Technology Screening for Natural Gas Liquids Treatment

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ABSTRACT

Natural Gas Liquids (NGL) streams may be contaminated with small amounts of organic sulfur species, H_2S, and/or CO_2. Removal of these impurity components to very low levels is often dictated by product specifications. While a variety of established technologies can be applied to remove many of these components, some components (e.g., COS) are considered more difficult to remove, and technologies applied to remove one component can result in the need to apply another downstream technology. This paper discusses in detail the screening of liquids treating technologies, including the consideration of the feed stream characteristics, the requirements for the product, and other factors that can influence technology selection (e.g., other existing unit operations in the gas plant). The basic parameters and features of technologies often applied in liquid treating are discussed. An NGL treating application requiring the removal of a variety of sulfur species is developed as an example; various treatment options consisting of multiple technologies are considered, with the competing technology solutions compared via technical applicability and economic factors.

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Introduction

A common byproduct of natural gas and oil production is natural gas liquids (NGL), which is a mixture that may contain ethane (C2), propane (C3), iso-butane (I-C4), butane (N-C4), and natural gasoline (C5+). The fractionated components of the stream are valuable to downstream users such as petrochemical companies and refineries. The NGL, also known as Y-grade liquids, must be of sufficient quality to be transported and accepted at the fractionation plants. Frequently, Y-grade product specification must be met in order for the stream to be allowed pipeline entry and transport. Y-grade requirements may include limits on product temperature range, hydrocarbon composition, vapor pressure, corrosiveness, carbon dioxide, hydrogen sulfide, other specific sulfur species, total sulfur, water content, and color.
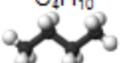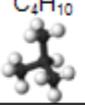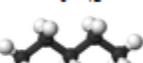
A variety of technologies have been employed to treat NGL to meet specifications. When significant amounts of multiple impurities are present, the treatment system required to yield an acceptable Y-grade product can be complex. This paper reviews many of the technologies that are available, and discusses the issues that might be considered in technology selection.

Liquid Feed Stream Characteristics

NGL streams are recovered at gas plants associated with field gas gathering and conventional crude oil processing as well as field flood CO_2 recycle treating. NGLs are also recovered in many instances at so-called "straddle" plants located on pipelines transporting natural gas, often from offshore fields. NGL are fractionated into various petroleum products, after which they can be used for many applications ranging from raw material in petrochemical plants and combustion engine fuel blending to commercial heating and cooking. Some of the uses for the various NGL components are detailed in Figure 1. Besides valuable hydrocarbons, NGL streams may contain impurities such as hydrogen sulfide (H_2S), organic sulfur compounds, CO_2, water, and others.

Common NGL Specifications

The level of purification required for an NGL stream is dependent upon pipeline and downstream requirements. NGL streams may often carry contaminants such as H_2S, methyl mercaptan (CH_3SH), ethyl mercaptans (C_2H_5SH), heavier mercaptans, carbonyl sulfide (COS), carbon disulfide (CS_2), miscellaneous other organic sulfur compounds (e.g., dialkyl sulfides, dialkyl disulfides, and thiophenes) and in cases involving high ethane recovery, carbon dioxide (CO_2). Sulfur compounds can cause problems in downstream processing equipment, and contamination of final products. In addition, high sulfur and/or CO_2 content can result in corrosion of equipment and piping.

NGL Attribute Summary				eia
Natural Gas Liquid	Chemical Formula	Applications	End Use Products	Primary Sectors
Ethane	C_2H_6	Ethylene for plastics production; petrochemical feedstock	Plastic bags; plastics; anti-freeze; detergent	Industrial
Propane	C_3H_8	Residential and commercial heating; cooking fuel; petrochemical feedstock	Home heating; small stoves and barbeques; LPG	Industrial, Residential, Commercial
Butane	C_4H_{10}	Petrochemical feedstock; blending with propane or gasoline	Synthetic rubber for tires; LPG; lighter fuel	Industrial, Transportation
Isobutane	C_4H_{10}	Refinery feedstock; petrochemical feedstock	Alkylate for gasoline; aerosols; refrigerant	Industrial
Pentane	C_5H_{12}	Natural gasoline; blowing agent for polystyrene foam	Gasoline; polystyrene; solvent	Transportation
Pentanes Plus*	Mix of C_5H_{12} and heavier	Blending with vehicle fuel; exported for bitumen production in oil sands	Gasoline; ethanol blends; oil sands production	Transportation

C indicates carbon, H indicates hydrogen; Ethane contains two carbon atoms and six hydrogen atoms
*Pentanes plus is also known as "natural gasoline." Contains pentane and heavier hydrocarbons.

Source: U.S. Energy Information Administration website

Figure 1 – NGL Fractions and Common Uses

Sources of NGL such as gas plants and EOR CO_2 recycle units often do not have fractionation infrastructure; therefore, the transport of NGL to downstream fractionation units via pipeline is often required (although truck or rail transport may also be done). Before transport, the NGL stream must meet the pipeline specification often referred to as the Y-grade specification.

There is not a universally-accepted Y-grade specification, but most specifications share some similarities. The specifications most relevant to this paper pertain to presence of various sulfur compounds; these specifications may include total sulfur (or total volatile sulfur), COS, H_2S, and corrosivity. One specification that is subject to quite a bit of variability is total sulfur. A survey of some publically available pipeline specifications (1) (2) (3) shows a total sulfur (or total volatile sulfur) limit varying from 120 to 1,200 ppmw. In the same specifications COS did not have a limit specified or had a specified limit of 10 or 15 ppmw. Overall, in newer specifications there appears to be a general trend to reduce total sulfur content allowance for Y-grade products.

Sulfur species in NGL can be problematic in that they can partition to various hydrocarbon products in fractionation plants. A complete review of the fate of all of the sulfur species that may be present in NGL is beyond the scope of this paper. Examination of the boiling points of

some of the sulfur species may provide some indication of which hydrocarbon product a sulfur compound would partition to in a NGL fractionation train; however, many reports have indicated that simple comparison of boiling points is not sufficient in determining the partitioning of some sulfur compounds in hydrocarbon fractions. Significant non-ideal vapor liquid equilibrium (VLE) appears to exist in these systems; some sulfur compounds may even have some significant reactivity at distillation conditions. Reports and papers published by the GPA (4) (5) (6) and others (7) (8) have characterized the VLE of some sulfur compounds with hydrocarbons. When trying to predict of the fate of sulfur compounds in an NGL fractionation train, VLE data should be sought in the literature or generated in the lab if necessary. The predictions of process simulation software should be compared with these data.

Table 1 shows a list of a few of the typical Y-grade pipeline specifications that were used in this work and that pertained to impurities such as sulfur compounds, CO_2, and water. An indication of which hydrocarbon fraction some specific impurities preferentially partition to is sometimes expressed in the Y-grade specification. For example, the specification for COS in Table 1 is given as "12 ppmw in contained propane". In an NGL fractionation train, most of the COS will partition with the propane product, so the fractionator of the NGL is primarily concerned with the amount of COS that will ultimately be in their propane product. In determining whether or not an NGL stream meets the COS specification in Table 1, the mass concentration of COS in the NGL would be divided by the mass concentration of propane.

Table 1 – Examples of Typical Y-Grade Specifications

Component	Specification
Carbon Dioxide	Maximum: 0.35 vol% of the Ethane / 500 ppmv
Corrosion, Copper strip at 100 °F	No. 1
Total Sulfur	Maximum: 150 ppmw
Hydrogen Sulfide	Must pass ASTM D-2420 test
Carbonyl Sulfide	Maximum: 12 ppmw in contained Propane
Water Content	No Free Water @ 34 °F

Sulfur species are often the most problematic to deal with in upgrading NGL to meet a Y-grade specification. For example, as little as 1 ppmw of H_2S may result in failure of the copper strip test, and small amounts of dissolved elemental sulfur can also cause copper strip test failure (9) (10) (11). Additionally, any residual COS (in the presence of water and a catalyzing agent) can hydrolyze to H_2S and CO_2 in transportation and storage systems. There are cases where an NGL stream passes the copper strip test at the production site, and then fails the test after transfer through a pipeline, probably due to the hydrolysis of residual COS.

The treatment of liquids can be complicated when there are multiple compounds to be removed. Multiple processing steps may be required. Some treatment methods may require or produce another species characterized as an impurity; for example, hydrolysis of COS requires the presence of water (liquids streams are often produced dry), and produces H_2S and CO_2. Additionally, the choice of technologies can be strongly dependent upon the amount of contaminants to be removed, on the type of facility it will be part of, and on the infrastructure and other processing units at the existing facility.

There are many technologies and approaches for removal of impurities such as H_2S, organic sulfur, and CO_2 from NGL streams. The following is a brief discussion of some of these approaches, including their applicability, advantages, and disadvantages. Other reviews of liquids treating technologies are found in the literature (12) (13) (14).

Liquids Treating Technologies for Impurity Removal

Alteration of Gas Treatment Train Prior to NGL Recovery

In general, for highly sour gas streams many operators prefer to remove contaminants to the extent possible by treating the inlet gas. Therefore the logical starting point for consideration of the improvement of NGL quality may be to consider changing the existing processes in the gas treating train prior to the NGL recovery. An example of this strategy would be to design or modify a molecular sieve gas dehydration unit upstream of the NGL recovery to maximize the removal of organic sulfur compounds (15). Another example would be to consider the replacement of an amine treating solvent with a hybrid solvent having both chemical and physical agents which have often been effective in removing organic sulfur compounds (16).

There are many cases where it is more efficient to remove the impurities from the recovered NGL rather than from the rich gas, because the gas stream feeding the NGL recovery unit is typically large compared to the NGL stream and the impurities will be more concentrated (leading to easier removal) in the NGL stream. Because the consideration of upstream gas treating equipment is very site and application specific, the remainder of the discussion in this paper will focus primarily on the treatment of the recovered NGL.

Molecular Sieve Adsorption (Regenerable)

Molecular sieves are commonly used to remove water from gas and liquid streams, but some sulfur species such as COS and some light mercaptans can also be removed by judicious choice of sieve type and operating and regeneration conditions. The adsorbent is then regenerated, usually by pressure and/or temperature swing, using a sweep gas. When evaluating the installation of a molecular sieve unit to treat NGL, consideration might also be given to whether it makes more sense to install it (or modify an existing unit) on the isolated NGL or on the gas feed to the NGL recovery unit.

One advantage of molecular sieves is the ability to remove some organic sulfur compounds concurrently with water. Disadvantages include concurrent adsorption of some of the hydrocarbons, complexity of operation, the need for a regeneration sweep gas (often a sweet product gas is used), and the need to deal with the regeneration sour off-gas. Also, there is a risk

of forming COS in the mole sieve bed if both H_2S and CO_2 are present. Molecular sieves are available over a range of pore sizes, depending on the contaminant removal objectives. For example, a 3X or 4X sieve will selectively remove smaller molecules such as water, while larger sieves up to 13X are used when removal of larger organic molecules is desired. General discussions of molecular sieves for gas treating can be found in the literature (17) (18) (19).

Molecular sieves might be applied most effectively at plants where there is an existing unit to treat the sour regeneration off-gas, or if that gas stream can be disposed of by some other method. An example of a situation where the sour regeneration off-gas is easily handled is in NGL recovery from an EOR CO_2 recycle stream; this small stream can sometimes be recompressed and mixed with the recycle CO_2 stream. Also, if installed at a gas plant or refinery with an existing amine unit, the regeneration gas may be treated in these existing systems.

Other Regenerable Adsorbents

There are other regenerable adsorbents besides molecular sieves that can be used for NGL treatment, and some of these adsorbents are targeted at removing specific compounds. These other regenerable adsorbents would typically have the same treating and regeneration scheme as molecular sieves, and would also have similar advantages and disadvantages. There are several adsorbents of this type that could be applied in NGL treatment service, many of which are described in a previous report (12); one example of a regenerable adsorbent that might be applicable to NGL treatment is Selexsorb COS®, which targets the removal of COS and few other species.

Non-regenerable Adsorbents

Many non-regenerable adsorbents are available that can be used in NGL treatment, mostly focused on the removal of sulfur species. Many of them use a chemical reaction with components of the adsorbent, yielding a non-volatile, non-dissolving product that is retained on the bed. Change-outs of the bed must be done occasionally, often requiring the need for multiple beds. Advantages of non-regenerable adsorbents include process simplicity for most applications, relatively low capital cost compared to regenerable processes, and very little operational complexity. A disadvantage of this approach is that the cost of the adsorbents is typically high, and as a result this approach can only be economically applied for the removal of relatively small amounts of impurities. Some adsorbents may also not removal all of the impurities of interest, leading to the need for multiple processing steps. Some adsorbents might also require the presence of water and/or require that the adsorption be done at an elevated temperature, which can complicate the process.

Many non-regenerable adsorbents contain a metal oxide or mixtures of metal oxides as the primary reactive species, often supported on an inert substrate. The choice of metal oxide may dependent upon the impurities to be removed and the operating conditions; the exact composition of the non-regenerable adsorbents and their performance for the removal of specific compounds may be propriety to the vendor.

Some of the least expensive non-regenerable adsorbents use iron oxide as the primary reactive metal and these materials can remove bulk amounts of H_2S readily, although the presence of

some water may be required for efficient use of the material. Other adsorbents with more expensive metals are often used to adsorb organic sulfur compounds and also remove H_2S down to very low levels. A zinc oxide absorbent can be used for deep H_2S removal, although depending on the application high temperatures may be required. For lower process temperatures and for less reactive organic sulfur species, a higher surface or promoted mixed metal oxide, often containing copper and zinc can be used. Some examples of non-regenerable adsorbents include various SULFATREAT®, PURASPEC®, and SULFURTRAP® products, UOP® GB-420, UNICAT® TSR-121G, and PuriStar® R3-12. An advantage of some non-regenerable adsorbents is that they have the capability to remove some organic sulfur species, such as dimethylsulfide and thiophene, that may be difficult to remove with many other technologies. (20)

Potassium Hydroxide/Methanol

Another non-regenerable process for the removal of various liquids impurities is the use of methanol with potassium hydroxide (KOH). This approach involves injecting methanol into the liquid hydrocarbon stream and contacting the liquid with a bed of KOH briquettes causing the following reaction to occur *(21)*. :

$$COS + KOH + CH_3OH \rightarrow H_2O + KSCOOCH_3$$

In addition to removing the COS at a high efficiency, residual CO_2 and H_2S will be removed by acid-base reaction with the KOH, as will a significant fraction of the mercaptans; some carbon disulfide (CS_2) removal is also reported to occur *(21)*. However, there does not appear to be published data that describes the efficiency of the KOH/methanol system for the removal of organic sulfur compounds other than COS.

Water is produced in all of the reactions of the KOH/methanol system with sulfur compounds and CO_2. Because of the hygroscopic nature of solid KOH, the water produced in the reactions will tend to be absorbed by the KOH to form various KOH hydrates depending on the temperature. Depending upon the water content of the feed liquid, the concentration of COS, the process conditions, and the extent of usage of the KOH bed, the KOH briquettes may eventually absorb enough water to cause a concentrated KOH aqueous phase to form, which can be decanted from the bottom of the treater vessel. Agglomeration of the KOH can also occur due to the wetting, which can make change-out more difficult, although experience has led to the use of "walnut" shape KOH briquettes to mitigate this issue; a picture of the KOH briquettes often used in this service is shown in Figure 2.

Advantages of this technology are that it removes COS down to very low levels and that it also can remove large portions of other impurities (e.g., mercaptans) in the feed NGL. Additionally, KOH and methanol are both relatively inexpensive chemicals. Disadvantages of the technology include the formation of a spent KOH aqueous liquid phase that must be disposed of, the need to change-out the solid bed of spent KOH that can become agglomerated, and the spent KOH material may be considered hazardous. Additionally, if the feed liquids have a very high water content the use of KOH/methanol may be uneconomical due to the excessive absorption of the water and subsequent loss of the KOH due to the dissolution of the KOH into an aqueous phase.

Figure 2. KOH Briquettes

Amine Treating

Amine treating is used throughout industry for removal of H_2S and CO_2 from gaseous and liquid hydrocarbon streams. The hydrocarbon is contacted with the amine where absorption and reversible chemical reaction remove these impurities from the hydrocarbon. Heat is applied to the amine in the regenerator where the H_2S and CO_2 are liberated from the amine. There are several different amines and specialty blends that have advantages to specific treating needs. The presence of specific organic sulfur compounds may result in the problems for the use of some amines; for example, monoethanolamine (MEA) will react irreversibly with COS.

Amine treating of NGL is fairly common and has been the subject of previous literature discussions (22) (23) (24). Diethanolamine (DEA), 2-(2-aminoethoxy) ethanol (commonly known as diglycolamine or DGA®), and diisopropanolamine (DIPA or ADIP) are often used for liquid treating when there are organic sulfur compounds present. Literature suggests that DGA® reacts with COS and is effective for COS removal from liquids (25); the DGA® that reacts with the COS is recovered in a conventional thermal reclaimer where the COS is hydrolyzed to CO_2 and H_2S. Some limited removal of mercaptans may also be accomplished with these amines depending on the specific operating conditions. For cases where CO_2 must be removed from the NGL, which may be the case in high-ethane recovery cryogenic plans, DEA is often used.

Amine treating is similar to the solid-based regenerable adsorption processes insofar as an acid gas stream is produced that must be disposed of. The economical application of amine treating may thus be dependent upon plant-specific issues. The presence of another amine plant and a Claus sulfur-recovery unit at the facility would be helpful if the acid gas streams could be comingled. Another possibility would be the application at a CO_2 recovery plant where the small acid gas stream could be compressed and added to the recovered lean CO_2 stream. Finally, the subsurface injection of the acid gas should be considered, if that is a viable option.

Advantages of amine treating include the capability to concurrently remove portions of all acidic impurity components from the NGL, and that amine treating is a familiar and well-established

technology in the gas treating industry. Disadvantages of amine treating for NGL include potential limitations of mercaptan removal (and non-acidic organic sulfur, such as dialkyl sulfides and disulfides), the need to remove water from the treated NGL, and the need to dispose of the acid gas byproduct.

Catalytic Hydrolysis

A catalyst can be used to hydrolyze COS, converting the COS to H_2S and CO_2 according to the following reversible reaction:

$$COS + H_2O \leftrightarrow H_2S + CO_2$$
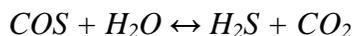
This process might logically be used upstream of a H_2S/CO_2 removal process that does not efficiently remove sulfur in the form of COS. Using certain catalysts, this reaction chemistry can be carried out in the liquid phase at relatively low temperatures (approximately < 200°F). This technology might be advantageous in situations where H_2S and/or CO_2 needs to be removed from the NGL anyway, and a downstream amine (or other H_2S and CO_2 removal technology) is planned. Some amines, such as COS, are also thought to hydrolyze COS given sufficient residence time.

This approach requires the presence of adequate amounts of water to hydrolyze the COS, probably with some stoichiometric excess, which may not always be present in NGL streams. These catalysts do not react appreciably with most other organic sulfur compounds, such as mercaptans.

Advantages of COS hydrolysis include that it is effective for COS removal to low levels, the process is very simple, and the catalyst bed should last a long time. Disadvantages include that other contaminants (CO_2 and H_2S) are produced, which must be removed downstream, and it is likely that some residual water will be present after the hydrolysis. A couple of examples of commercialized COS hydrolysis catalysts include Sud Chemie® C53-2-01, PURASPEC® 5312, and others.
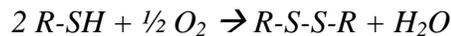
Caustic Wash

This approach involves contacting the liquid hydrocarbon stream with caustic solution (usually in the 5 to 20 wt. % range). Spent/diluted caustic is exported and replaced with fresh caustic to maintain removal efficiency. The caustic wash process is primarily used for removing relatively small amounts of hydrogen sulfide and methyl and ethyl mercaptans, but can also remove CO_2 (although large amounts of CO_2 absorption can lead to carbonate salt precipitation, and may require operating the caustic at a low concentration). Typically a water wash is done after the caustic wash to remove any dissolved or entrained salts.

Advantages of caustic wash include the relative simplicity of the process and the high removal efficiency. Some disadvantages of caustic wash include the lack of capability to remove COS, the potential for the contamination of the treated NGL with salts, and the associated costs for handling and disposal of spent caustic; additionally, the treated NGL stream will contain water as a result of the caustic wash process.

Regenerable Caustic Wash

Regenerated caustic systems are primarily used for removing methyl, ethyl and some higher mercaptans from liquids. The process involves contacting the untreated hydrocarbon stream with a caustic stream which extracts the mercaptans into the aqueous phase. The spent caustic is sent to a regeneration unit, where the caustic is recovered. Two different regeneration technologies are common. In a simple regeneration process the spent caustic is heated to reverse the mercaptan-NaOH reaction, with the mercaptan stripped out as an acid gas stream, and the NaOH recovered; this approach may be advantageous when there is a convenient market for the mercaptan stream (e.g., odorants). A different regeneration scheme involves using contact with oxygen (from air) and using a catalyst to regenerate the spent caustic and catalytically convert the mercaptan to a disulfide:

$$2 \ R\text{-}SH + \tfrac{1}{2} \ O_2 \rightarrow R\text{-}S\text{-}S\text{-}R + H_2O$$

The resulting disulfide oil can be decanted from the regenerated caustic. Because regenerable caustic wash processes typically target mercaptan removal, the process may be combined with a non-regenerated caustic pre-wash (or other technology) intended to remove H_2S and CO_2 prior to the process.

Some advantages of this process are that it can handle large volumes and significant mercaptan concentrations, and that it reduces the cost associated with single use caustic and disposal of spent caustic. Disadvantages of this process include the need for disposition of the byproduct streams: mercaptan acid gas that results from simple regeneration, or disulfide oil liquid and spent air from the catalytic regeneration process. Examples of the catalytic regeneration technology are the MEROX® and THIOLEX/REGEN® processes.

Hydrodesulfurization

Hydrodesulfurization is a catalytic chemical process used to remove organic sulfur contaminants from hydrocarbon streams. This technology is frequently used in refineries to remove sulfur compounds from a variety of intermediate product streams. The hydrodesufurization is achieved through the reaction of the organic sulfur with hydrogen at elevated temperature and pressure in a fixed bed reactor, where the sulfur containing contaminants are all converted to hydrogen sulfide. The treated hydrocarbon liquid is separated from the gas and flows through a stripper column in which the H_2S is removed from the hydrocarbon product liquid. The hydrogen rich gas is treated in an amine column to remove hydrogen sulfide. The sulfur-free hydrogen gas is returned to the fixed-bed reactor. Acid gas from the amine regenerator and stripper require further treatment or disposal.

Hydrodesulfurization is a common unit operation at refineries, where heavy organic sulfur compounds are common, and hydrogen is usually available. An advantage of hydrodesulfurization is the ability to treat a wide variety of organic sulfur species. The disadvantages of this technology are high capital cost, complexity of the process, and the need for a hydrogen source. This approach would typically only be applied to large applications that are part of an integrated facility. The high cost and lack of a hydrogen source at most field gas plants would result in this technology not being a reasonable fit for the majority of cases.

Important Factors in Technology Screening

Some of the factors that are important in the screening of technologies for use in NGL treatment are discussed below.

- *Amount of impurities to be removed.* Non-regenerable adsorbents are often the simplest, lowest capital cost method for removing an impurity from a liquid or gas stream. The use of non-regenerable adsorbents for H_2S removal from NGL is well-established; the removal of organic sulfur compounds with non-regenerable adsorbents is more difficult, although several suppliers report that their adsorbents can remove certain organic sulfur compounds in addition to H_2S. If the compound to be removed is at a low enough concentration and/or the NGL stream is small enough then non-regenerable adsorption may be economically justifiable because of the low capital cost of implementation. The costs and technical viability of non-regenerable adsorption is dependent upon the specific application; so a limit to the amount of a sulfur compound for which removal by non-regenerable adsorption is economically viable is not obvious. However, for applications where the amount of sulfur to be removed is less than roughly a few hundred pounds per day non-regenerable adsorption should be considered.

- *Presence of existing amine plants and a Claus unit.* Some of the options discussed here produce an acid gas stream, either from the regeneration of an adsorbent, or from the regeneration of an amine. The installation of a regenerable adsorbent or an amine unit for NGL treatment would be favored if there are existing amine and Claus units that could accept the acid gas stream.

- *Other disposition route for acid gas.* Even if an amine and Claus plant does not exist at the facility, it still may be possible to route an acid gas stream created by amine or adsorbent regeneration to an acceptable location. An example of this is for some CO_2 recovery plants, acid gas recovered from NGL treatment can sometimes be combined with the compressed recovered lean CO_2. Another example is to consider if the acid gas can be disposed of by subsurface injection. Overall, the ability to dispose of a acid gas stream in an economical fashion is an important consideration in technology screening. Although systems can be built to dispose of the acid gas streams, the cost of such units (e.g. Claus) would result in a significant economic penalty to those NGL treatment technologies that produce an acid gas stream.

Case Study

The following is a case study for a generic NGL stream generated from an EOR CO_2 recovery process, as a distillation bottoms stream in an NGL recovery unit. The composition and conditions of the off-spec NGL stream are shown in Table 2. Based on this composition and flowrate, various options for treatment were considered to yield an NGL product that meets Y-grade specifications.

Considering the Y-grade specifications of concern listed in Table 1, the treatment needs for this stream to consider are reduction of H_2S, COS, and total sulfur. The impact of the treatment options on the stream hydrocarbon characteristic, CO_2 content, and water must also be considered in the options evaluation.

Table 2 – Case Study Basis

Case Study NGL Treating Inlet Conditions		
Temperature	°F	100
Pressure	Psig	300
Flow rate	lb/h	30,000
Components	Mole %	
C3	24	
iC4	13	
nC4	28	
iC5	11	
nC5	10	
C6+	14	
H2O	Dry	
Components	ppmw	
CO_2	<<1	
H_2S	1 - 2	
COS	650	
Methyl Mercaptans	100	
C2+ Mercaptans	150	
Other Mercaptans	150	

Treatment Options Development

Several treatment options for meeting the Y-grade pipeline specification can be considered for each contaminant; these options are described below.

COS Removal

The COS content of this stream greatly exceeds the Y-grade specification. The COS removal methods considered in detail for this case study include catalytic hydrolysis, KOH/methanol reaction, amine (DGA®) absorption, and regenerable adsorption. Other removal methods, such as using other amines like DIPA, may be feasible but were not considered in detail.

H_2S

Although the level of H_2S is low in the NGL, it is still at a concentration (1 - 2 ppmw) that could result in failure of the copper strip test. Additionally, some of the COS treating processes may produce H_2S, so the removal of H_2S must be considered. The technologies considered for H_2S removal include caustic wash, amine treating, and regenerable adsorption. H_2S removal could

have been done with non-regenerable adsorption, but this was not included because in all of the options considered H$_2$S was removed as a "byproduct" of a different treatment technology.

Mercaptans

Mercaptans in the NGL stream will likely cause the stream to exceed pipeline specifications for total sulfur. A (non-regenerated) caustic wash may be considered for removal of the mercaptans. But due to the relatively large amount of mercaptans that need to be removed (about 300 lb/day), a regenerable caustic wash system would both reduce spent caustic disposal costs as well as being more effective in removing more of the higher mercaptans that may be present.

Some of the other technologies considered, will likely achieve some mercaptan removal. KOH/methanol and amine treating with DGA$^®$ will likely remove some of the mercaptans, but it neither appeared to be capable of achieving the depth of removal of mercaptan desired, therefore a regenerable caustic wash was assumed to follow these other technologies.

Water

The NGL stream for this case is dry before treatment, however; some of the technologies used to remove some of the sulfur containing species will result in water saturation of the treated NGL stream. The solubility of water in NGL decreases with decreasing temperature. So, even if any free water is decanted from the treated NGL, if it is cooled *further* to 34°F some water would phase separate. The Y-Grade specification states no free water at 34°F; therefore, drying of the final product may be required for some options.

Technical Evaluation – Summary of Treatment Schemes

The goal of the NGL treatment is to reduce COS, mercaptans, and H$_2$S concentrations while not introducing any other significant contaminants, so that the NGL meets Y-grade pipeline standards.

Several sulfur removal technologies discussed earlier were not further considered as part of this case study, including the following.

- Caustic wash (non-regenerable) is most economical when removing trace amounts of H$_2$S and methyl and ethyl mercaptans at low levels and thus would likely be less uneconomical in removing the high levels of mercaptan for this case. However, caustic wash is included for trace H$_2$S removal prior to a regenerable caustic wash process.

- Non-regenerable mixed metal oxide adsorbents have been reported by some vendors to be capable of removing many of the organic sulfur species in the NGL, although the required operating conditions (e.g., temperature) may need to be adjusted. However, in general the use of these relatively expensive non-regenerable materials to remove over 700 lb/day of total organic sulfur compounds was assumed to be economically prohibitive when compared to other regenerable technologies.

- Hydrodesulfurization would be an effective way to remove all of the organic sulfur from this stream. However, given the high capital cost of this technology and the lack of a hydrogen source, hydrodesulfuration was ruled out.

Five different conceptual processing schemes were developed using various combinations of the aforementioned technologies, and these four schemes were then compared with respect to technical and economic feasibility.

Option A

Option A is a COS hydrolysis bed followed by a regenerable caustic wash (RCW) for mercaptan removal (Figure 2). The RCW unit includes a (non-regenerated) caustic prescrubber for removal of H_2S and CO_2 that is produced in the COS hydrolysis. Examples of commercially available RCW processes are Merichem's THIOLEX® with REGEN® and UOP's Merox®. Merox® was the primary RCW process considered in detail for this application.

Water would be added to the raw NGL, and the stream passed through one or more COS hydrolysis beds. The hydrolysis would convert the COS to H_2S and CO_2, so the NGL from this step would contain H_2S, CO_2, mercaptans, and water as the primary contaminants. H_2S and CO_2 when scrubbed into caustic are not regenerable in the Merox® process, so a caustic pre-scrubber is used to remove the CO_2 and H_2S from the NGL prior to the main Merox® process. The amount of H_2S and CO_2 generated by the COS hydrolysis is actually quite substantial – about 600 lb/day of CO_2 and H_2S total – so caustic requirements for the prescrubber would be substantial.
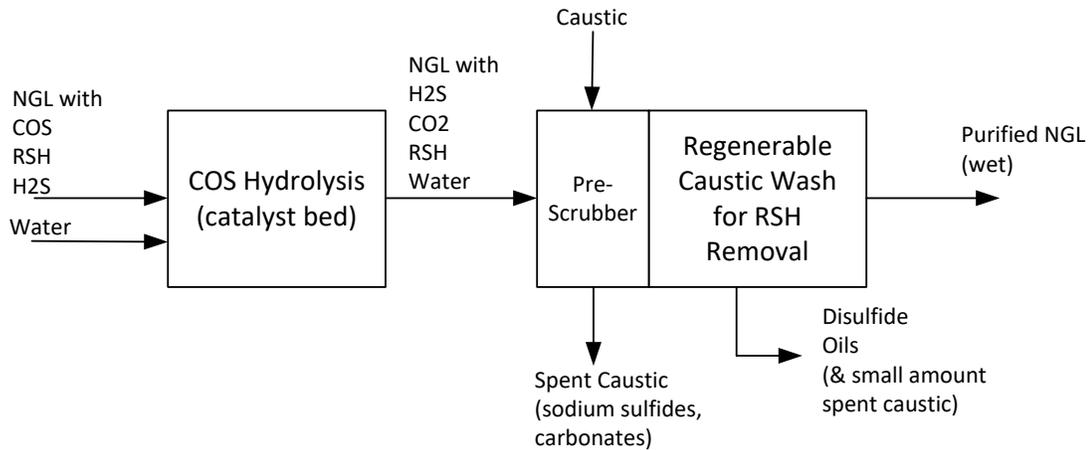

Figure 2: Option A - COS hydrolysis, Caustic Pre-Wash, and RCW

The disulfide oils generated in the Merox® process would be sent for disposal, sent to a hydrotreater, or sold as a specialty product. The spent caustic stream from the prescrubber would also have to be disposed of. The purified NGL from the Merox® unit would contain some water, and drying would be required to meet the Y-grade specification.

Option B

If the amount of H_2S and CO_2 generated in the COS hydrolysis in Option A cannot be treated with a simple caustic wash – due to technical issues and/or the cost of caustic and spent caustic disposal – an amine treater can be considered as a replacement for the prewash. Option B shown in Figure 3 depicts replacing the caustic pre-scrubber part of the RCW unit with an amine treater

using DEA, DGA®, or DIPA to remove the H_2S and CO_2 before the Merox® unit. This option creates an acid gas stream that will require disposition. The feasibility of the application of the amine treater will likely be dependent upon the ability to deal with the acid gas stream at the subject plant. The most common would be a Claus type sulfur plant or acid gas injection.
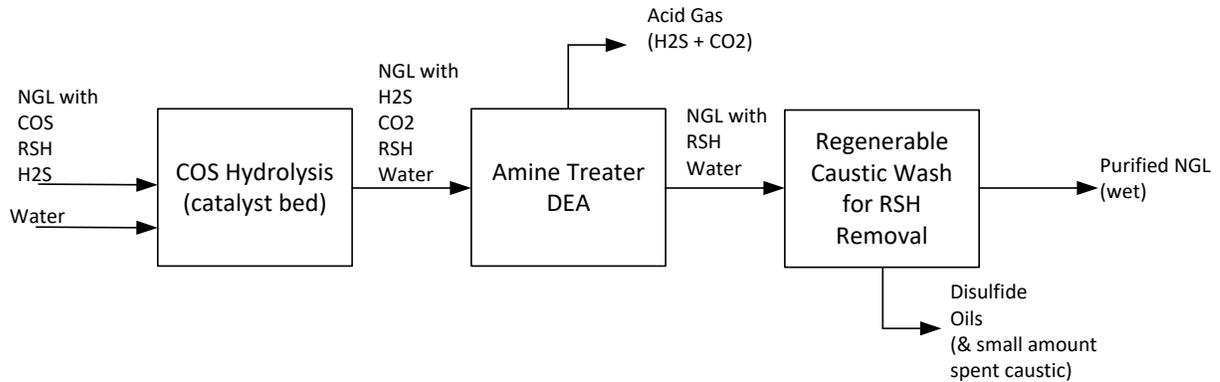
Figure 3: Option B – COS hydrolysis, Amine Treater, and RCW.

Option C

Option C shown in Figure 4 uses an amine treater to remove COS (and any residual H_2S and CO_2) from the NGL, followed by an RCW unit for mercaptan removal. The amine system is assumed to be DGA® with a reclaimer, which allows for efficient COS removal. Another amine that is believed to have some capability for COS removal, but may not require a reclaimer, is DIPA; therefore DIPA could also be considered in this scheme. The acid gas stream from the amine unit would primarily be H_2S and CO_2, and would have to be handled in some other process, so the viability of this option is also strongly site/plant specific.
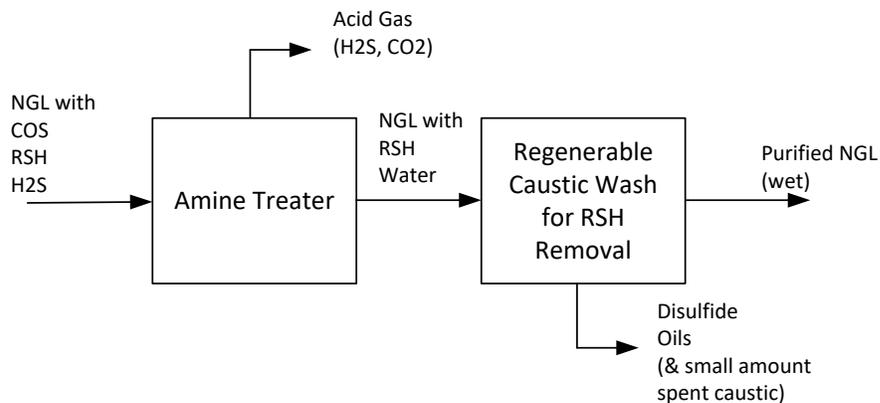

Figure 4: Option C – Amine Treater with RCW.

Option D

Option D shown in Figure 5 depicts the concept of using a regenerable COS adsorbent, such as Selexsorb COS®, to remove COS and H_2S upstream of a mercaptan removal unit. A heated sweet

gas would be required as a sweep gas for the regeneration, which creates a regeneration off-gas stream containing the H_2S and CO_2; the regeneration off gas would require disposition. Due to the large amount of COS in this NGL stream and the low COS specification in the treated NGL, one adsorbent vendor offered that the use of regenerable adsorption would be difficult to economically justify, although it would be justifiable if the COS concentration was much lower than that assumed in this study. In this concept the designer would also have to take into consideration the cyclical/irregular flow rate and composition of the regeneration gas from the Selexsorb COS® unit, and its potential impact on its disposition method.
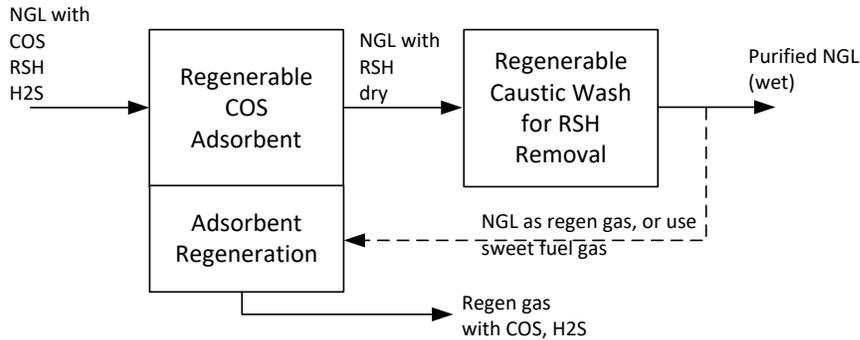
Figure 5: Option D – Regenerable COS Adsorption, with RCW.

Option E

Another option for removing COS (along with H_2S and CO_2) prior to an RCW unit is to use the KOH/methanol process. In this option, some methanol is added to the NGL and it is passed through a bed of solid KOH. The KOH bed would require occasional replacement, and a small aqueous KOH stream with other salts would be decanted from the KOH bed during operation. The KOH bed would likely remove some of the mercaptans, but it is not known if it would remove mercaptans to the level required by the Y-grade specification. It is possible that by sizing the KOH bed larger than required for COS removal could result in the attainment of sufficient mercaptan removal, but there does not appear to be data available in the literature to suggest a design practice. Therefore, it is assumed that a regenerated caustic wash unit would be placed downstream of the KOH bed to remove mercaptans; the RCW unit would not require a prewash because the KOH bed should remove all of the CO_2 and H_2S from the NGL.
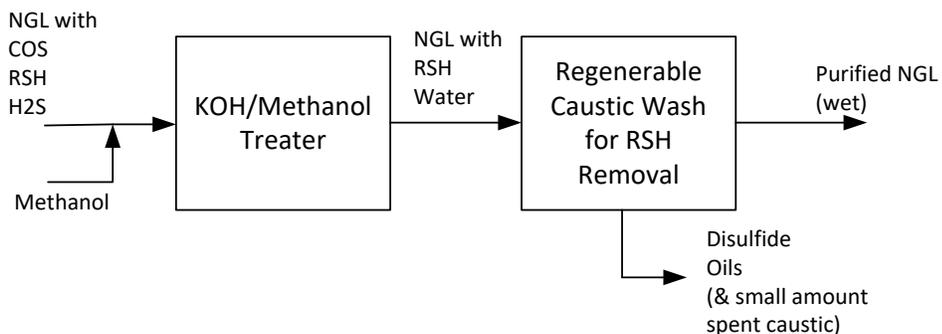
Figure 6: Option E – KOH/Methanol Treater, with RCW.

Economic Factors

Many of the details of the process technologies considered in this paper are proprietary to the vendors, thus common economics variables like cost/unit of hydrocarbon treated or cost/lb sulfur removed are difficult to define in a generic fashion. Additionally, costs are highly dependent upon other factors. As previously described the existence of a route for handling an acid gas adsorbent or amine regeneration stream is economically important: a plant with such a route can dispose of the acid gas regeneration stream at little cost, while a plant without such a route would have to add significant additional equipment and costs to handle the stream. Therefore, it will not be attempted to specify any costs in detail, since they would be situation dependent, and could portray an incorrect conclusion for other situations. However, there are economic factors to be considered that can help determine which options are best to promote to further evaluation.

All of the schemes considered include a regenerated caustic wash unit, typically place at the end of the treatment train. Some of the intermediate technologies, such as the amine treaters and the KOH/methanol process would remove some of the mercaptans, but the removal efficiencies are not (for this case) known to be high enough to displace the RCW unit. Limited information for the removal of mercaptans by the KOH/methanol process is available and in the absence of data it may be deemed necessary to approach the development of a treatment scheme conservatively.

Option A utilizes COS hydrolysis that results in the generation of H_2S and CO_2 that must be removed before the stream is treated for mercaptans. If the quantity of H_2S and CO_2 generated in the hydrolysis is small (due to a small COS amount in the feed), a non-regenerated caustic scrubber upstream of a Merox$^{®}$ unit (Option A) is likely to be feasible and the economic penalty of the non-regenerated caustic scrub would be low. However, if the quantity of H_2S and CO_2 is relatively high, as is the case in this example, the operating cost of a caustic scrubber (i.e. caustic consumption and spent caustic disposal) may be high enough to make economic justification more difficult. For this case the non-regenerable caustic prewash would consume over one half ton per day of NaOH, and also produce a substantial volume of spent caustic.

Depending upon the cost of caustic and spent caustic disposal, one might also consider using an amine treater downstream of the COS hydrolysis (Option B); the relatively high operating costs associated with the caustic prewash would be replaced by the higher capital cost, but lower operating cost, of the amine. However, an amine treater would generate an H_2S/CO_2 stream from the regenerator/reclaimer that could require additional unit operations. For applications where the acid gas can be slipped into another stream, as might be the case at a EOR CO_2 recycle facility or at a larger gas treatment facility, then the amine approach might be merited.

The KOH/methanol process requires roughly equimolar amounts of KOH and methanol to COS. Residual CO_2 and H_2S will also be removed, requiring a 2:1 stoichiometric KOH ratio; mercaptans may also consume some KOH. If Option E is compared with Option A, it can be concluded that the molar consumption of base for Option E (in the RCW prewash) will be lower than Option A by greater than a 2:1 ratio, albeit the base used in Option E (KOH) is more expensive than that used in the caustic prewash (NaOH) in Option A. The factor that might favor the KOH/methanol process over the COS catalytic hydrolysis is when the amount of COS to be removed is high. The COS catalytic hydrolysis process is simpler and less maintenance intensive, whereas the KOH process requires routine change-outs of the KOH bed and draining and disposal of the concentrated KOH/salt solution.

Conclusions

The treatment of NGL for the removal of contaminants can be a complex endeavor, particularly when large amounts of a variety of sulfur species are present. A number of strategies can be considered, the first of which may be the evaluation of upstream gas processes to determine if these processes can be modified to minimize the NGL treatment requirement. It is not reasonable to identify best technologies or combinations of technologies for the removal of specific sulfur compounds; the selection of technologies may be dependent upon other systems that are available at the facility, the amount of the sulfur compounds being removed, and other factors. This paper outlined the characteristics, advantages, and disadvantages of the processes that can be used in NGL treatment, and the other factors that are important in technology selection; the example schemes considered in this paper should be of use in helping NGL treaters select the best treatment processes from both technical and economic perspectives.

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