer where the spent catalyst is regenerated by contact with oxygen. The elemental sulfur is then concentrated into a sulfur slurry, which moves to the sulfur handling unit to recover any entrained catalyst solution.

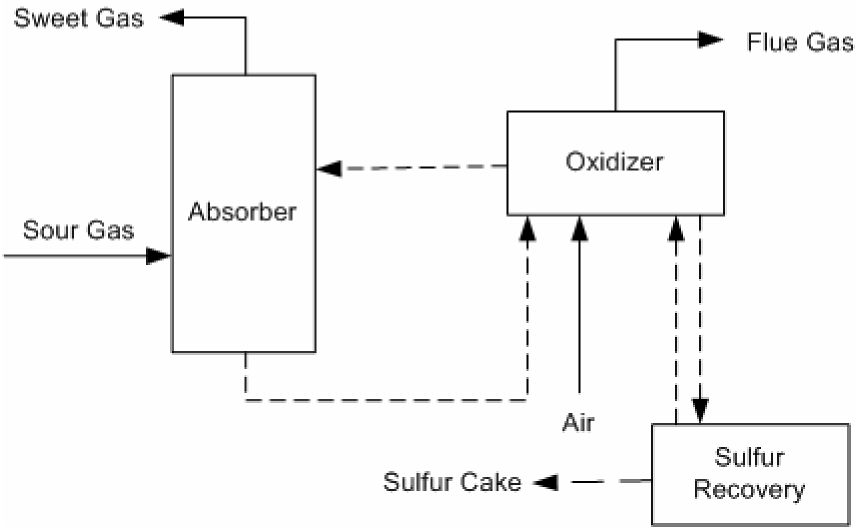

Figure 4 Typical LO-CAT® System Flow Diagram

Commercial Manufacturers and Applications

As mentioned above, GTP and LGI are the two active manufacturers of catalytic sulfur removal technology. GTP first commercialized the LO-CAT® technology in 1978, with the SulFerox process coming to market in the early 1980's. 300 to 400 units are currently in operation in a number of different industries that require recovery of low levels of sulfur[16]. These include natural gas sweetening, syngas operations, air purification, biogas/landfill gas units, and refinery "off-gas" streams.

Environmental Footprint

Due to the simpler make-up of the catalytic recovery process relative to the Claus process, the direct and indirect emissions are lower. Similar to the Claus process, sulfur, tail gas, and spent catalysts are all process products. The sulfur removed from this process is not directly suitable for industrial use; the product is a "cake" that contains up to 70% water. The sulfur recovered contains a small amount of entrained residual catalyst and is considered low-value sulfur that is suitable for agricultural purposes but is undesirable as a chemical feedstock.

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[16] Combination of information provided by both GTP/Merichem and Shell.

The catalyst can either be landfilled or used as an agricultural fertilizer. Finally, the tail gas stream, depending on composition, can either be vented or burned in a thermal oxidizer. While this stream may still be a source of SO_2, CO_2, and CO, the concentrations tend to be lower than in a Claus process.

Since no additional process equipment is required outside of what is listed in Figure 4, the indirect emissions are negligible.

Appendix A Technologies Summary

Appendix A includes a summary of the technologies discussed in the above sections. Information is provided on the operating conditions, clean-up parameters, advantages, and disadvantages.

Summary of Acid Gas Removal Technologies

Technologies	Size range	Operating range	Cleanup Parameters	Advantages	Disadvantages
Chemical Solvents	Designed for specific application	Low-temperature operations-inlet gas at about 110°F Low to medium operating pressures (70-360 psi) with many solvents; some can be used for > 500 psi (nat. gas)	Can remove H_2S down to 1ppm with a high solvent circulation rate CO_2 removal dependent on amine selected	Proven technologies; can selectively remove H_2S only, if desired	Limited in what compounds can be removed Corrosion is a major operating concern
Physical Solvents	Designed for specific application	Low-temperature operation-process conditions from 80 to –80°F High pressure operation (500 to 1200 psi)	Can remove to ~0.1 ppm H_2S with Rectisol, 1 ppm H_2S with Selexol	Can provide wide depth or breadth for contaminant removal	Capital costs can be significant for some systems Usually have high power requirements
Catalytic Absorbents	Feed gas with inlet H_2S < 10-20 ppm	Operating temperatures range of 660 – 750°F Operable over a wide range of pressures	50 ppb H_2S achievable	Able to meet stringent sulfur specs Ease of use	Cannot be regenerated, may require landfilling Inlet H_2S concentration must be low to be economic
Sulfur Recovery: Catalytic Redox	Used for < 20 TPD sulfur recovery	Low-temperature operations-inlet gas at about 110°F Operating pressures range from 15 to 600 psi, but is normally used in low-pressure applications	99.9%+ removal efficiency	Low cost and significant turndown flexibility Ability to treat wide range of gas compositions	H_2S is the only compound removed; not suitable if feed gas contains other sulfur compounds Low-value sulfur recovered
Sulfur Recovery: Claus	Greater than 20 TPD sulfur recovery, acid gas H_2S concentrations >40%	1800 to 2800°F in the combustion chamber, 400 to 600°F in the catalytic reactors Close to atmospheric pressure	94 to 97% S recovery, depending on process configuration Can increase recovery if additional tail gas treatment performed	Extensive operating experience Sulfur recovered is pure; can be sold as a commodity	Can be very expensive relative to Redox processes for low sulfur recovery rates (<20 TPD) High temperature process

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This deliverable is Subtask 2.3 of Task 2, Gas Cleanup Design and Cost Estimates, of NREL Award ACO-5-44027, “Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup and Oxygen Separation Equipment”. Subtask 2.3 builds upon the sulfur removal information first presented in Subtask 2.1, “Gas Cleanup Technologies for Biomass Gasification” by adding additional information on the commercial applications, manufacturers, environmental footprint, and technical specifications for sulfur removal technologies. The data was obtained from Nexant’s experience, input from GTI and other vendors, past and current facility data, and existing literature.

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