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ARTICLE

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TO EACH PROJECT ITS UNIQUE SOLUTION!

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SSWEET
Sulfurex Selection Work Expert Tool
How to select the right DMT desulphurization technology

Keywords
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1 Introduction

Biogas streams from fermentation processes of organic matter normally contain hydrogen sulfide (H_2S). H_2S is a colorless and toxic gas that has a strong odor of rotten eggs. It forms flammable mixtures in air in the range of 4.5 – 45.0 % vol. and its combustion leads to sulfur dioxide emissions (SOx), which have harmful environmental effects. H_2S is corrosive to most equipment (pipelines, compressors, storage tanks, engines, etc.) and decreases the lifetime of CHP units. Therefore, H_2S has to be removed due to potential mechanical, environmental and safety reasons. DMT Environmental Technology has over twenty years of experience in desulfurization with a portfolio including Sulfurex® CR (Caustic Reuse), Sulfurex® BF (Biotrickling Filter), Sulfurex® BR (Biological Regeneration) and activated carbon. Since the selection of the best desulfurization technology depends on many factors, such as e.g. site conditions, uptime, final application of the biogas, DMT has developed a tool. This tool is the Sulfurex® Selection Work Expert Tool (SSweet) which helps our clients deciding on the most suitable technology for their projects.

2 Biogas desulfurization technologies

H_2S can be removed in-situ during its anaerobic production in digesters, or from crude/raw biogas before its final application. In digesters, H_2S can be removed by air injection or addition of iron salts/oxides. In the case of raw biogas, desulfurization by physical-chemical separation processes has traditionally dominated the market; however increasing attention has been paid to biotechnological methods in the last two decades for biological degradation of H_2S. In addition, the combination of physical-chemical processes with biotechnological processes have also been developed to combine the advantages of both technologies.

For boilers or engines, the addition of iron chloride or air/oxygen to the digester is the common process for bulk removal of hydrogen sulfide.

In case of simultaneous production of heat and electricity in CPH units, biological processes are commonly used to perform the desulfurization. If concentrations below 100 ppm(v) are required, a post-treatment is regularly required after the biological process. For high concentrations of H_2S, chemical scrubbers are the best suitable choice, with the possibility of integrating a regeneration step to reduce the OPEX.

In the case of biogas upgrading, there are strict regulations on end products such as biomethane, CNG or bio-LNG hence the amount of oxygen in the biogas is a critical issue (e.g. maximum oxygen concentrations of 0.5 % for gas grid requirements). Activated carbon filters are typically used as a pre-treatment to remove H_2S prior to the upgrading process for low H_2S concentrations and loads. For medium or high loads, alkaline scrubbers are normally used, with the integration of regeneration processes at high flows and/or high concentrations. Upgrading technologies based on physical absorption, such as water scrubbers or non-water sorbents, can simultaneously remove H_2S and CO_2, but usually require a pretreatment to achieve low concentrations. Otherwise a post treatment is required to remove H_2S from the exhaust air

3 DMT desulfurization technologies

DMT is aware that no biogas stream has the same properties, and that more than one technology can fit for one project. As a specialist in gas treatment technologies, we offer a wide portfolio for biogas and landfill gas desulfurization purposes.

The principle of the technologies is the absorption of H_2S in a liquid and further oxidization to elemental sulfur or sulfate.

• Sulfurex® CR (Caustic Reuse) is a chemical scrubber in which H_2S is absorbed into a liquid at high pH to enhance the absorption capacity of the solvent, and then further oxidized during the aerobic treatment of the effluent in a wastewater treatment plant (WWTP).

•Sulfurex® BF (Biotrickling Filter) is a biological process in which the H_2S is absorbed in an aqueous solution at low pH and then biologically oxidized to sulfur/sulfate in-situ.

• Sulfurex® BR (Biological Regeneration) is the

combination of Sulfurex® CR with a bioreactor for the biological regeneration of caustic. In the Sulfurex® BR, H_2S is absorbed into a solvent under alkaline conditions, then further oxidized into sulfur in the bioreactor.

The principles of the Sulfurex® products are described in more details in the following chapters.

Sulfurex® CR – Action Reaction

Sulfurex® CR is a chemical desulfurization process specifically designed to treat biogas streams with high concentrations of H_2S, with fast adaptation to fluctuations in gas inlet. The principle of the technology is the neutralization of H_2S by caustic soda according to the following reaction:

$H_2S + NaOH \leftrightarrow NaHS + H_2O$ [1]

However, part of the caustic also reacts with carbon dioxide present in the biogas, producing carbonates:

$CO_2 + 2NaOH \leftrightarrow Na_2CO_3 + H_2O$ [2]

Figure 1 shows a process flow diagram of the process. The main element of the system is one packed column, which is used to increase the contact between the biogas and the caustic solution in countercurrent. H_2S is absorbed into the liquid phase and then reacts with caustic. The technology incorporates an automatic system control to continuously measure the outgoing concentration of H_2S. The dosing of caustic is adjusted to guarantee high efficiency, providing a total control on H_2S outlet concentration.

DMT gives the possibility of adding an extra column, in a double stage process. The spent solvent in the first column is recirculated in the extra column, where the caustic is reused and more H_2S is removed according to the reaction:

$H_2S + Na_2CO_3 \leftrightarrow NaHS + NaHCO_3$ [3]

Both processes can integrate a cooling step for biogas conditioning. Here the biogas is simultaneously cooled down and dried in one step. Since the scrubbing process of H_2S has been proved to be more efficient at low temperature, caustic consumption can be reduced. In addition, dried biogas prevents condensation and mechanical problems during the final application of the biogas. The integration of a second column in addition with the cooling step can save up to 30 % of caustic.

The chemical scrubber is a robust and flexible technology that allows an exhaustive control of the outlet concentration. It is a compact unit which requires low initial investment, but leads to higher operational expenses than Sulfurex® BF due to caustic consumption. Since oxygen is not injected, this technology is suitable for biogas upgrading purposes.

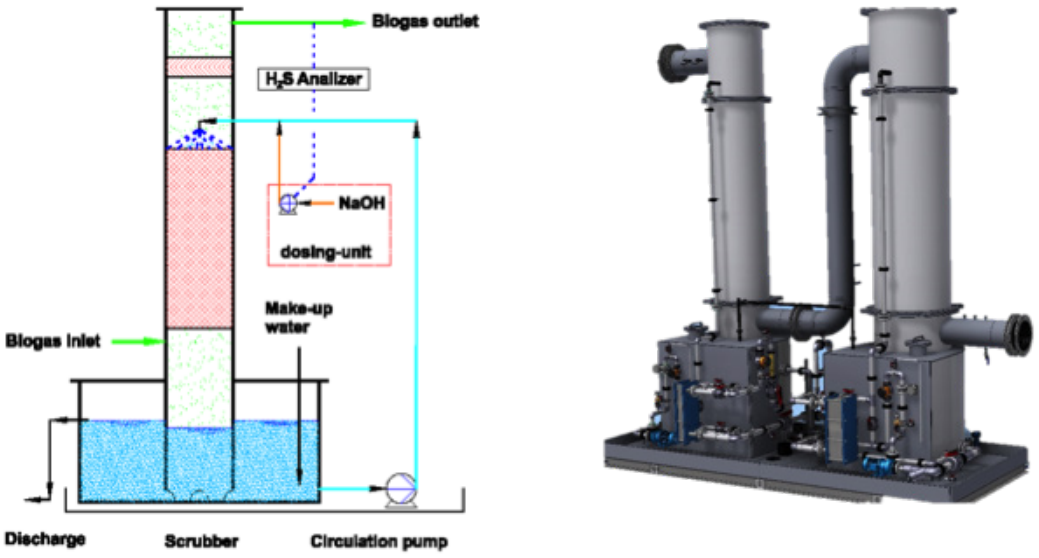

Figure 1. Schematic process of Sulfurex® CR, 1-stage (left). 3-D drawing of a Sulfurex® CR 2-stage (right)

Sulfurex® BF – Let bacteria do the work

Sulfurex® BF is a biological desulfurization technology to remove H_2S from biogas and landfill gas. The principle of the technology is the biological oxidation of H_2S by Thiobacillus bacteria, with the addition of air. Depending on the amount of oxygen available, H_2S is biologically oxidized into elemental sulfur or sulfuric acid according to the following reactions:

$$2H_2S + O_2 \leftrightarrow 2S + 2H_2O \quad [4]$$

$$H_2S + 2O_2 \leftrightarrow H_2SO_4 \quad [5]$$

Figure 2 shows a process flow diagram of the process. The main element of the system is a packed column. The packing material is simultaneously used for attaching the microorganisms and enhancing the contact between the bacteria and H_2S. Water is continuously recirculated and sprayed over the bacteria, and H_2S is absorbed into the liquid phase and then biologically converted. Oxygen is added by an automatic control system, which adjusts the air flow injected, to produce selectively sulfuric acid. The process incorporates a heat exchanger to maintain an optimal temperature. Nutrients are added for the biological growth. The produced sulfuric acid and excess of biomass are removed from the process through the drain.

Sulfurex® BF is cost effective, requires low investment (CAPEX) and provides efficient removal of H_2S (95 % of removal efficiency) without use of chemicals. The system only requires water and nutrients, which leads to low operational expenses. However, the process is not suitable for all applications since the addition of oxygen is limiting the final application of the biogas (such as biogas upgrading).

Sulfurex® BF can be used for biogas and landfill gas desulfurization before its utilization in CHP units for low and medium loads. The main cost of this technology is make-up water and its disposal, so Sulfurex® BF is interesting in locations with easy access to make-up water and disposal, such as WWTP.

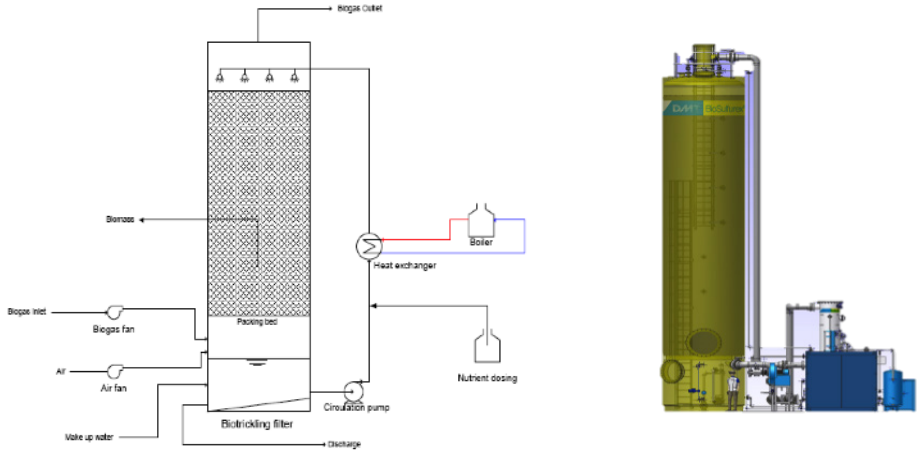

Figure 2. Schematic process of Sulfurex BF (left).). 3-D drawing of a Sulfurex® BF (right).

Sulfurex® BR – Best of both worlds

Sulfurex® BR is a desulfurization process that combines chemical desulfurization at medium to high pH with biological regeneration of the solvent. The system consists of a packed column, a biological reactor and a settler which can be integrated in the bioreactor. Figure 3 shows a basic process flow diagram of a Sulfurex® BR process. In the packed column, an alkali solution containing caustic is sprayed over the column in countercurrent. H_2S is absorbed into the liquid phase and reacts with caustic according to the following reaction:

$$H_2S + NaOH \leftrightarrow NaHS + H_2O \quad [6]$$

The absorbed sulfide is then, with the addition of air, biologically converted into elemental sulfur by the Thiobacillus bacteria in the bioreactor, according to the main reaction:

$2NaHS + O_2 \leftrightarrow 2S^0 + 2NaOH$ [7]

The sulfur produced is then recovered from the washing liquid in settler for further treatment. The liquid is recirculated in the packed column to remove more H_2S.

Sulfurex® BR is a flexible desulfurization technology that achieves low hydrogen sulfide outlet concentrations with low operational expenses thanks to the regeneration step. Since the air injection takes place in the bioreactor, the technology is suitable for biogas upgrading purposes. This technology is more suitable for high loads of sulfur, in which the reduction of the OPEX compensates the higher initial investment.

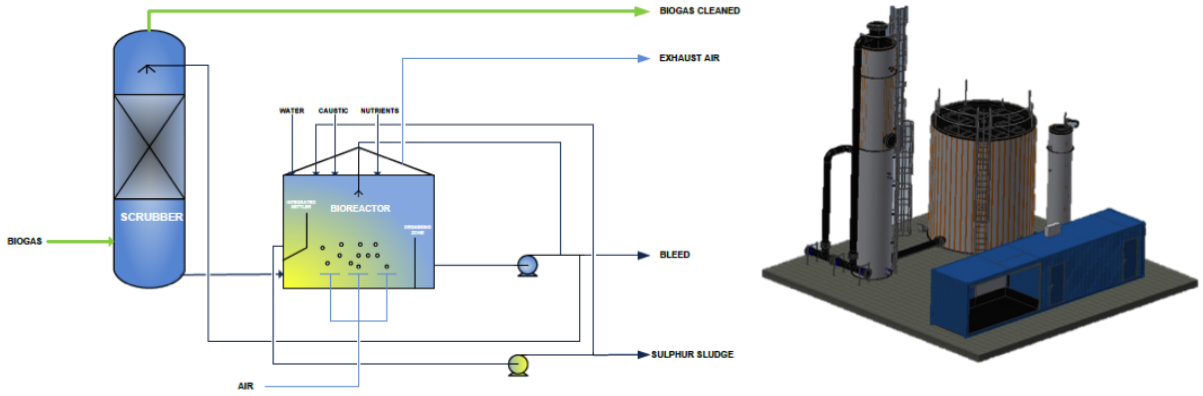

Figure 3. Schematic process of Sulfurex® BR with an integrated settler (left). 3-D drawing of a Sulfurex® BR (right).

4 Selecting the Right Technology with SSWeet

The selection of the right desulfurization technology can be a challenging exercise, with many factors playing an important role such as e.g. CAPEX, OPEX, final application of the gas, site conditions, uptime, reliability. In many cases, more than one desulfurization technology can be applied as a solution. It is very important to guide clients to the best solution for their projects, so we have developed our very own tool, the Sulfurex Selection Work Expert Tool (SSweet).

The SSweet uses a mathematical model to estimate the Total Cost of Ownership (TCO). A graph is used as a preselection overview of the most suitable technology for the project based on biogas flow rate and inlet H_2S concentration. In addition to this graph, a tailor-made business case is generated by considering specific site conditions of the client (such as electricity price, water price, caustic price, discharge cost or labor cost), providing the final CAPEX and OPEX for the project. With the SSweet, customers can be provided with an otherwise complex business case and therefore choose the ideal solution for their projects by making decisions based on CAPEX versus OPEX or reliability versus costs.

The following paragraphs illustrate the features of the SSweet and the impact of project specific conditions and requirements on technology selection. A project for the desulfurization of a biogas stream of 350 Nm^3/h, containing 55% of CH_4, 44% of CO_2 and 4000 ppm(v) of H_2S is used as a general example. In the preselection phase, based on inlet flow and concentration, more than one desulfurization technology is suitable without any additional information (Figure 5). This example is then applied in three very different contexts (paper industry (anaerobic WWTP), domestic water treatment (anaerobic WWTP) and anaerobic digester – AD)). From experience, these industries are common desulfurization markets (Figure 4).

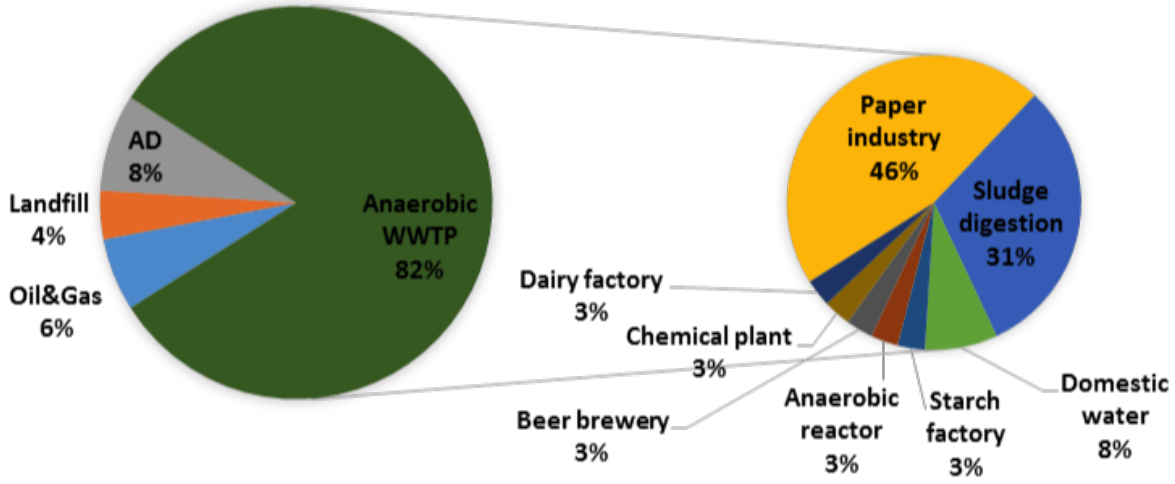

Figure 4: Desulfurization markets (DMT)

Paper Industry

Biogas is naturally produced from the anaerobic treatment of the wastewater in the paper factory. Since paper factories require a large amount of heat during the production process, the biogas can be used in a boiler. In this way, the energy efficiency of the plant is improved.

However, the boiler is sensitive to H_2S due to risks of corrosion and formation of SOx from the combustion of H_2S is under legislation. Prior utilization, the biogas has to be desulfurized down to 100 ppm(v) H_2S. This is where DMT comes in. Through discussions with the customer, DMT gathers information on specific sites conditions and customer's requirements:

• Since caustic is used during the pulping process, it is already available in-situ and extra-consumption will not be perceived as a major inconvenient.

• Uptime and easy operation will be leading parameters in the final decision.

From customer requirements and caustic availability, DMT is inclined to favor Sulfurex® CR as a solution. The business case and the TCO, based on the specific site conditions and preferences of the client, confirms that Sulfurex® CR is indeed the most attractive solution for the customer (see Figure 5). It combines the advantage of a reduced OPEX (due to caustic availability) with high reliability and uptime.

Wastewater Treatment Plant (WWTP)

Biogas is produced from the secondary treatment of a municipal wastewater treatment plant. Here, the biogas is a by-product that can be valorized in the form of electricity in a CHP (Combined Heat and Power) unit.

According to the supplier of the CHP, the concentration of H_2S in the biogas cannot exceed 200 ppm(v) in order to reduce maintenance cost and preserve lifetime of the unit.

After discussing with the customer, DMT builds the business case around the following site conditions and extra-requirements:

• The desulfurization process can be easily integrated within the main process (wastewater treatment) as supply of water can be easily arranged and the discharge can be disposed into the main process and directly treated.

• The client prioritizes a cost-effective and environmental friendly solution.

From the site conditions (water supply and water discharge), DMT already lean towards a Sulfurex® BF since then wastewater from the main process could be used as supply water without further treatment. The business case (Figure 5) validates this initial assumption – only qualitative and based on experience – and selects the Sulfurex® BF as the most attractive solution for the client. Compared to Sulfurex® CR and Sulfurex® BR, its OPEX is significantly reduced with the

easy access and discharge of water and it is the most environmental friendly solution.

Anaerobic Digester (AD)

Biogas is produced in a mono-digester from a feedstock rich in sulfur-containing proteins as a main product. It is then upgraded before injection into the local gas grid as biomethane. The upgrading process cannot handle H_2S and there are strict gas grid requirements (H_2S < 3 ppm(v)) so desulfurization has to be carried out in two steps: bulk removal down to 100 ppm(v) followed by polishing with activated carbon. Oxygen is also subjected to strict regulations and should not exceed 0.5% in the biomethane so oxygen injection is not allowed.

During dialogs, the customer also specifies that the technology should be reliable with high uptime to optimize the profit and reduce active carbon consumption.

Due the strict requirements on oxygen, DMT does not consider the Sulfurex® BF as an option. Accounting for the specific requirements from the customer and the process, the most attractive choice of desulfurization technology (prior to upgrading) is Sulfurex® BR. The biological regeneration reduces significantly the OPEX of the process, compensates the higher initial investment costs and provides a reliable solution with high uptime.

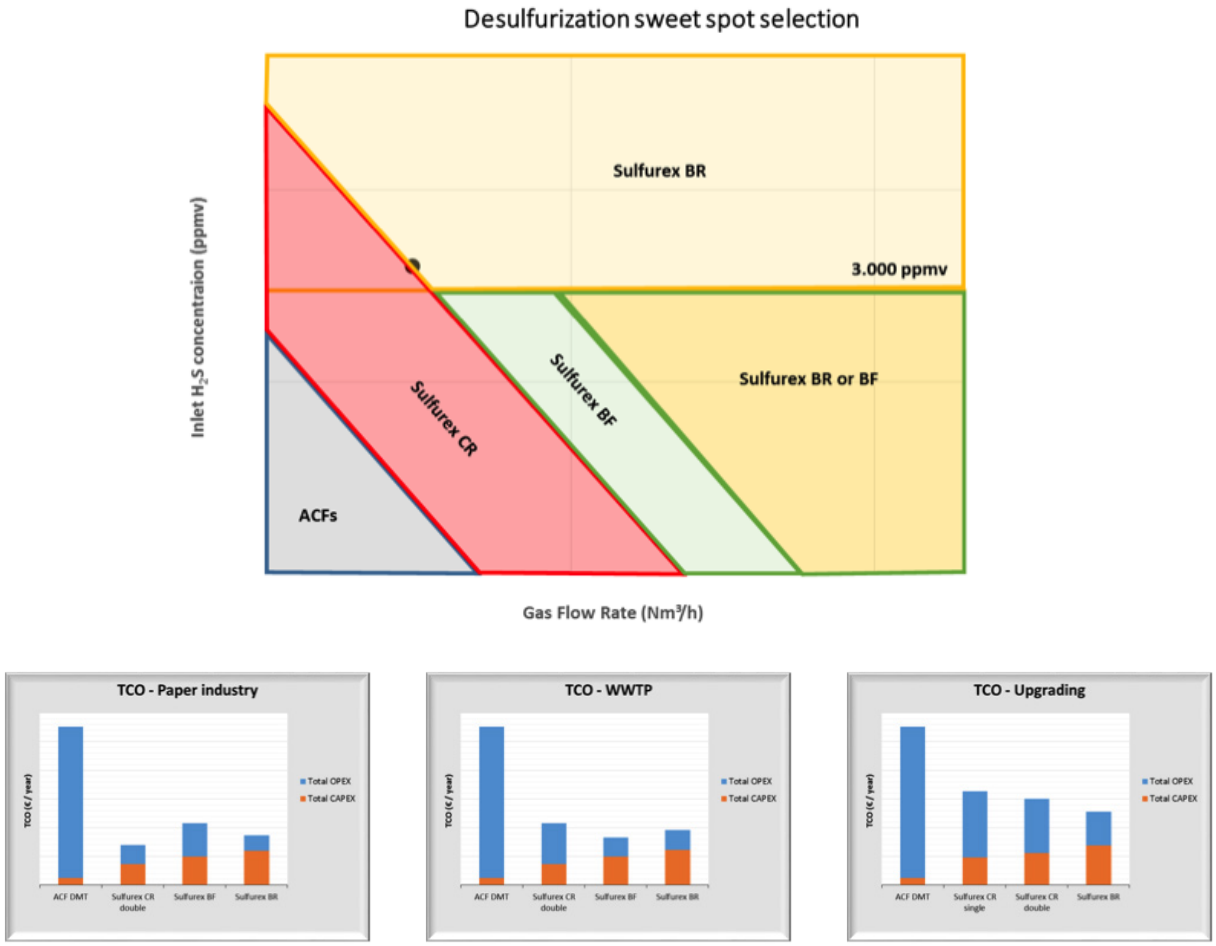

Figure 4. Business case analysis for a general case (Flow 350 Nm³/h, 55% of CH_4, 44% of CO_2 and 4000 ppm of H_2S). Above Desulfurization selection sweet spot selection. Below, Total Cost of Ownerships for three different cases.

5 Best solutions

Hydrogen sulfide (H_2S) is produced by many industries as an undesirable gaseous by-product. Due to its characteristics (high toxicity, corrosive attributes and environmental restrictions), an H_2S removal step is usually required before the final application of the biogas.

DMT has more than twenty years of experience in gas desulfurization. Our technologies includes a chemical process (Sulfurex® CR), a biological process (Sulfurex® BF), a biochemical process (Sulfurex® BR) and activated carbon for small loads. The versatility of these technologies, enhanced with the possibility of combination, enables us to respond to most customers' specific needs, from small loads and flows to high loads and high flows, from Oil & Gas industries to AD plants owners' needs.

Nevertheless, offering a solution is not enough. Offering the best solution to our customers is essential. The choice of the best technology for a specific project is dependent on innumerous factors such as final application of gas, TCO, conditions on site and many other factors, which complicates the selection.

This challenge led us to design the Sulfurex Selection Work Expert Tool (SSweet). Combining a preselection step based on years of experience in the field of desulfurization with a tailor-made business case, this tool enables us to select, together with the customers, the most attractive technology for their project – both from a technical and financial standpoint. Each project has its unique characteristics and so it should have its unique business case, and that is what DMT wants to offer.

With the Sulfurex Selection Work Expert Tool (SSweet) and our expertise, we believe that helping our customers with building their tailor-made business case and choosing the best solution based on facts contributes to the success of a project and to a **clear and prosperous future.**