# TROUBLESHOOTING A PROPANE DESULFURIZATION PLANT TOWARD ULTRA LOW SULFUR PRODUCTION

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**Abstract:** Liquefied petroleum gas (LPG) should comply with legislation concerning low sulfur content (less than 10 ppm wt.) before being used as an automotive fuel. Mercaptans and hydrogen sulfide are the most significant sulfur compounds which should be mandatory removed from any transportation fuel. To do such a task, using selective catalytic oxidation (SCO) process followed by TSA (temperature swing adsorption) process can be an appropriate option to remove such odorous and harmful compounds. In this paper, a commercial scale selective catalytic oxidation (SCO) plant followed by adsorption (as a case study) is studied. At first, it is shown that the presence of water and sulfur compounds in the product stream of the target propane desulfurization plant is due to the desulfurization section installed before the adsorption unit. So, to tackle with this problem, the molecular sieve of the adsorption tower is replaced with a synthetic zeolite of X-type. Results has shown that this revamp can successfully remove all undesired compounds from the final product such to meet all universal standards.

**Keywords:** Desulfurization, Molecular Sieve, Disulphide

## 1. INTRODUCTION

Liquefied petroleum gas, known as LPG, is increasingly used as a transportation fuel, and necessity it should comply with legislation concerning low sulfur content of automotive fuels. The amount of sulfur allowed in transportation fuels is reducing across the world. For instance, the United States Environmental Protection Agency's Tier 3 specifications, which come into effect in 2017, will reduce gasoline sulfur content to less than 10 wt. ppm from the Tier 2 maximum of 30 wt. ppm. Therefore, the need for low sulfur feed in fuel cell industry is a growing trend. Moreover, LPG and light hydrocarbons such as propane can be used as feedstock for fuel cells which are generally sulfur intolerant. Additionally, odor problem is a serious concern as environmental and public nuisance with high economic growth. Odor has been known as a sensory pollution that gives an unpleasant feeling and it is linked directly to the life quality. It is well known that mercaptans, sulfur compounds and hydrogen sulfide are representative mal-odorants. For all these reasons, desulfurization needs to be carried out when the product is for sale or as the final product.

Up to now, the sulfide removal or sweetening processes for hydrocarbon fuels are mainly hydrodesulphurization (HDS), adsorptive desulfurization, and selective catalytic oxidation (SCO) followed by adsorption. The latter process, involves two main processes: 1. in the first section, called desulfurization plant, using liquid/liquid extraction process in the presence of a liquid catalyst the mercaptans (RSH) is removed with a caustic solution, and 2. In the second part, the product of the de-sulfurization plant is conducted to TSA (temperature swing adsorption) process to remove all remained sulphur compounds.

In this paper, a commercial scale selective catalytic oxidation (SCO) plant followed by adsorption (as a case study) is studied. It was observed that the presence of water, RSH and sulfur compounds in the product stream of the target petrochemical plant was mainly due to the desulphurization section located in the upstream of adsorption unit. Therefore to troubleshoot the desulphurization plant, it was recommended that the molecular sieve of the adsorption tower should be replaced with a synthetic zeolite of X-type with a pore opening of 10 angstrom (13X). Then, the effect of this recommendation to complete removal of undesired compounds from the final product the target plant is discussed.

## 2. PROCESS DESCRIPTION

The feed of propane treatment section is the product of propane desulfurization unit. Propane desulfurization unit performs on four main processes to remove sulfur compounds from propane and prepare it for the end user. Refer to Figure 1, the first process, the pre-alkalization, removes hydrogen sulfide, carbon dioxide and a small portion of carbonyl sulfide from the propane stream using an alkaline solution by the following reactions:

$$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$$
$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$
$$COS + 4\ NaOH \longrightarrow Na_2S + Na_2CO_3 + 2\ H_2O$$

From the top of the pre-alkalization vessel, the feed of the second process, Extraction, enters the bottom of an extraction column, after being heated through a heat exchanger. Mercaptans and Carbonyl Sulfide are removed from the Propane Stream in presence of an aqueous caustic solution and a small amount of catalyst, according to the following reactions:

$$RSH + NaOH \longleftrightarrow RSNa + H_2O$$

$$COS + 4\ NaOH \xrightarrow{\text{Activator}} Na_2S + Na_2CO_3 + 2\ H_2O$$

The caustic solutions are from caustic solution regeneration stage and Tanks improvised in the Plant for storing materials.
Water washing Stage, performed by bubbling the Propane streams through the Water, to remove caustic traces from the bulk of Propane. Finally, the Water droplets are adsorbed by a salt filter and flows to the Propane Treatment section.

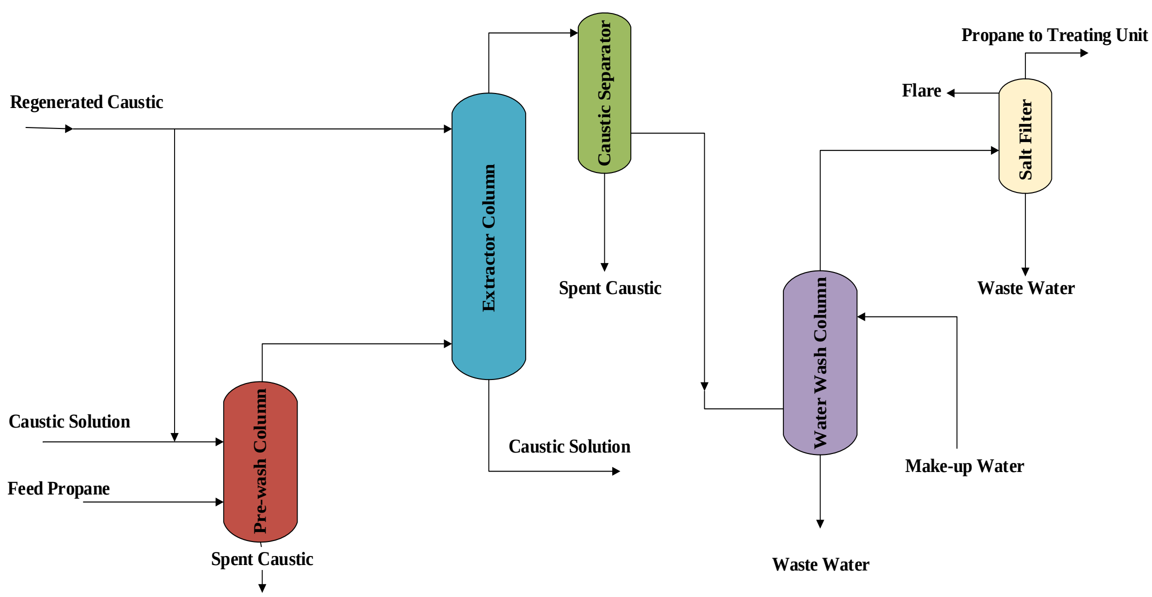


Figure 1. Propane desulfurization unit

The Mechanism of the propane treatment plant is based on physical adsorption by an adsorbent in the format of TSA (Temperature Swing Adsorption) process. As shown in the Figure 2, TSA process consists of two or more towers and associated regeneration equipment. One tower is in adsorption mode while the other one is being regenerated with a hot gas to desorb impurities from the desiccant.

The adsorbent used in the aforementioned section was a commercial Molecular Sieve 5A to adsorb Water and other impurities (Carbonyl Sulfide, Mercaptans). The Molecular Sieve was loaded in each tower with about 7.3 $m^3$ tower capacity by sock loading method. The adsorbent was expected to remove water to less than 0.1 ppm wt.


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and sulfur compounds to less than 10 ppm wt., while the input feed stream is expected to have not more than 200 ppm wt. Water and 20 ppm wt. Sulfur compounds. The Treatment capacity is about 21,000 kg/hr. feed stream with pressure of 25.3 bara and temperature of 60-61 °C which flows through the vessel upward, in the liquid state in order to distribute the fluid uniformly through the bed cross section area. The regeneration gas is Low Pressure Off-Gas of the Plant which flows through the adsorption vessel downward and through a distributer and desorb the impurities from the adsorbent surface. For cooling the vessel and the adsorbents, dried product in low pressure enters the vessel. In normal conditions, the mentioned adsorbent with all of the characteristics should work fine and produced an acceptable Propane product with specifications appropriate for delivering to the end user. However, deficiencies in a side-process caused a problem that made the loaded adsorbent useless and the final product out of acceptable range of standard products.

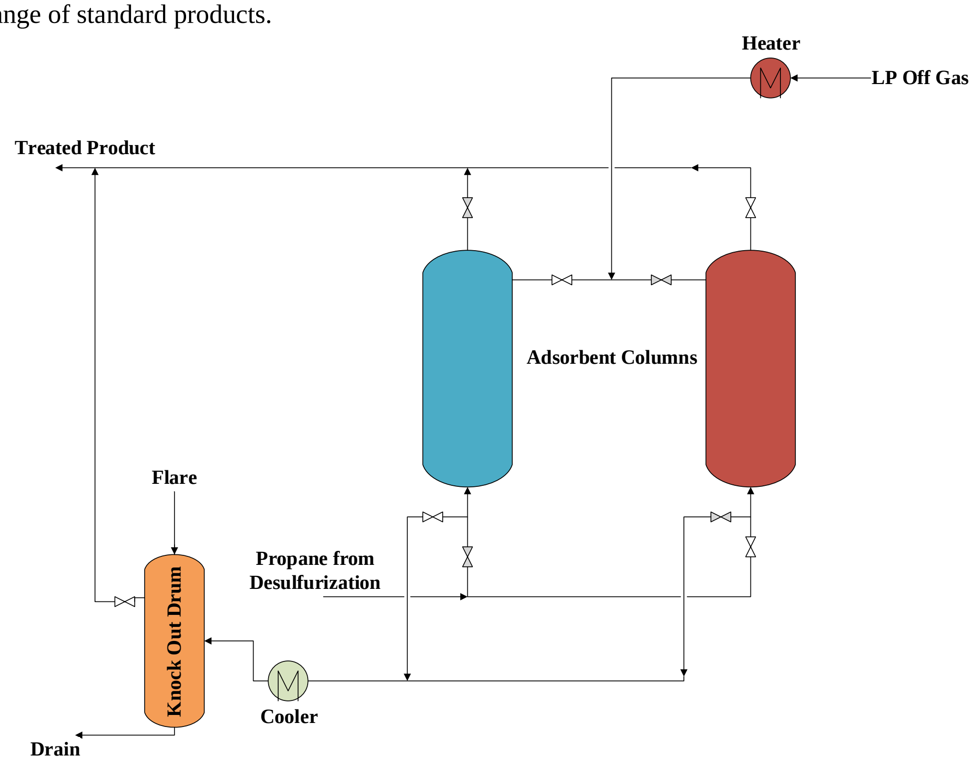


Figure 2. Adsorption Unit

The side process is caustic regeneration section, in which the spent caustic used in Desulfurization Unit is regenerated and all of its sulfur compounds are expected to be removed. However, a low efficient separator caused presence of sulfur compound more than expected quantity.

As shown in Figure 3, the feed stream of caustic regeneration process is a caustic saturated with sodium mercaptides and sodium sulfide in which dissolved hydrocarbons are present. This feed is fed to a degasser to remove the dissolved hydrocarbons and send them to the flare. After being heated through a heat exchanger, degassed caustic solution enters the bottom of the regeneration tower along with an injected stream of pressurized air. Sodium mercaptides and sodium sulfide is oxidized in the regenerator over a catalyst by the following reaction:

$$2\ RSNa + 0.5\ O_2 + H_2O \longrightarrow RSSR + 2\ NaOH$$
$$3\ Na_2S + 4\ O_2 + H_2O \longrightarrow Na_2S_2O_3 + Na_2SO_4 + 2NaOH$$

To separate the Caustic and Air, their mixture is passed through an Air separator. The caustic, containing disulfide compounds is guided from the bottom of the separator to disulfide separator. To provide more efficient separation of the disulfides from the caustic solution, it is mixed with naphtha in static mixer before the separator inlet. The regenerated caustic solution is fed from the bottom of to the top of extraction tower of propane desulfurization.



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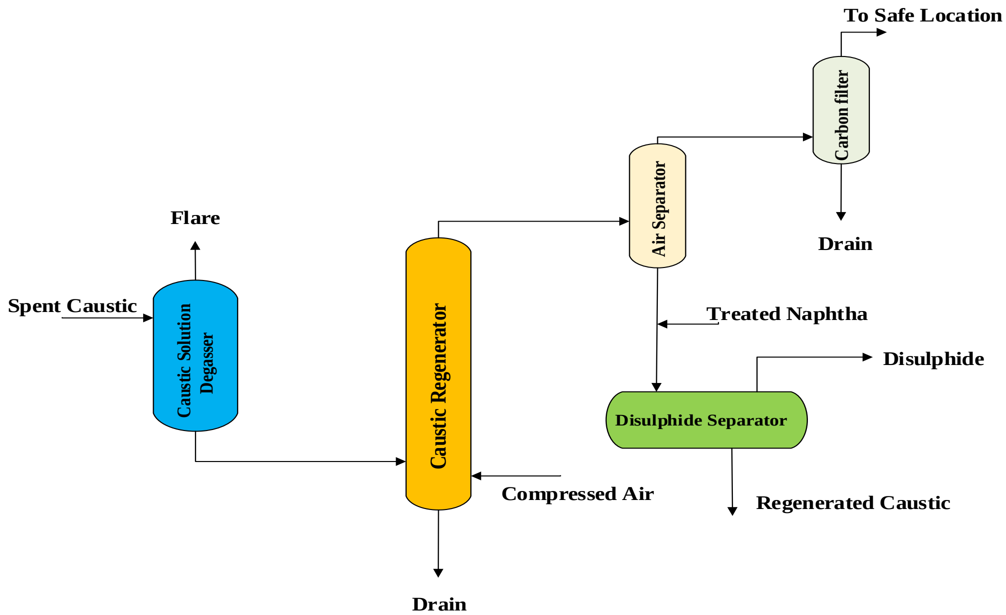


Figure 3. Caustic Regeneration Unit

## 3. RESULTS

The final separation stage in caustic regeneration process is designed to reduce sulfur as disulfide compounds of the caustic. However, analysis reports show that the feed stream of Propane treatment unit has much quantities of disulfide components. This means that the final separator has low efficiency and as a result, the regularly loaded commercial 5A Molecular sieve was unable to adsorb them effectively.

As neither the propane desulfurization plant nor propane treatment section was not expected to remove disulfide compounds. Consequently, the total sulfur of final product became more than 10 ppm wt. and made it an un-usable product because of failing to pass EURO 5 standard. The operating conditions and a typical analysis report of treatment feed stream are reported in Table 1.

**Table 1: Operating Conditions and Feed Composition**

| Composition | | | Impurities | | | Operating conditions | | |
|---|---|---|---|---|---|---|---|---|
| Ethane | mass% | 0.73 | Water | ppm wt. | 200 | Temperature | °C | 60-61 |
| Propane | mass% | 97.96 | Carbonyl Sulfide | ppm wt. | 20 | Pressure | bara | 25.3 |
| i-Butane | mass% | 1.26 | Methyl Mercaptan | ppm wt. | 4.2 | Total Flow Rate | kg/hr | 20,652 |
| n-Butane | mass% | 0.02 | Ethyl Mercaptan | ppm wt. | 1.5 | | | |

Note: Reported values for sulfur compounds are typical. In some cases, the total sulfur compounds reach up to 70 ppm wt.

Also, sulfur analysis for three different time shows that the feed stream of Propane Treatment section has oscillation and more than expected values. Reported values in three different time are as Table 2.

**Table 2: Composition of sulfur compounds in the feed stream**

| COMPONENT | Sulfur as S (ppm) | | |
|---|---|---|---|
| | **Date 1 (2013.02.16)** | **Date 2 (2013.06.10)** | **Date 3 (2013.06.29)** |
| Hydrogen Sulfide | 0.0 | --- | --- |
| Carbonyl Sulfide | 4.28 | 25.6 | 7.1 |
| Methyl Mercaptan | 6.34 | 4.2 | 0.24 |
| Ethyl Mercaptan | 1.4 | 1.5 | 0.0 |
| iso-Propyl Mercaptan | 0.48 | 0.0 | 0.0 |
| Diethyl sulfide | 0.0 | --- | --- |
| Alkyl Disulfide Components | 38.5 | 20.7 | 34.66 |
| Total Sulfur | 51 | 52 | 42 |

As mentioned before, previously designed treatment unit was based on adsorbing water and carbonyl sulfide by 5A molecular sieve. However, this type of molecular sieve was unable to adsorb disulfide compounds. To tackle with this problem, it was recommended that 5A molecular sieve could be replaced with a synthetic zeolite of X-type crystal structure in sodium form with a pore opening of 10 angstroms. The specifications of the loaded 13X molecular sieve are presented in Table 3.

**Table 3: Specifications of 13X molecular sieve**

| **Properties** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Beads** | | | | | | | | |
| Size | Diameter | Bulk density | Crush strength | Static water adsorption | Static $CO_2$ adsorption | Static $H_2S$ adsorption | Attrition | Moisture content |
| mesh | mm | g/ml | N | wt% | wt% | wt% | wt% | wt% |
| 8×12 | 1.6-2.5 | 0.63-0.69 | ≥40 | ≥29 | ≥18 | ≥13 | ≤0.1 | ≤1 |

As can be observed from Figure 4, Alumina is a three-valance cation while silicon is a four-valance one. If Alumina acts as “T” element in TO4 structure, then a negative charge is gained., This is due to the fact that Alumina is three valances, and a cation is needed to be added to the system to balance the charges of the structure. Therefore, higher alumina to silicon ratio, leads to more negative charges in the crystal structure, so more cations should be added to the system which subsequently results in more polarity in the structure. The type of the zeolite is affected by the following composition of the mixture:

- Al/Si Ratio: Molecular Sieve with High Al/Si Ratio, has high Adsorption Capacity to Adsorb low polarity Molecules, such as COS and $CS_2$.
- Nucleation time enhanced by modifying $OH^-$ due to influencing transportation of silicates from the solid phase to solution.
- Inorganic cations act as structure directing agents and balance the framework charge. They affect the crystal purity and product yield.

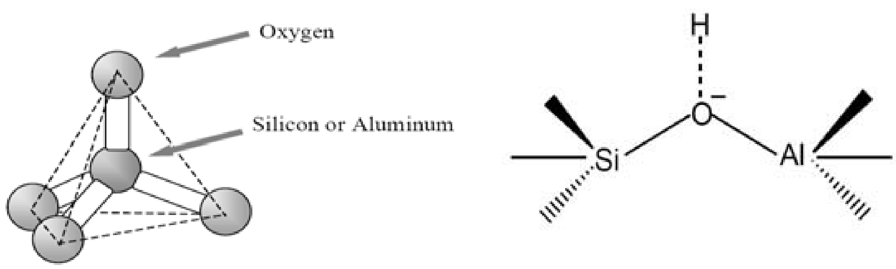


Figure 4: Structure of Molecular Sieve

Nitel Pars / HENGYE Chemical Co. developed special type of medium silicate Molecular Sieve for adsorbing heavy and low/weak polar molecules. This molecular Sieve type is capable of deep desulfurization and also adsorbing heavy sulfur compounds such as disulfide and water simultaneously. Moreover, in regeneration step, it desorbs all of the impurities and got refreshed for next adsorption cycle. It is noticeable that the new design of the Propane treatment process is based on Physical adsorption, while the commonly used method is adsorption by an irreversible chemical process.

Table 4 shows most important components of the feed stream and their molecular properties. It is obvious that the Special type of mentioned Molecular Sieve has the ability to adsorb a wide range of impurities of the stream.

**Table 4: Important components of the feed stream**

| Components | Polarity | Hydrogen bond | Kinetic Diameter (Å) |
|---|---|---|---|
| **Water** | Polar | Hydrogen Bond | ~ 2.6 |
| **Methyl Mercaptan** | Medium-Polar | Not-Applicable | 9 > D > 3 |
| **Alkyl Disulfide** | Medium-Polar | Not-Applicable | 9 > D > 3 |
| **Carbonyl Sulfide** | Weak-Polar | Not-Applicable | 9 > D > 3 |
| **Propane** | Non-Polar | Not-Applicable | 9 > D > 3 |

## 4. CONCLUSIONS

Using a special type of 13X molecular sieve instead of a commercial 5A one in the downstream of a propane desulfurization plant, shows better efficiency of removal of water, $H_2S$, mercaptane and high molecular weight sulfur compounds. The product meets the special requirement of ultra-low sulfur production. Table 5 shows Sulfur Components Analysis results after loading specially developed Molecular sieve during adsorption cycle which are reported by the petrochemical company studied. The results obviously show that the mentioned Molecular sieve has the desired capability to adsorb undesired di-sulphides and other impurities. Therefore, it can reduce the total sulfur compounds and water to less than 2 and 1 ppm wt., respectively. Figs 4 &5 demonstrate the trend of sulfur compounds in the product during 8 month from start of run.

Also, the outlet regeneration gas analysis results reported by Kharg Petrochemical Co. in the Table 6, shows that the regeneration step is done properly and the beds is ready for next cycle. The physical adsorption mechanism in the desired process is obvious from sulfur compounds in the analysis of regeneration gas outlet.

**Table 5. Sulfur components analysis after loading 13X molecular sieve**

| COMPONENT | METHOD | Sulfur compounds as S (ppm) | | | |
|---|---|---|---|---|---|
| | | Inlet 2014/02/20 | Outlet 2014/02/20 | Inlet 2014/02/23 | Outlet 2014/02/23 |
| Hydrogen sulfide | ASTM D-5504 | 0 | 0 | 0 | 0 |
| Carbonyl sulfide | ASTM D-5504 | 0.6 | 0.4 | 0.5 | 0.4 |
| Methyl mercaptan | ASTM D-5504 | 4.65 | 0 | 4.84 | 0 |
| Ethyl mercaptan | ASTM D-5504 | 0.8 | 0 | 1.4 | 0 |
| Carbon disulfide | ASTM D-5504 | 0 | 0 | 0 | 0 |
| Iso-propyl mercaptan | ASTM D-5504 | 0 | 0 | 0.36 | 0 |
| Alkyl disulfide | ASTM D-5504 | 33.95 | 1.6 | 40.9 | 0.2 |
| Total sulfur | ASTM D-5504 | 40 | 2 | 48 | 0.6 |

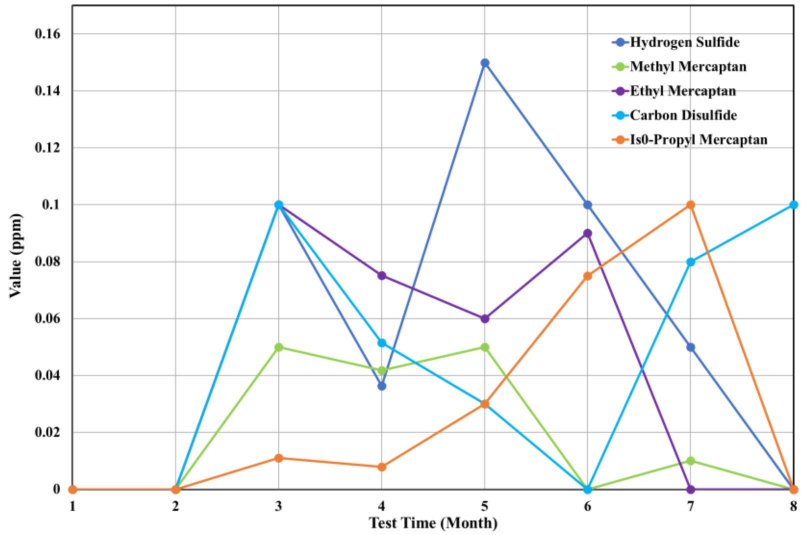


Figure 5: Light sulfur compounds in the product during 8 months

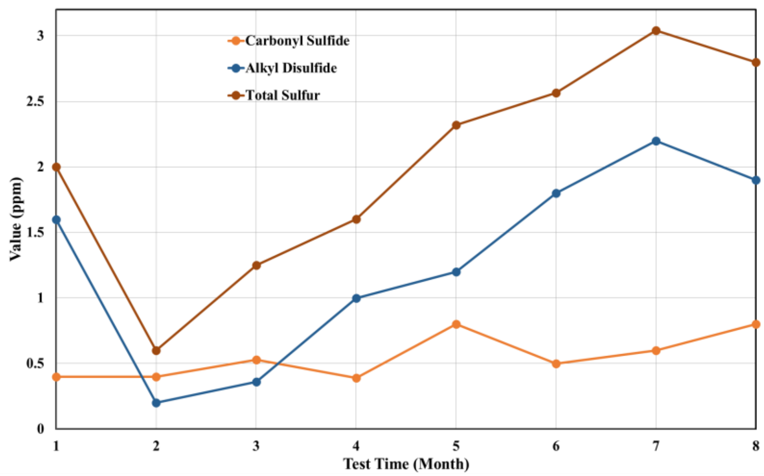


Figure 6: Heavy sulfur compounds in the product during 8 months

**Table 6: Composition of the outlet regeneration gas**

| COMPONENT | METHOD | Sulfur Compounds as S (ppm) | | | | |
|---|---|---|---|---|---|---|
| | | Time 12:30 | Time 14:00 | Time 15:00 | Time 16:30 | Time 19:00 |
| **Hydrogen Sulfide** | ASTM D-5504 | 21 | 10.2 | 3.6 | 2.7 | 0.5 |
| **Carbonyl Sulfide** | ASTM D-5504 | 10.5 | 26.8 | 25.3 | 49.3 | 19.4 |
| **Methyl Mercaptan** | ASTM D-5504 | 435 | 150 | 69.1 | 43 | 19.1 |
| **Ethyl Mercaptan** | ASTM D-5504 | 915 | 1139 | 1059 | 948 | 618 |
| **Nor-Propyl Mercaptan** | ASTM D-5504 | 6 | Nil | Nil | Nil | Nil |
| **Unknown sulfur Components** | ASTM D-5504 | 112.5 | 34 | 23 | 7 | 3 |
| **Total Sulfur** | ASTM D-6667 | 1500 | 1360 | 1180 | 1050 | 660 |

## 5. ACKNOWLEDGMENT

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