SRU-TGTU Analyzer Best Practices

RefComm Galveston 2016
Sulfur Recovery

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SRU-TGT Analyzer Tags

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AT-1 (Acid Gas)

\[ \text{H}_2\text{S} + \text{Total Hydrocarbon} \]
\[ \text{(CO}_2, \text{H}_2\text{O, NH}_3) \]
\[ \text{(BTEX, MeOH)} \]
O\textsubscript{2} Required to Burn Hydrocarbons Compared to an Equal Amount of H\textsubscript{2}S

<table>
<thead>
<tr>
<th>Compound</th>
<th>Moles O\textsubscript{2} per Mole HC</th>
<th>Ratio of O\textsubscript{2} needed per mole HC compared to mole of H\textsubscript{2}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Ethane</td>
<td>3.5</td>
<td>7</td>
</tr>
<tr>
<td>Propane</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Butane</td>
<td>6.5</td>
<td>13</td>
</tr>
<tr>
<td>Pentane</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>Hexane</td>
<td>9.5</td>
<td>19</td>
</tr>
</tbody>
</table>
Field Data / HC Process Upset

H$_2$S swings from 83 to 87%

THC = 0.25%

12 fold increase in THC from 0.02 to 0.25% lasting ~3 minutes

THC = 0.02%
Feed Forward Analysis: Actual Control Response to Hydro-Carbons
(Courtesy of Jacobs Comprimo)
Acid Gas Analyzer / Summary

• Benefits
  – For SRUs with TGTU: Mitigation of SO₂ breakthrough to the amine absorber…It’s not when the HC comes that makes the problem, its when the HC goes away
• To be “ready” install a heated acid gas probe at shutdown
AT-4 (SRU Tail Gas)

$H_2S / SO_2$

($COS, CS_2$)
Ratio vs Excess H$_2$S vs Air Demand

• Ratio is the non linear expression of $2 \text{H}_2\text{S} / \text{SO}_2$

• Excess H$_2$S is the linear expression of $[\text{H}_2\text{S}] - 2[\text{SO}_2] = -1\%...0\%...+1\% \text{H}_2\text{S}$

• Air Demand uses a scaling factor $AD\{2[\text{SO}_2] - [\text{H}_2\text{S}] \} = -5\%...0\%...+5\% \text{AIR}$

        (AD factor is nominal 3.5)
Tail Gas: Efficiency as a Function of Excess Air
Tail Gas: Process Upset & Over-Range Event
SRU at Turndown
(slow response vs plugging)
COS & CS$_2$ in SRU Tail Gas

COS: 0 to 4,500 ppm
CS$_2$: 0 to 1,200 ppm
Putting the Analyzer in Control After Start-up

“After start up when is the analyser put into control mode?”
- Catalyst preference for H2S over SO2 can skew true air control.
- Sulphur Experts recommends control mode after 8 hours.

“Do you consider tail gas analysers to be reliable?”
- Thankfully yes was common response
- Responses capture the evolution of the tail gas products.
- Time for a 3rd generation.

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Tail Gas / Best Practices

Top of the Pipe Analyzer

Sample Line Analyzer 900 ADA

Insulated steam jacketed nozzle

Weather cover for ASR probe and jacket

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Tail Gas Best Practices / Weather Protection

“Each 10C increase in operating temp above 25C reduces mean electronics component operating life by 50%”
Tail Gas “Sample Line” / Best Practices

Installed at 45° between Cd4 & RGG (bad piping design…good installation) Slope the sample line, no pockets
Tail Gas Analyzer / Summary

• Heat integrity at the sample point is paramount
  – Regulated MP steam is best, trapped LP if a must
  – Solve heat integrity problems with Conto-Trace (do not wrap tubing around a nozzle (which does not work))

• Observe the H₂S/SO₂ indicating outputs
  – They can give non predictive results
  – When the analyzer is moving…its working

• Connect the analyzer into the AIT data network
AT-5/6/7 (TGTU)

H₂ / H₂S
(COS / SO₂)
Analytical Measurements on a TGTU

• The critical (gas) measurements are $\text{H}_2$ and $\text{H}_2\text{S}$

• COS is a secondary measurement in combination with $\text{H}_2 + \text{H}_2\text{S}$

• $\text{CS}_2$ for certain applications but COS considered more important

• SO$_2$ can be measured at the quench inlet or outlet (not common)

• pH is measured in the quench water (not addressed here)
Amine-Based Tail Gas Treating Unit

Claus Tail Gas

Substoichiometric Air + H₂

Inline Burner (RGG)

Tail Gas

Fuel

Reduction Reactor

Quench Tower

Analyzer Sample Point #1

Analyzer Sample Point #2

H₂S 0-5%

H₂ 0-5%

H₂S 0-500 PPM

H₂ 0-5%

COS 0-200 PPM

To Incinerator Stack

Absorber

H₂O

To Amine Regenerator

Amine from Regenerator

Start Up Sample Point

LPS

WHE

CW

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Ranges for \( \text{H}_2\text{S}/\text{COS}/\text{CS}_2 \)
Location for \( \text{H}_2 \) Measurement

- Optimal analytical ranges
  - \([\text{H}_2\text{S}] > [\text{COS}] > [\text{CS}_2]\) generally exist in < concentrations
  - Ranges subject to spectroscopy matrix, optimal ranges are;
    - \( \text{H}_2\text{S} \) 0-100 ppm (up to 0-500 ppm FSR depending on permit levels)
    - \( \text{COS} \) 0-200 ppm
    - \( \text{CS}_2 \) 0-50 ppm

- \( \text{H}_2 \) sample point location when there are 2 analyzers
  - Locate the \( \text{H}2 \) measurement at the Absorber outlet (slightly cleaner)
  - If using Flexsorb locate the \( \text{H}2 \) measurement at the Quench outlet
HAG Particulate Filter After $\text{SO}_2$ TGTU Upset
Low $H_2$ (TGTU) vs High $SO_2$ (Tail Gas)
TGTU (COS & H$_2$S)  Steady State & Upset
TGTU Analyzer Summary

• A $\text{H}_2 / \text{H}_2\text{S}$ analyzer is critical to the operation of a TGTU

• When replacing a legacy $\text{H}_2 / \text{H}_2\text{S}$ analyzer add the COS/CS$_2$ measurements

• If there is a diverter valve have a “start up” sample point

• If there is an analyzer at both the Quench and Absorber outlet put a $\text{H}_2$ sensor at both locations

• This survey is based on ~190 analyzers
  – Of which ~150 are at Abs outlet, ~35 at Quench outlet. ~5 at Quench inlet
AT-8 (Emissions)

**SO₂**

**SO₂ Mass Emission**

**(H₂S, O₂, NOx)**
Other Parameters

- **SO₂**
  - Dual range for TGTU bypass periods

- **H₂S**
  - Measurement of residual value after incineration (~10 ppm)
  - The part of EPA sub-part J(a) that was not promulgated
  - Accounting for un-combusted reduced S compounds by oxidizing the residual H₂S to SO₂

- **O₂**
  - Stand alone analyzer or on board with CEMS SO₂ analyzer
  - Combustion control can only be done with stand alone

- **NOx**
  - NOx values are low, not normally required
Emission Analyzers

▪ “The Color of Plumes”
  ▪ White: Steam plume caused by water condensation (cold, Canada)
  ▪ Bluish white: SO$_3$ plume usually caused by high SO$_2$ emissions
  ▪ (….Confirmed by “Green Slime” in the CEMS sample system)
  ▪ Orange: NO$_x$ plume
  ▪ Brown: Unburned hydrocarbon / soot plume
  ▪ Green: Burning H$_2$S plume
AT-2 (O₂ / SRU Start up)

O₂
(CO, Combustibles)
Process Oxygen Measurement

- For start-ups and shut-downs of the SRU
  - Requires excess O\textsubscript{2} to near stochiometric conditions of 0.1\% xs air

- Measurement typically done by operators using portable unit
  - Safety considerations: exposure of personnel during start up
  - SRU-TGTU tend to be all at one time and not in sequence

- A fixed (permanent) system can consist of;
  - Laser based “non contact” type analyzer (capable of sampling into “Claus” mode but shut-in after transition to “Claus” mode)
  - Isolated between start ups with "ASR" probes
AT-3 (Sulfur Pit)

$\text{H}_2\text{S}$ (LEL)

$\text{SO}_2$ (Pyrophoric sulfur fire)
Sulfur Pit Gas: Solubility of H₂S in Sulfur

- Produced sulfur has ~600 ppm of dissolved H₂S + hydrogenpolysulfide
- Spontaneous degassing and concentration in the gas phase can increase to explosive levels (3.25%)
- Pit gas analyzer requires same sample integrity as tail gas analyzer
- H₂S is measured to warn of LEL, SO₂ is measured to warn of S-fire
- Used to quantify addition to emissions (Pit can be 1/3rd or more of emissions)
H$_2$S / SO$_2$ values
S-Tank sweep gas
Sulphur Pit High H₂S & SO₂ Values (Just prior to an incident)

CFD modeling confirms H₂S can exist ~16x The mean value

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## Maintenance: Analyzer Categories

<table>
<thead>
<tr>
<th>Complexity Factor Category</th>
<th>Type of Analyzer</th>
<th>Estimated PM (h/month)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (Simple)</td>
<td>pH, Conductivity, Gas Detection, O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2</td>
</tr>
<tr>
<td>2. (Physical Property)</td>
<td>Boiling Point, Flash Point, Freeze Point, RVP, Viscosity</td>
<td>3</td>
</tr>
<tr>
<td>3. (Environmental)</td>
<td>CEMs SO&lt;sub&gt;2&lt;/sub&gt;, CO, Opacity, H&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>2.5</td>
</tr>
<tr>
<td>4. (Complex)</td>
<td>Tail Gas, GC, Mass Spec, NIR, FTIR, H&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>4</td>
</tr>
</tbody>
</table>

Outside Training

Courtesy of Chevron ETC, Analyzer Engineering Group

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Q&A

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