VOC reduction at Raffineria di Milazzo's SRU complex–Part 2

Based on new environmental regulations focusing on volatile organic compounds (VOCs) at the emissions point of a refinery's sulfur recovery unit (SRU), Raffineria di Milazzo–a JV between Eni and Kuwait Petroleum Italia–carried out troubleshooting activities to identify and implement suitable actions to minimize the concentration of VOCs at the emissions point of the SRU complex.

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Based on new environmental regulations focusing on volatile organic compounds (VOCs) at the emissions point of a refinery's sulfur recovery unit (SRU), Raffineria di Milazzo–a JV between Eni and Kuwait Petroleum Italia–carried out troubleshooting activities to identify and implement suitable actions to minimize the concentration of VOCs at the emissions point of the SRU complex.

Many definitions of VOCs exist in scientific literature and technical references. In this article, VOCs refer to the sum of the contributions of methane and non-methane VOCs (C_1 and C_1+). The technological arrangement of Raffineria di Milazzo's SRU complex ensures high sulfur recovery performance.

This article shares a troubleshooting case study (analysis and related solutions) as a support reference when facing similar environmental topics.

As described in **Part 1** (https://www.hydrocarbonprocessing.com/magazine/2023/march-2023/environment-and-safety/voc-reduction-at-raffineria-di-milazzo-s-sru-complex-part-1) of this work (published in the March issue of *Hydrocarbon Processing*), Raffineria di Milazzo's sulfur complex arrangement consists of three SRUs. Each SRU includes a Claus section (with two catalytic stages), a tail gas treatment (TGT) section [utilizing the Shell Claus Offgas Treating (SCOT) process or a derivative technology] and a final conversion section (incinerators). The incinerators' tail gas outlets are combined into a common stack.

Theoretical analyses, combined with analytical activities on each SRU section, enabled refinery personnel to identify the key factors of VOCs present in the complex. The first step consisted of identifying inlet streams with a relevant impact on VOC content at the emissions point. The removal of VOCs from these streams enabled a reduction of VOCs at the stack by an order of magnitude.

A second step consisted of identifying and eliminating the VOC contribution in the SRUs' internal process streams. In SRU3, a carryover of the sweetening amine solution in the tail gas outlet led to a significant contribution of VOCs (due to thermal degradation of the amine solution itself in the incinerator section). A new design of sweetening column internals has allowed the minimization of amine solution entrainment and, eventually, a further reduction of the VOCs at the stack.
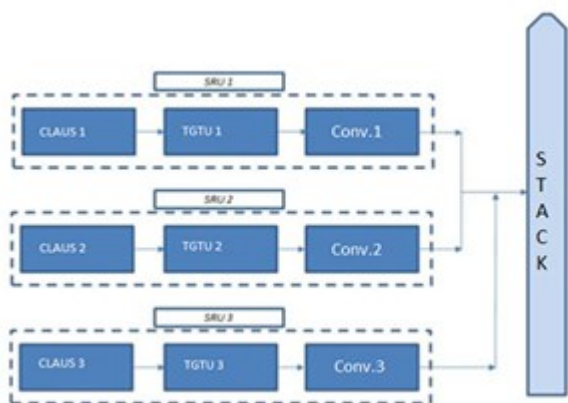
A third (and final) step investigated possible VOC generation due to chemical reactions in the SRUs. A methanation reaction in the TGT unit's (TGTU's) reduction reactor was identified, illustrating that the presence of carbonyl sulfide (COS) and carbon disulfide (CS_2) in a reducing environment (excess of hydrogen) can generate methane. By minimizing the precursors involved in the reaction, it has been possible to reduce the content of "methane VOC" at the stack to a very low level. The synergy of these actions led to an overall VOC reduction at the SRU complex stack by two orders of magnitude vs. the original value (target achieved VOCs < 5 mg/Nm^3).

Oil and gas products [e.g., naphtha, gasoil, liquefied petroleum gas (LPG)] must be desulfurized to minimize sulfur oxide (SO_x) emissions of internal combustion engines. Over the past several decades, different refinery processes (including sweeting and hydrotreating) have been developed to achieve more restrictive limits of residual sulfur in refined products. The extracted sulfur from products must be recovered as elemental sulfur, and this is possible through the Claus process (and associated tail gas treatment processes), where 99.9% of sulfur is retrieved in liquid form to be utilized in the chemicals industry (e.g., sulfuric acid production, the vulcanization of tires) or farming (especially as fertilizer).

Sulfur recovery at Raffineria di Milazzo

Three different SRUs at Raffineria di Milazzo are dedicated to sulfur recovery. Each unit comprises a Claus section, a TGTU section and a final conversion section (**FIG. 10**). Every Claus section has two catalytic Claus reactors. The TGTU sections utilize the SCOT process (SRU1 and SRU2) and a high Claus ratio (HCR) (SRU3). The final conversion section includes catalytic incinerators for SRU2 and SRU3, along with a thermal incinerator for SRU1. **Note:** For process flow diagrams of these sections, please refer to Part 1 of this article (https://www.hydrocarbonprocessing.com/magazine/2023/march-2023/environment-and-safety/voc-reduction-at-raffineria-di-milazzo-s-sru-complex-part-1).

(/media/18400/falzone-fig-10.jpg)

FIG. 10. Block diagram of Raffineria di Milazzo's SRU complex.

TROUBLESHOOTING ACTIVITIES

According to European Commission (EC) Directive 1999/13/EC (Solvent Emissions Directive), VOCs are functionally defined as organic compounds having, at 293.15 K (20°C), a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under conditions of use.

The aim of this work is to identify the sources of VOCs at Raffineria di Milazzo and to minimize their concentrations in the SRU complex's stack to adhere to new environmental constraints (i.e., 20 mgC$_{eq}$/Nm^3).

Analytical troubleshooting Step 2: Identifying VOC sources in SRU3

Part 1 (https://www.hydrocarbonprocessing.com/magazine/2023/march-2023/environment-and-safety/voc-reduction-at-raffineria-di-milazzo-s-sru-complex-part-1) of this article covered theoretical considerations, a description of the analytical setup for VOC detection, the investigation's starting point and Step 1. **TABLE 4** details the configuration of Raffineria di Milazzo's SRU complex at the beginning of the deeper investigation into SRU3.


(/media/18411/falzone-table-04.jpg)

Comparing the configuration of the starting point and Step 1, the configuration of Step 2 was the following:

- SRU1 was in a hot stand-by arrangement–the Claus section was kept warm by the thermal reactor where fuel gas is burned in stoichiometric conditions, and the final conversion unit was kept warm by a thermal incinerator. In this arrangement, TGTU1 was shut down, and the flue gas from the Claus section reached the final conversion section directly (TGTU1 was bypassed).

- SRU2's load was lower than the previous configuration–the acid gas feedstock was moved to SRU3 to provide a higher load for the test on the unit.

- The greater load in SRU3 allowed a spit-flow configuration to reach the proper temperature on the thermal reactor (> 1,250°C). In the previous configuration, the oxygen enrichment arrangement was used due to the lower load.

FIG. 11 shows the configuration of SRU3 in Step 2. Some considerations can be deduced by the analytical overview shown in **FIG. 11**:

- As in SRU2, no relevant VOC concentration was found in the outlet of the Claus section. This confirms that a complete removal of hydrocarbons occurred in the thermal reactor.[1]

- At the outlet of the reduction reactor, the VOC concentration increased slightly and remained constant until it entered the catalytic incinerator. This was probably due to a slight contamination of VOCs in the hydrogen reduction stream and/or a VOC generation chemical reaction that took place in the reduction reactor. However, the values detected are not concerning since they were less than 20 mgC_{eq}/Nm^3.

- An increase in the VOC concentration of one order of magnitude was detected at the outlet of the catalytic incinerator. In this case, methane represented the biggest portion of the VOC concentration measured (> 85%). It is worth remembering that the tail gas preheating to catalytic incinerator reaction temperature is performed by a furnace, where natural gas (≈ 85% of CH_4) with excess air is burned. Therefore, a burning check in the tail gas preheater was necessary.
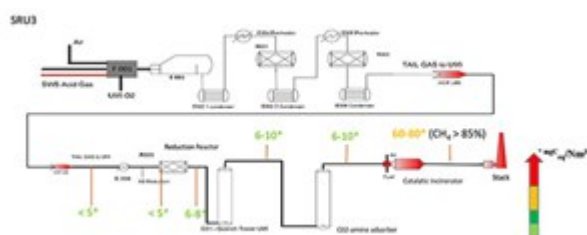
(/media/18403/falzone-fig-11.jpg)

FIG. 11. Process flow diagram of SRU3 with the VOC concentration measured in different unit sections.

A check on the burning condition in the tail gas preheater of the final conversion section was carried out. First, the burner was replaced with a new one, followed by several tests (**TABLE 5**).

(/media/18412/falzone-table-05.jpg)

The burning in hot standby condition and in different unit loads seemed to be different. Conversely, the VOC concentration at the final conversion outlet, with a bypass of TGTU3 (the tail gas from the Claus section was sent directly to the final conversion section), was less than 5 mgC$_{eq}$/Nm^3.

During the different tests, the composition of VOCs did not change with different fuels: CH$_4$ content in the refinery's fuel gas was 30 vol% and it was higher than 85 vol% of natural gas. If a burning issue occurred using a different fuel, a different composition of VOCs in the final conversion section's outlet stream had to be detected. The tests suggested that the source of VOCs was not identified, but it could be found in TGTU3 (the VOC concentration went to very low values by bypassing TGTU3).

To determine the source of VOCs in TGTU3, a review of the analytical setup was performed. It was discovered that all analyses were carried out using the H$_2$S neutralization step (with a caustic solution). In this condition, if a liquid carryover had occurred from the amine absorber, it could not have been detected (the liquid would have remained in the caustic solution). For this reason, the neutralization step was removed, and a direct sampling was carried out from the amine absorber tail gas outlet stream.

A substantial increase in the concentration of the VOCs in the amine absorbing tail gas was measured after the analytical setup modification (**FIG. 12**). Lab tests were performed to verify that the flame ionization detector (FID) could detect the amine in terms of the VOC output. To simulate an amine solution carryover, a stream of gas (air/nitrogen) was injected into the amine solution sample at different temperatures (**FIG. 13**).
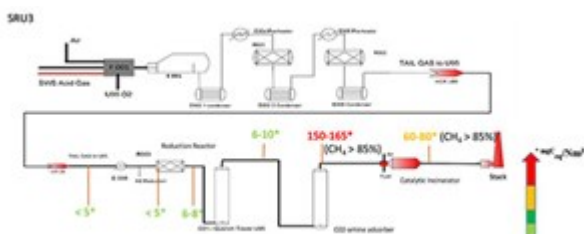
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FIG. 12. SRU3's process flow diagram with VOC concentration measured after analytical setup modifications.
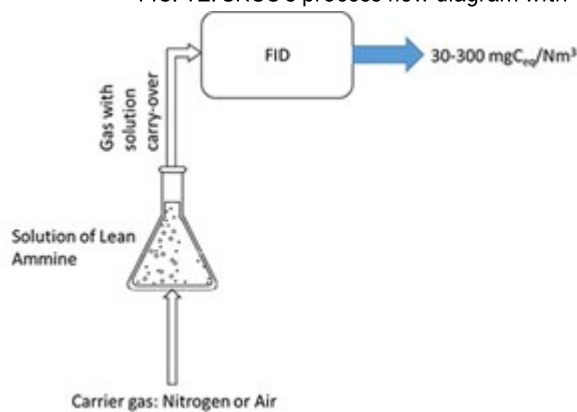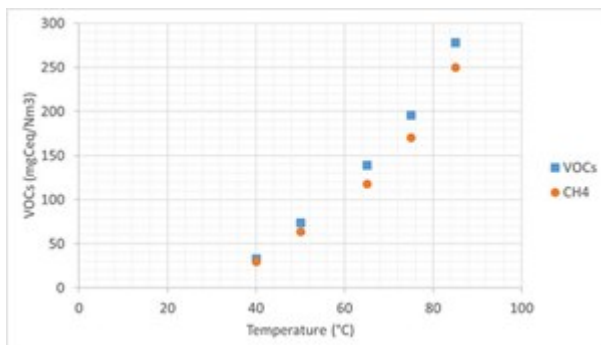

(/media/18404/falzone-fig-13.jpg)

FIG. 13. Lab analytical setup for amine solution carryover verification.

FIG. 14 shows the VOC concentrations detected by the FID vs. amine solution temperature. The graph indicates that the VOC concentration detected by the FID increased with the temperature due to the increase in methyl diethanolamine (MDEA) vapor pressure with the temperature. Another result was that the methane concentration was higher than 85% within the VOC concentration. Finally, lab tests

confirmed the VOC measurements at the amine absorber output stream. An amine solution is very likely to be entrained, and its thermal degradation occurred at the incinerator or FID itself. Therefore, a deeper analysis of the vapor-liquid separation performance at the head section of the absorber was required.

(/media/18405/falzone-fig-14.jpg)

FIG. 14. VOC concentration detected by an FID at different temperatures of the amine solution.

The design of SRU3's absorber column is different from that of the SRU1 and SRU2 absorber columns, especially in the head separation section where SRU1 and SRU2 have a gas-liquid separator installed, while, at the SRU3 absorber, there is a demister inside the column immediately before the gas outlet (**FIG. 15**). Therefore, in SRU1 and SRU2, the additional gas-liquid separation step minimized the possible amine solution carryover. A VOC contamination source from the amine absorbing column was not detected in these units.
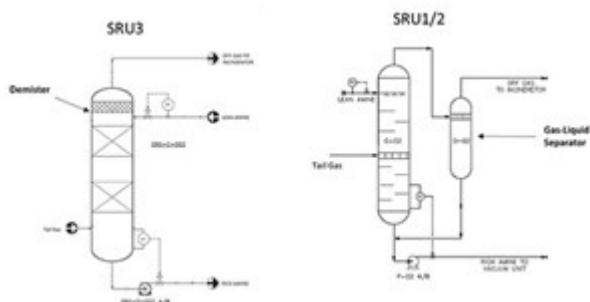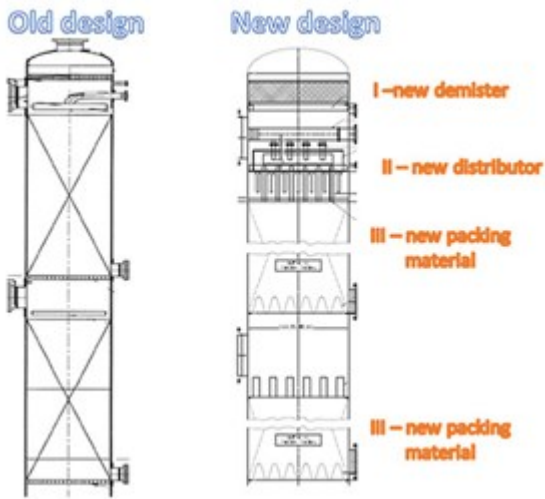

(/media/18406/falzone-fig-15.jpg)

FIG. 15. Comparison of SRU1's and SRU2's absorbing columns and SRU3's absorbing column.

To minimize the amine carryover phenomena at SRU3's amine absorbing column, a revamping of internals was proposed by a leading internal design company (**FIG. 16**). The project consisted of the following:

- The packing column material was replaced to guarantee high gas-liquid separation efficiency.
- The disengagement at the upper part of the column was increased to improve gas-liquid separation in that section.
- The lean amine distributor was replaced. The old distributor did not guarantee a uniform distribution of lean amine solution, so it caused a different gradient of gas velocity with a high likelihood of the liquid entrainment phenomena.
- The demister was replaced with a high-efficiency unit. The new demister can separate droplets with a characteristic dimension of ≥ 2 µm from gas (the old unit could guarantee ≥ 9 µm).

(/media/18407/falzone-fig-16.jpg)

FIG. 16. A comparison of SRU3's amine absorbing column before and after the internals revamp project.

After revamping the amine absorber internals, new measurements with the new analytical setup were carried out. The VOC concentration at the outlet of the amine absorber had decreased substantially (**FIG. 17**). Conversely, a slight increase in the VOC concentration from the reduction outlet reactor was detected. In addition, a different composition of VOCs at the outlet of the final conversion section was discovered (only CH_4 was detected). This led the authors to think that a new source of VOCs had been identified: CH_4 generation in the reduction reactor.
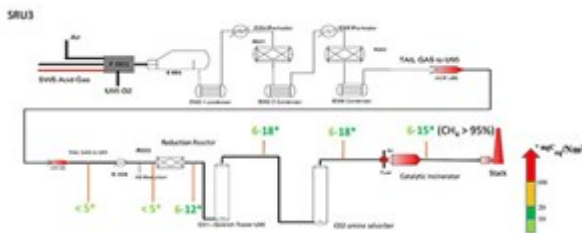
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FIG. 17. An SRU3 process flow diagram with the VOC concentration measured after the internals revamping of the amine absorbing column.

In the reduction reactor, the Claus tail gas sulfur compounds (SO_2, CS_2 and COS) reacted with hydrogen to produce H_2S through a CoMo catalyst action. When the CS_2 concentration increased in the tail gas, the following reactions (Eq. 1 and 2) took place:

$$CS_2 + 3H_2 \rightarrow CH_3SH \qquad\qquad\qquad\qquad\qquad \text{(Eq. 1)}$$

$$CH_3SH + H_2 \rightarrow CH_4 + H_2S \qquad\qquad\qquad\qquad \text{(Eq. 2)}$$

These reactions showed that hydrogen partial pressure plays a role—if the hydrogen concentration is higher in the reactor, then the CH_4 concentration will also be higher at the reactor's outlet stream.

The first catalytic Claus reactor did not contain a titanium dioxide (TiO_2) layer to maximize the COS and CS_2 hydrolysis. Therefore, the COS and CS_2 hydrolysis had to be maximized at the thermal reactor—the oxygen enrichment configuration was employed to maximize both temperature and residence time in the thermal reactor.[1] Simultaneously, the hydrogen rate to the reduction reactor had been minimized to reduce the hydrogen partial pressure in it.

Following these actions, the concentration of VOCs in SRU3 was measured, which is shown in **FIG. 18.** After identifying the VOC sources and taking proper actions to minimize their concentration, very low values were measured at the SRU3 outlet stream.
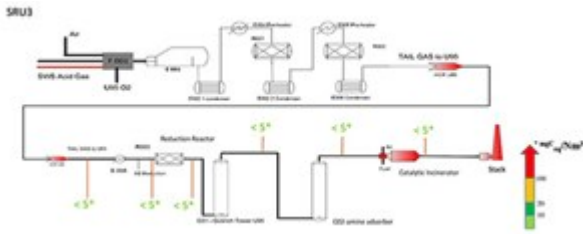
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FIG. 18. SRU3's process flow diagram with the concentration of VOCs measured after actions were taken to reduce the methanation reaction.

Results

At the conclusion of these troubleshooting activities, all possible sources of VOCs had been investigated. The most relevant sources detected were:

- **Contamination of the hydrogen stream in the TGTUs:** TGTU1 and TGTU2 were fed with a catalytic reforming hydrogen stream. A relevant hydrocarbon concentration was present in this stream. Therefore, this stream was replaced with a high-purity hydrogen stream ($H_2 > 99.5$ mol%).
- **The TGTU amine absorber section:** An amine solution carryover was detected at TGTU3's absorbing column. The revamping of the column internals minimized any possible physiological entrainment (**FIG. 16**).
- **VOC generation in the SRU complex:** A CH_4 generation reaction was identified in the TGTU3 reduction reactor. SRU3's configuration was changed to remove the CH_4 precursors and minimize their generation.

The final SRU complex configuration after troubleshooting activities is detailed in **TABLE 6**.

TABLE 6. Final SRU complex configuration				
Unit	Split-flow configuration	Oxygen enrichment arrangement	SWS offgas feed	Load, based on liquid sulfur production
SRU1	-	-	No	60%
SRU2	-	Yes	Yes	70%
SRU3	No	Yes	Yes	80%

(/media/18413/falzone-table-06.jpg)

FIG. 19 shows that the VOC concentration at the outlet of each SRU was lower than 5 mgC$_{eq}$/Nm^3. It is worth noting that the VOC concentration that was detected in SRU2 at the end of the troubleshooting activities was even lower than the concentration measured after the first troubleshooting step. This was because the hydrogen rate to the reduction reactor was optimized to inhibit the methanation reaction in TGTU2.
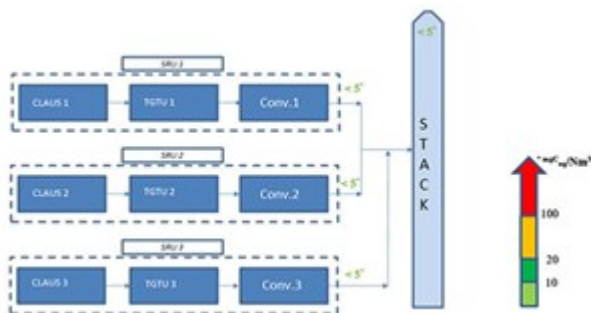
(/media/18410/falzone-fig-19.jpg)

FIG. 19. The concentration of VOCs at the conclusion of the troubleshooting activities.

After the sources of VOCs were identified and actions were taken to minimize them, VOC concentration was reduced by two orders of magnitude at the SRUs' outlet streams.

Takeaways

Troubleshooting was performed to reduce VOCs at the SRU complex. A theoretical analysis to identify the sources of VOCs in each SRU was conducted, and a series of measurements at different SRU streams was carried out to detect the most relevant ones. These analyses were carried out through a proper analytical setup based on FID.

Initially, the VOC concentration was 480 mgC_{eq}/Nm^3, with different contributions of each SRU. The highest VOC concentration was detected at SRU2's outlet stream (1,100 mgC_{eq}/Nm^3)–a hydrogen stream from the catalytic reforming unit was fed to the reduction reactors of TGTU1 and TGTU2. VOCs entered the system due to the low hydrogen purity of this stream (58 mol%–82 mol%). The existing stream was replaced with a high hydrogen-purity stream (> 99.5 mol%), which led to the reduction of VOCs at the outlet streams of SRU1 and SRU2 (< 5 mgC_{eq}/Nm^3 and < 10 mgC_{eq}/Nm^3, respectively) and, in turn, at the stack (40 mgC_{eq}/Nm^3).

An investigation for the sources of VOCs was carried out at SRU3, where the concentration of VOCs at the outlet stream was 60 mgC_{eq}/Nm^3–80 mgC_{eq}/Nm^3. A slight modification of the analytical setup was necessary to identify that a carryover of amine solution occurred at the TGTU3 absorbing column. The amine degradation occurred at incinerator temperatures (300°C–320°C), and the VOC concentration was measured at the SRU3 outlet stream. A revamping of the column internals was essential to minimize the amine solution carryover, which led to a VOC reduction at SRU3's outlet stream (10 mgC_{eq}/Nm^3–15 mgC_{eq}/Nm^3).

The final step consisted of an investigation into the possible chemical reaction for VOC generation, as a methanation reaction in the TGTU reduction reactor had been identified. The presence of COS and CS_2 in a reducing environment (excess of hydrogen) can create CH_4. By minimizing the precursors involved in the reaction, it was possible to reduce the content of CH_4 VOCs at the stack to a very low level.

The synergy of these actions led to an overall reduction of VOCs at the SRU complex by two orders of magnitude vs. the original value (target achieved VOCs < 5 mgC_{eq}/Nm^3). **HP**

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