DELIVERING A GREENER PRODUCT

Michael F. Ray and Michael J. Ray, ThioSolv, USA,
discuss the use of refinery sulfur processing in anaerobic digester gas clean-up.

With concerns about climate change and carbon dioxide (CO_2) emissions on the rise, many countries are shifting towards renewable fuels. One source of renewable energy that is becoming more widespread is biogas, particularly from anaerobic digestion. As of January 2023, 20 000 full-scale anaerobic digestion systems are operational around the world, and it is estimated that 1000 new projects are being built per year.[1] These biogas streams, as with most natural gas streams, contain hydrogen sulfide (H_2S) which must be removed from the biogas in order to maintain low sulfur emissions. Anaerobic digesters also produce a liquid byproduct known as digestate that contains ammonia and H_2S. This needs to be removed and processed before reuse or discharge of the water. Air stripping or steam stripping the ammonia from the water is a technique that is often used. This produces a stream with concentrations of ammonia of less than 1%, and H_2S of fractions of a percent. Ammonia and H_2S must be removed for discharge into waterways.

Because biogas has similar contaminates to natural gas or refinery off-gas streams, process technologies from the oil and gas industry can be explored for treating biogas. However, there are limitations due to the differences in equipment and production outputs.

Traditional technologies used in refining, such as Claus units, may not be practical, considering the small H_2S output of the biogas plants. The use of amine units is becoming more common for the removal of H_2S and CO_2 from the biogas, but the H_2S remains with the CO_2 and needs to be further processed. Iron sponge is common in H_2S removal in the biogas industry, but still requires further handling of the pyrophoric spent material before it can be disposed of or the remaining sulfur can be land applied.

Processes from the refining industry can be used to treat the anaerobic digestate. Refineries strip the ammonia from sour water streams using a sour water stripper, a technology that is very efficient at removing the ammonia and H_2S in the water to very low levels. In biogas applications, the sour water stripper can provide a discharge stream of water that can be low enough in ammonia and H_2S for discharge into a waterway. A sour water stripper would be a great choice for a larger digestate operation but may be not be practical for a smaller operation.

In anaerobic digesters, the biogas and digestate ratio of ammonia to H_2S highly favours ammonia in almost all cases. After stripping the sour ammonia gas from the digestate and sour CO_2 streams from the digester's biogas, one option is to convert the streams into ammonium thiosulfate (ATS) – a nutrient-rich green fertilizer. Processes such as SWAATS (patented), SimpliSWAATS or BioSWAATS (patents pending) can be used in most large or small digester gas streams. To provide the stoichiometric balance in the processing of the gases to ATS, purchased sulfur will likely need to be oxidised to provide sulfur dioxide (SO_2) for the process. The required ratio of sulfur to nitrogen in the ATS [$(NH_4)_2S_2O_3$] is 1:1, which can be achieved by using sulfur or ammonia as necessary for the balance.

SimpliSWAATS is a process that has been previously used at Transmix facilities, for processing H_2S and small amounts of ammonia contained in a gas stream at process pressure, producing ATS. A Transmix facility processes

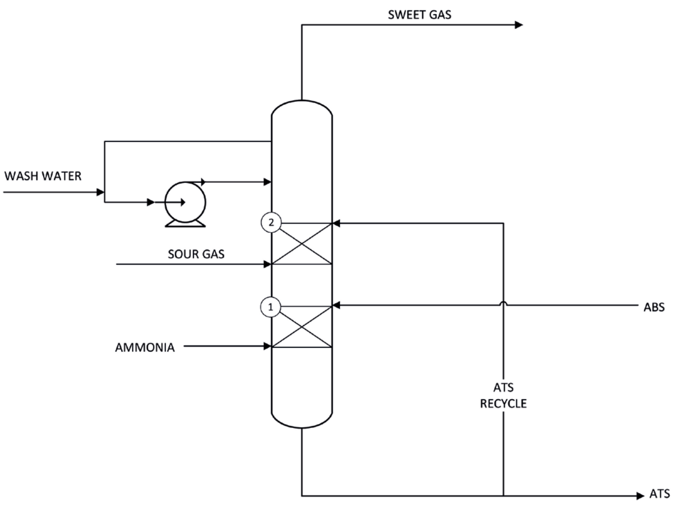

Figure 1. A block flow diagram of the SimpliSWAATS process.

various grades of diesel and kerosene that are transported through a common pipeline and no longer meet one specification. The SimpliSWAATS process selectively removes the H_2S and ammonia from the gas stream and converts it to ATS. It creates the ATS by adding ammonium bisulphite (ABS) and the necessary supplemental ammonia to react with the H_2S and create the ATS. Reaction 1 outlines the stoichiometry of this process:

$4NH_4HSO_3$ [ABS] + $2NH_3$ + $2H_2S \rightarrow 3(NH_4)2S_2O_3$ [ATS] + $3H_2O$ (1)

The ABS can be purchased as a 70% aqueous solution and added directly into the process, or produced by reacting SO_2, ammonia and water. Reaction 2 occurs in the latter case:

$NH_3 + SO_2 + H_2O \rightarrow NH_4HSO_3$
(2)

SO_2 can be produced by combusting molten sulfur or H_2S, or can be purchased as a reagent. One major advantage of purchasing the ABS directly is the removal of the capital cost requirements for a burner, and the removal of the need to purchase SO_2 gas. The ABS solution typically has a pH range of 4.8 – 5.2 in the commercial grade. However, ABS can be made in situ if there is a source of excess ammonia or the operator is willing to purchase the ammonia. To produce ABS, SO_2 is added in a 1:1 molar ratio to the excess NH_3; or NH_3 is added in a 1:1 molar ratio to the excess SO_2. It is important to keep the circulating solution operating between 4.5 – 5.1 pH.

The sourcing of the ammonia will be different depending on the size of the digester. For larger digesters, adding a sour water stripper to remove the ammonia and H_2S may be necessary. For smaller digesters where a sour water stripper or an air stripper may not be practical, the digestate can be filtered to separate the ammonia and H_2S into a liquid stream and remove the solids and other substances.

The SimpliSWAATS process starts by taking the gas, which can be at its current pressure and temperature. Near-atmospheric pressures will work for the process, but a higher pressure will allow for smaller sized equipment than a lower pressure gas. The licensee of the process will have to determine the cost benefit analysis of raising the design pressure if necessary.

The biogas to be processed passes through a circulating solution containing ABS and ammonium sulfite. A portion of the circulating solution is sent to be mixed with a solution containing a higher ABS concentration and lower pH. The ABS in circulation lowers the pH of the circulating solution. The solution that mixes into this circulation will have a higher pH, creating a high sulfite to bisulfite ratio. Additionally, the gas exiting the first contactor will contain a small amount of ammonia. These sources of ammonia raise the pH of the circulating solution. The ABS added has a pH of approximately 5.0 from production and most commercially-available sources. A 6.1 – 6.3 pH at the top of the circulation is the target to control the process and minimise emissions; operating below 5.5 pH could cause the ATS to decompose within the solution; a pH below 5.9 means that there is a potential for increased SO_2 emissions; a pH of above 6.3 means that there is a potential for increased ammonia emissions.

Between the two is the best operating pH to minimise overall plant emissions. Using these pH guidelines as an indication, the ATS is formed in the solution as the H_2S is reacted from the gas. This ATS solution will eventually reach a salt concentration of around 60% by weight, and it can then be sold and marketed as ATS fertilizer. The ATS product is usually a clear or slightly yellow liquid and may have a slight smell of ammonia or SO_2. The final liquid product will typically have a specific gravity of around 1.34, and a pH of 7.0 – 7.5. The circulating solution is usually around 50 – 100 times more volume than the product draw.

At the top of the reactor column, a circulating water solution is used to scrub out any of the remaining ammonia and SO_2 from the gas stream. From there, the gas can be reinserted into the process with on-spec H_2S and SO_2 concentrations.

The SimpliSWAATS process, along with other processes in the SWAATS family, has a number of advantages. There are no side streams or waste streams produced in the process. The only streams that exit the process are the fertilizer and the sweetened gas stream. The stripped water from upstream is available for reuse or discharge. There are no catalysts in the system, or other materials that are consumed and disposed of in the reactions. The process can be conducted at relatively low pressures and temperatures, which allows for the equipment to have lower design pressures and temperature and reduces the potential for hazards. Another major advantage of the SimpliSWAATS process is the production of a marketable fertilizer. This enhances the return, as the fertilizer can be sold on the market to help offset the cost of operation.

BioSWAATS operates in a similar manner, the primary difference is that biogas is used as a feed instead of a gas stream from a fossil fuel-based source, and the ammonia in the reaction is stripped from the digestate. It allows for the creation of organic ATS, which can be used to grow organic crops, with any excess ammonia being used to either enhance the nitrogen level of the fertilizer, or further processed to produce additional ABS.

In the case of a small biogas application, BioSWAATS has other advantages over typical sulfur removal processes in the industry. The process can use the liquid from the anaerobic digester to treat the H_2S, and using ammonia entrained in the digestate. In filtered digestate from small digesters, SO_2 can be added to the system to create ABS and ATS.

For larger digesters, the entrained ammonia and H_2S may need to be air stripped or may require a sour water stripper. SO_2 can be added to the air stripper gas or sour water stripper gas. For either system, the ABS can in turn be used to treat the biogas. Another major advantage of producing ATS using this method is that it is possible to produce ATS without the use of fossil fuels. This could lead to the ability to produce and market organic fertilizer, which could then potentially create a higher market value for the fertilizer as the demand for organic produce continues to increase there.

Conclusion

As the biogas market emerges, a quality process for removing the H_2S from the final product is necessary in order to keep emissions low. While processes that have been used in the traditional oil and gas industry are a great place to start in the design process, the relatively smaller size of the equipment and output capacity may make some processes impractical. Processes that have worked historically in the refinery process, and work in both large-scale and small-scale digesters, are the sour water stripper, amine unit and the SimpliSWAATS process. BioSWAATS can treat ammonia and H_2S emissions from biogas and digestate while producing a quality ATS fertilizer – ultimately achieving a greener product.

Reference

1. SIMET, A. and FLETCHER, K., 'Biogas Advances in the US', *Biomass Magazine*, (27 January 2017).

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Contact:
Michael J. Ray
(210) 870-0291
michael.j.ray@thiosolv.com
www.Thiosolv.com