

Challenges with the Transition to Biofuels

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Introduction

Sour water can be found in most industrial facilities including refineries, gas plants, power plants and chemical factories. Depending on the source of the water, the components in the sour water will be completely different.

In a sour gas processing facility, the sour water typically originates as either produced water or condensed water and may contain low levels of H₂S and CO₂ as well as salts and hydrate/corrosion inhibitors. Any condensed sour water is normally salt-free, however may contain carry over products from the production cycle, such as amines, glycols, methanol and other items that may have been injected into the process.¹

In an oil refining facility, the sour water can originate from desalters and processing units, such as the Fluid Catalytic Cracker (FCC) or hydrotreaters, as well as amine and sulphur recovery units (SRU), including the Tail Gas Treatment Unit (TGTU). These sour water streams distinguish themselves from a gas processing facility sour water streams through their higher hydrogen sulphide (H₂S) content, the presence of large amounts of ammonia (NH₃) and the much larger volumes that need to be processed.

The processing of these sour water streams in a sour water stripper has been well-documented in literature^{2,3} and it is not the intent of this article to go into design details of these units or what can be done with the stripped water. The focus of this article is to discuss the impact that sour water stripping technology selection may have on the produced sour gas streams, also called sour water acid gas (SWAG). As well, the article covers the options available to process these gases, considering the current shift in the industry to produce biofuels instead of conventional oil products.

Conventional Sour Water Stripper Acid Gas processing

Sour water produced in a plant where no ammonia is present, such as a gas plant, typically contains very low concentrations of H₂S and CO₂ as neither gases dissolve in high concentrations in the sour water based

on Henry's law. One can expect concentrations in hundreds of ppmwt. As a result, the SWAG flow rates are very small, and, in most facilities, will be routed to the flare directly, where they may add a small amount of SO₂ to the environmental emissions.

This is not the case in refineries where a large portion of the nitrogen present in the crude oil is converted to ammonia in the hydroprocessing units. Due to the rapid dissolution of ammonia in water and the formation of ammonium bisulphide in water, with equimolar amounts of ammonia and H₂S, the sour water will contain high concentrations of ammonia and H₂S. There are usually two different methodologies for removing the H₂S and ammonia from the sour water. In Figure 1, a typical process flow scheme for a single stage sour water stripper is provided. This configuration removes both ammonia and H₂S from the water to produce a SWAG stream containing about one third H₂S, one third ammonia and one third water.

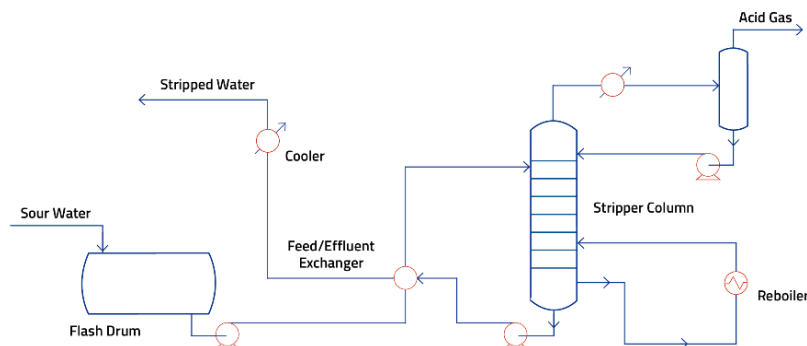


Figure 1. Process flow scheme of a single-stage sour water stripper

Some facilities may elect to segregate the ammonia and H₂S in a two-stage sour water stripper. This results in a high purity ammonia product, which can be sold as anhydrous or aqueous ammonia and a high purity H₂S product, which is processed in an SRU. Alternatively, the segregated ammonia can be destroyed in a CO boiler or other furnace. It can also be routed as a separate feed source to the SRU, which is often the destination for SWAG from a sour water stripper in a refinery environment. In Figure 2, a typical configuration for a two-stage sour water stripper is provided.

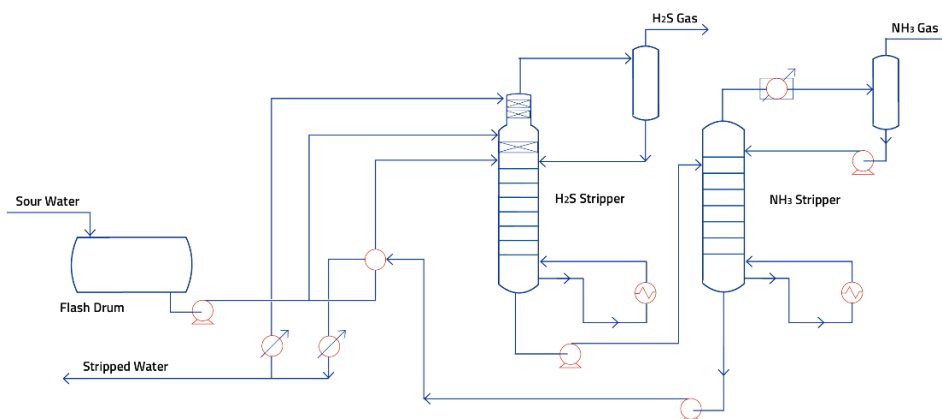


Figure 2. Process flow scheme of a two-stage sour water stripper

The traditional method to process SWAG in a refinery is in the thermal stage of the SRU. Due to the potential for ammonia to form salts with H_2S , CO_2 and SO_2 in colder sections of the SRU, it is essential to destroy the ammonia to a very high level (<50 ppmv). This is normally accomplished in the thermal reactor by integrating the three Ts into the design: Temperature, Time and Turbulence.

The turbulence portion can be accomplished by installing a high intensity burner to provide good mixing of the acid gas streams and air/oxygen. A minimum temperature of $1300^{\circ}C$ is recommended for the destruction of ammonia. This can be done by designing the SRU with air and acid gas preheat or by installing a front-side split thermal reactor, where a portion of the amine acid gas bypasses the main burner, thereby artificially raising the air stoichiometry in the front zone to provide a higher temperature. It is recommended to limit the bypass of amine acid gas to the second zone of the thermal reactor such that the front zone remains a reducing environment as oxidizing conditions can impact the integrity of the refractory. And finally, time is simply a matter of residence time in the thermal reactor. It can range anywhere from 0.8 seconds to 2 seconds depending on the ammonia concentration in the mixed acid gas or the presence of hydrogen cyanide.

The impact of biofuels on how to process sour water acid gas

With the emergence of biofuels facilities, there are new challenges with respect to sour water strippers and where and how to process the sour water stripper acid gas that is produced.

There are essentially two different methods for processing biofeedstocks in refineries.

In the first case, biofeedstocks are co-processed with conventional hydrocarbon feedstocks. This results in somewhat modified SWAG streams, without much of an impact to the downstream SRU where the SWAG is processed. Similarly, the impact on the performance of a two-stage sour water stripper to segregate ammonia and H_2S is also marginal.

The second method is a standalone biofuels facility, for which the most common technology chosen nowadays is the application of hydrotreating. In this process, water is produced due to the oxygen atoms in the biomass feeding the hydrotreater, and some wash water may be required to remove any ammonia produced in the unit. As biomass is typically very low in sulphur, these sour water streams will not have the traditional equimolar ammonia and H_2S composition but will contain much higher concentrations of ammonia compared to the H_2S . These water streams may also contain a substantial amount of CO_2 . In addition to the change in the sour water composition, due to the absence of sulphur components in the feed, there is usually no large amine acid gas stream associated with the unit, which traditionally would be fed with the SWAG to the SRU. As a result, in most cases these facilities will not have a SRU, which makes the question of where and how to process SWAG more important.

So, what options are there to deal with SWAG when there is very little amine acid gas available and there is still a requirement to meet certain environmental limitations for SO_2 emissions? The key is how to deal

with ammonia. Ammonia by itself is a very dangerous product with a TLV of 25 ppmv and cannot be released to atmosphere without destroying or removing it first.

Due to the presence of H₂S, even though in smaller quantities than for conventional refineries, the treatment of the SWAG will need to be combined with the removal of the H₂S before effluents can be sent to the atmosphere.

The first option discussed here is to route both SWAG and the amine acid gas that are produced together to a thermal oxidizer. Due to the presence of ammonia, the thermal oxidizer design needs to be modified to ensure that full ammonia destruction can occur, and the formation of NO_x is limited. This will require special thermal oxidizer technologies like the John Zink Noxidizer or the LD Duiker SCO technology. The custom designed thermal oxidizer employs a staged process, whereby NH₃ destruction is achieved in a reduction chamber with a high-temperature and sub-stoichiometric environment to prevent NO_x formation. The gases from the reduction chamber are quenched before entering the oxidation chamber where air is injected to complete combustion. A fire tube waste heat boiler provides heat recovery and cooling of the flue gases. Due to the presence of H₂S in the SWAG, SO₂ is produced and can be removed using a flue gas desulphurization technology, which in most cases uses caustic to meet the environmental targets. The absorbed SO₂ is typically converted to a sulphate by introducing air in the waste stream and routed to a wastewater treatment facility.

Alternative technologies such as Eutectic Freeze Crystallization could be considered to produce a solid product instead of a wastewater stream. Depending on the amount of sulphur present in the sour water and amine acid gas streams, the consumption of caustic in this configuration could lead to high operating costs. Figure 3 shows the process scheme for this line up.

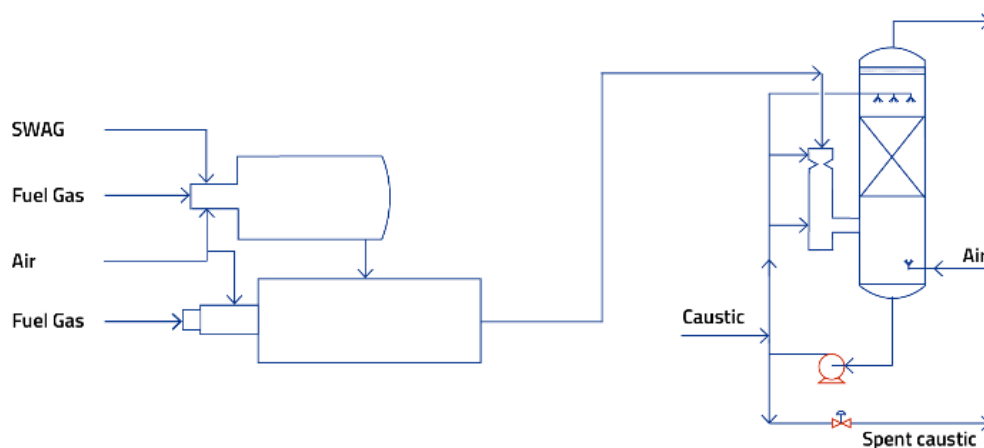


Figure 3. Process flow scheme for Ammonia-burning Thermal Oxidizer with Scrubber

An alternative methodology for dealing with the ammonia in SWAG is to install an Ammonia Scrubbing System (ASS) which is designed to remove ammonia before it is routed to an H₂S scavenging unit.

The Ammonia Scrubbing system consists of a dual stage absorption system designed to remove 99.9% of the ammonia from the gas stream. In this unit, the gas is passed through two towers where the gas is contacted with an acidic scrubber solution to remove the ammonia by forming ammonium bisulphate or ammonium sulphate in solution. As the H_2S in the gas phase is a weak acid, it will not be picked up by the scrubber solution, which is a strong acid. The remaining gas will contain mostly H_2S and CO_2 and can then be processed together with the amine acid gas (if present) in an H_2S scavenging system such as LOCAT, Thiopaq or Sulfatreat. The process scheme for this solution is provided in Figure 4.

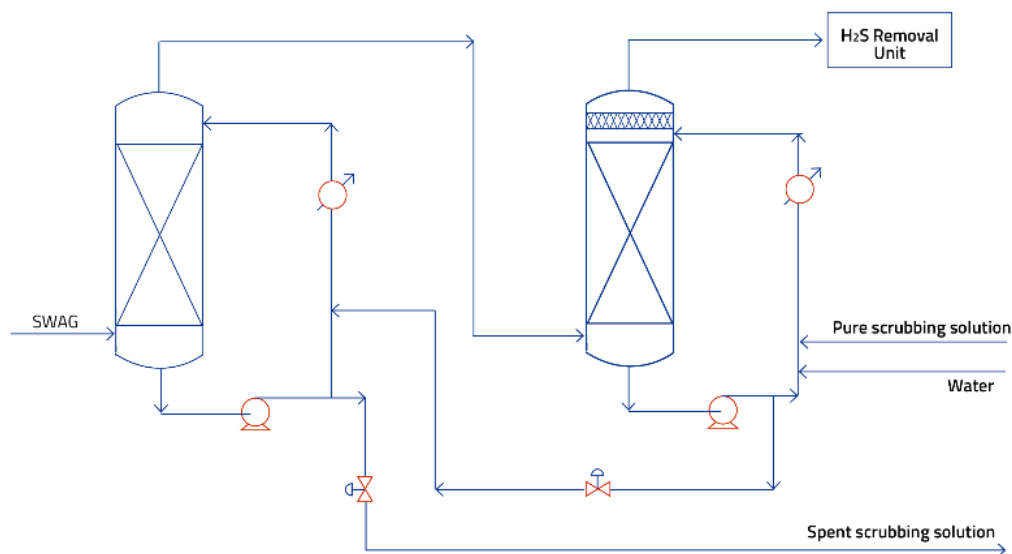


Figure 4. Process flow scheme for acidic removal of ammonia prior to sulphur scavenging unit

For a biofuels facility, the primary key for processing sour water and SWAG is how to integrate the processing with the available infrastructure that may or may not be present.⁴ It is pretty much always the preference to use the existing sour water stripper(s) and SRU to manage the new sour water and/or reduced SWAG flow rates. In the case of a full conversion from conventional oil processing to bio feedstock, the acid gas flows may be insufficient to maintain proper operation of an existing and likely oversized SRU. In that case, the economics of the above mentioned two configurations need to be evaluated for CAPEX, OPEX and integration into existing infrastructures of caustic supply as well as ability to handle the waste streams from the units.

Conclusion

With the emergence of the (co)processing of bio feedstocks in hydrotreaters, the balance of amine acid gas and sour water acid gas produced in refineries is swinging more to the SWAG side. This results in a requirement to re-evaluate how to process this SWAG.

For co-processing, the impact on the existing sulphur block is typically limited to a debottlenecking of the existing sour water system with minimal impact on the SRU.

In standalone biofuels facilities, alternative methods may need to be explored on how to handle SWAG in combination with the required SO₂ emissions. Ammonia is the key component to deal with and in absence of the SRU thermal stage requires alternative methods for removal with additional waste streams.

References

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