Industry Survey of Safety and Operational Considerations for Sulfur Complex Thermal Oxidizers

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Executive Summary

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A particularly difficult situation exists with how to manage a trip of sulfur complex thermal oxidizer. Over the years, many discussions have taken place within industry all ending up with the conclusion that a simple one-size-fits-all solution does not exist due to configuration difference in the plant, potential variability in the operation of upstream equipment, local regulatory and environmental requirements, and event specifics. A blind survey was sent to the Amine Best Practices Group (ABPG) to collect information on the current safety and operational considerations focused around sulfur recovery unit (SRU) thermal oxidizers (TO) being utilized by operating companies.

Survey results indicated that there is majority agreement on the required automated shutdowns for high temperature and loss of flame for all thermal oxidizer configurations. Most respondents indicated that they evaluate high temperature as being caused by either high hydrogen, fuel gas, or hydrogen sulfide flow. The survey highlighted that industry is not in agreement on whether an incinerator trip should be immediate around high temperature or if the SRU upstream of the incinerator should also trip when a thermal oxidizer trips. Operating companies were also split on if it was an acceptable practice to allow tail gas or pit gas to be flowing to the thermal oxidizer during an ignition attempt; when permitted there were generally well defined LEL or flammability targets to reduce likelihood of a safety event. Many operators find it difficult to meet temperature corrected LEL or flammability targets during both normal operation and unit upsets. For instance, hydrogen LEL at 482°C/900°F is reduced from 4.1% vol to 2.0% vol.

Description of Operating Configurations Considered in this Survey

The specific sulfur complex configuration within each refinery could impact how an operating company decides when or how the thermal oxidizer trips. Configuration could also influence the decision on whether a thermal oxidizer trip also trips the associated upstream Sulfur Recovery Unit (SRU). With these influences in mind, the survey questions were broken down by sulfur complex configuration and type of thermal oxidizer. The various configurations used in the survey are described below.

Sulfur Complex Configuration

- Single SRU at Site: Sites that operate a single SRU are confronted with the conundrum of balancing the safety inside the SRU compared with environmental and safety risks associated with site acid gas shedding response.

- Multiple SRUs at Site: Sites that operate multiple SRUs have the benefit of shutting down a single SRU, which can minimize site emissions and safety risk during acid gas shedding response.
- Single Thermal Oxidizer: SRUs that have a single thermal oxidizer without the ability to route to another thermal oxidizer during startup have to answer the question "Can a tripped thermal oxidizer be re-lit while the tail gas is still flowing gas to it?"
- Spare Thermal Oxidizer: Some sulfur complexes have either a dedicated spare thermal oxidizer or a header that allows for diverting flow to another thermal oxidizer. This benefit allows for process gas that often contains LEL above safety targets to be quickly moved away from the tripped a thermal oxidizer to allow for light off.

Thermal Oxidizer Configuration

- Natural Draft: a natural draft thermal oxidizer relies on density difference between hot and cold gases to create pressure differential that pulls the air into the combustion chamber and up the stack.
- Forced Draft without WHSG: a forced draft thermal oxidizer uses a blower to drive the air into the combustion chamber and up the stack
- Forced Draft with WHSG: a forced draft thermal oxidizer with a waste heat steam generator (WHSG) can be added to generate steam from the waste heat from combustion.

Description of Safety Events Impacting Thermal Oxidizers

The survey posed the question as to which automated shutdowns are implemented for the three different thermal oxidizer configurations. The responses are reported in Table 1. There was strong alignment on requiring high temperature and loss of flame shutdowns for all 3 configurations and low air and low steam generator level for oxidizers with a WHSG. It should be noted that the WHSG low level shutdown was not specifically called out on the survey as an answer choice; but was added as an "other" response. Industry is aligned on requiring a WHSG low level shutdown.

Table 1*: Survey results indicating percent of respondents that implement the shutdown for each thermal oxidizer configuration. Blue highlights indicate a high level of agreement*

What will initiate a thermal oxidizer automated shutdown?			
Shutdown Activation	**Natural Draft**	**Forced draft w/o WHSG**	**Forced draft w/ WHSG**
High temperature	80%	80%	82%
Loss of flame	90%	90%	91%
Low O_2	0%	0%	0%
Low air flow	20%	60%	73%
Low fuel gas flow or pressure	30%	30%	36%
High fuel gas flow	20%	10%	9%
Other (please specify)	20%[a]	30%[b]	64%[c]
a- local shutdown (1)			
b- local shutdown(1) / high FG pressure(1)			
c- low WHSG level (4) / local shutdown (1) / low air header pressure (1)			

The initiating events for high temperature and loss of flame were chosen to be discussed in more detail as they were highlighted as highest alignment. Low combustion chamber oxygen (measured in stack) is also briefly discussed as there have been several recent examples in industry of events causing a flame at the top of the thermal oxidizer stack.

<u>High Temperature Initiating Events (All Thermal Oxidizer Configurations)</u>

The survey evaluated which high temperature events are generally evaluated as part of a hazard assessment. Results shown in Table 2 indicate that the three main hazards that are evaluated are high hydrogen, fuel gas, or H_2S. Exceeding the fire box design temperature is the primary risk for a high temperature event. This temperature is often set at the refractory design limit.

Table 2*: Survey results indicating percent of respondents that evaluate different high temperature initiating events. Blue highlights indicate a high level of agreement.*

Which causes of high temperature in thermal oxidizer do you evaluate in hazard assessment?	
Initiating Causes	**% of Responses**
High hydrogen to thermal oxidizer	90.00%
High fuel gas to thermal oxidizer	100.00%
High H_2S to thermal oxidizer	90.00%
High hydrocarbon in acid gas to SRU	60.00%
High hydrocarbon in hydrogen	20.00%
Un-combusted fuel gas in SRU to thermal oxidizer	50.00%
Other (please specify)	20.00%

Numerous causes of each initiating event should be considered in hazard review and Table 3 outlines several of the high temperature causes.

***Table 3**: Initiating events that can lead to high temperatures in the SRU thermal oxidizer. This list is not exhaustive but contains most common causes for each hazard.*

Hazard	Cause 1	Cause 2	Cause 3
High H_2S Concentration	Inadequate air flow required for acid gas feed rate • Air flow control loop failure • Acid gas control loop failure • Air flow backed out by SRU pressure	Hydrocarbon contamination in acid gas • Amine unit upset • Sour water stripper upset • Off ratio fuel gas operation during cofiring	Loss of TGTU Amine • Loss of amine circulation • Loss of amine regeneration
High Fuel Gas Flow	High fuel flow from thermal oxidizer • Fuel gas control loop failure • Temperature control loop failure	High fuel flow from SRU • Fuel gas control loop failure during SU/SD or cofiring • Off ratio fuel gas operation during SU/SD or cofiring	
High H_2 Concentration	Hydrogen makeup control loop failure		

According to survey results the most common safeguards credited for high temperature were high temperature safety shutdown and high temperature critical alarm as shown in Figure 1.

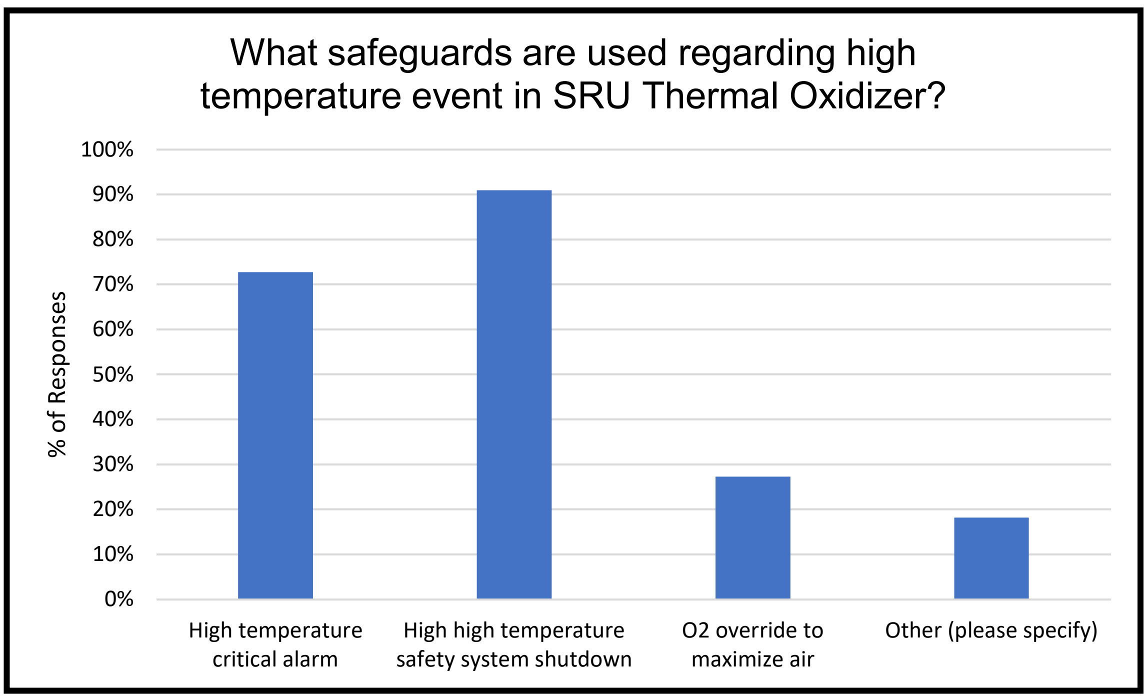

***Figure 1:** Survey results on credited safeguards surrounding SRU thermal oxidizer high temperatures. The other response was for a high fuel gas pressure trip.*

Loss of Flame (All Thermal Oxidizer Configurations)

Loss of thermal oxidizer flame can lead to an accumulation of combustible gases, resulting in dangerous toxic or deflagration outcomes. Table 4 contains a list of common initiating events that can lead to loss of flame. Flame detection is used as a direct measurement for the existence of the flame. Air flow (forced) and fuel gas high and low pressure are often included as part of the safety shutdown systems as shown in Table 1.

***Table 4**: Initiating events that can lead to loss of flame in the SRU thermal oxidizer. This list is not exhaustive but contains most common causes for each hazard.*

Hazard	Initiating Event
Low Air Flow	Air flow control loop failure (low)
	Air blower trip (if forced)
	Air backed out by downstream pressure drop (WHSG leak)
Low Fuel Gas Flow	Fuel gas control loop failure (low)
	Temperature control loop failure (high)
High Fuel Gas Flow	Fuel gas control loop failure (high)
Unit Upset	Dynamics of SRU Divert event blows out flame

Low Combustion Chamber Oxygen

While none of the respondents indicated that they trip their thermal oxidizers on low O_2, there have been several recent examples of industry events where thermal oxidizers have taken the form of a flare when insufficient oxygen exists inside the combustion chamber. This event most often occurs when excess H_2S or hydrocarbon passing into the thermal oxidizer above the available air rate to fully combust. When this happens, the high contaminate laden flue gas will pass up the stack and find excess O_2 at the stack outlet. The gas at the stack outlet has the potential to be hot enough to autoignite in the presence of O_2 and create a sustainable flame at the top of the stack. One consideration for this event response is to have air controller override any air to fuel ratios to maintain a minimum O_2 content. The high contamination event may coincide with a high temperature in the firebox, but not always. Figure 2 shows a thermal oxidizer with a flame on the top of the stack during a high H_2S event. Dispersion analysis is often used to understand risk of sending high levels of contamination out the stack. Natural draft thermal oxidizers have an elevated risk of toxicity at grade compared to other configurations when draft is lost, which needs to be considered for hazard analysis.

Figure 2: *Thermal oxidizer experiencing low fire box O_2 during a high H_2S event.*

Instantaneous or Delayed High Temperature Shutdown of Thermal Oxidizer

Industry appeared to have poor alignment on whether a high temperature trip should be instantaneous or delayed. The survey posed this question by breaking down each type of sulfur complex configuration for each type of thermal oxidizer configuration. Figure 3 shows the breakdown of responses for each configuration. It should be noted that there were less responses for single site SRU configuration (A and B). The data supports the impression that there is not agreement in industry on immediate versus delayed shutdown. Immediate thermal oxidizer shutdown is the primary response for most configurations. Some responses indicated that internal guidelines allow for a delayed shutdown, but were not being utilized. There were also many “varied” responses, indicating that inside operating companies there may be some variation in approach as well. Several of these operating companies have expressed that they are working towards a company-wide standard.

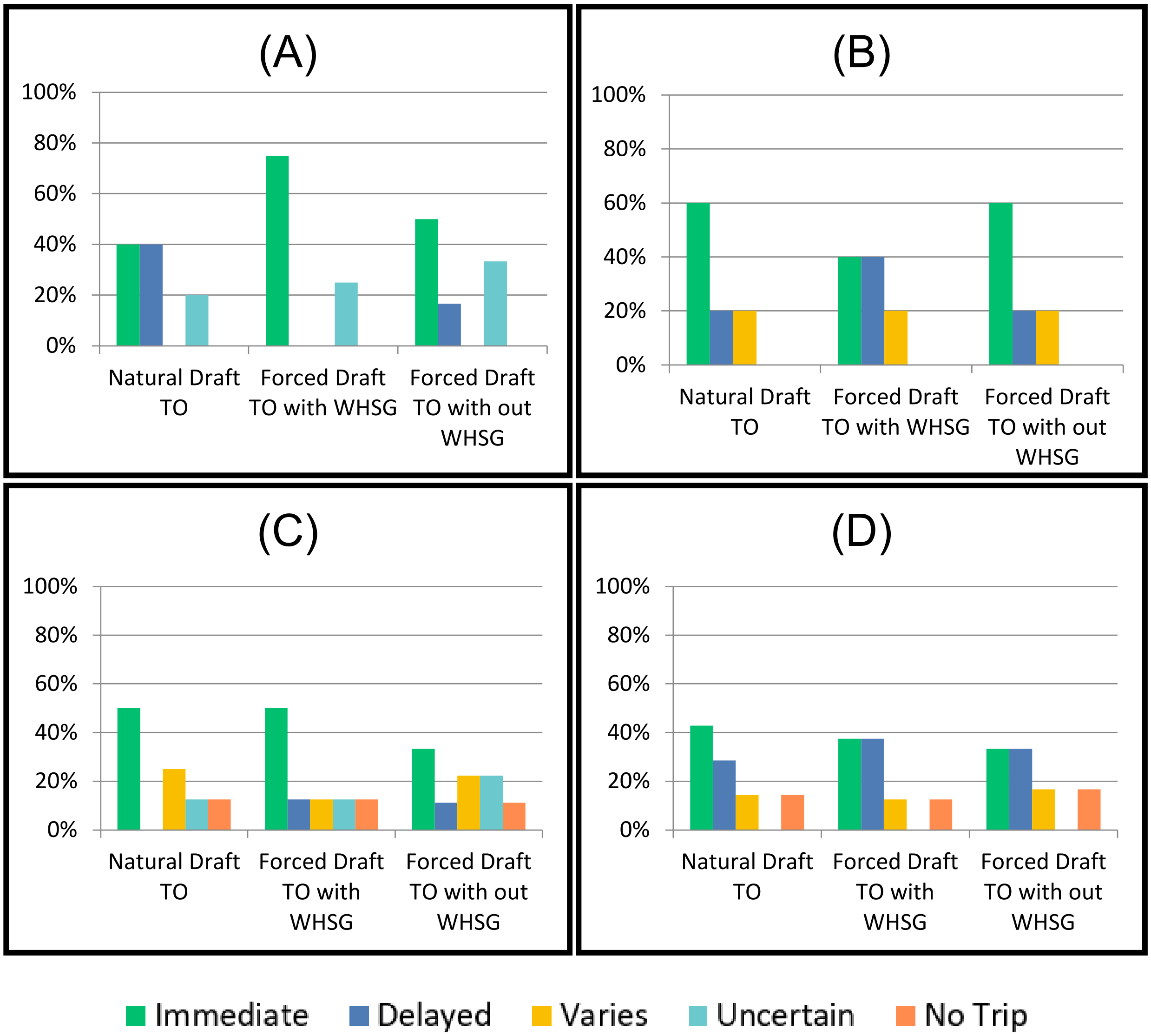

Figure 3. *Survey results for "Is a high temperature trip instantaneous or delayed?" Values shown as percent of respondents. (A) Single SRU train at site without spare thermal oxidizer (B) Single SRU train at site with spare thermal oxidizer (C) Not singular site SRU without spare thermal oxidizer (D) Not singular site SRU with spare thermal oxidizer.*

Tripping Upstream SRU Following a Thermal Oxidizer Trip

Another question that is often discussed in industry is "How can I safely relight a tripped thermal oxidizer?". One pathway to proving a safe ignition attempt is to remove SRU tail gas completely from the thermal oxidizer. Figure 4 contains the results from the survey asking operating companies if they trip the SRU when a thermal oxidizer trips. It should be noted that there were less responses for single site SRU configuration (A and B). Results from the survey show that there is variation between operating companies and inside operating companies.

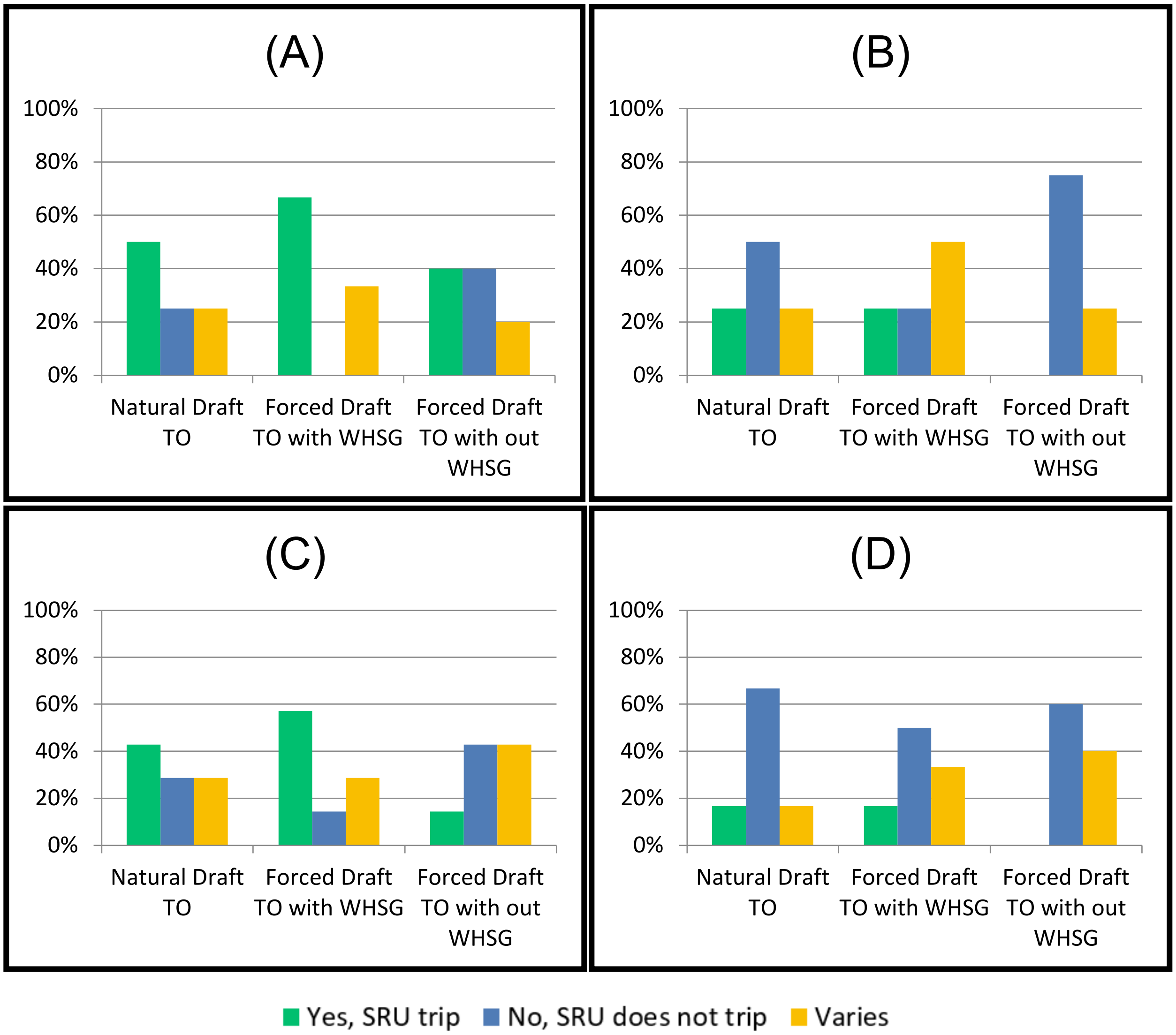

Figure 4*. Survey results for "Does a trip of a thermal oxidizer also trip the upstream SRU?" Values shown as percent of respondents (A) Single SRU train at site without spare thermal oxidizer (B) Single SRU train at site with spare* thermal oxidizer *(C) Not singular site SRU without spare* thermal oxidizer *(D) Not singular site SRU with spare* thermal oxidizer*.*

Data shows that SRU configurations that have a spare thermal oxidizer, or a shared thermal oxidizer header were less likely to trip the SRU. These configurations appear to provide robustness in terms of safety and emission considerations. Unfortunately, these options can be high in capital or not feasible for a variety of reasons.

Safety Considerations Following a Thermal Oxidizer Trip

While some locations have redundancy in thermal oxidizers or backup systems such as caustic scrubbers, others would need to run the SRU tail gas or tail gas unit off gas through an unlit thermal oxidizer to maintain production. Depending on the individual configuration of the sulfur complex and the duration of the trip event, relighting a thermal oxidizer while running process gas though could result in a serious safety outcome for the operator if adequate safety verifications are not followed. For those scenarios where the safety cannot be proven, the correct response to a thermal oxidizer shutdown is to trip the SRU. This will often involve production cuts in the plant and temporarily flaring of acid gases for units equipped with an acid gas flare. For configurations where there is no acid gas flare available or spare sulfur plant, the ultimate pathway could result in H_2S being emitted to refinery furnaces or hydrocarbon flares.

Two additional questions were asked to the ABPG. Members were asked if they allow for tail gas or pit off-gas to be routed to the thermal oxidizer during ignition and if they do, the safety verifications they require. These results are shown in Table 5. Each "Yes" respondent also commented with details on their safety verification requirements, the common themes from those answers are shown in the "Summary of Comments" column. Operating companies are split on this question.

Table 5*: Survey results for if respondents allow for tail gas or pit off gas to be routed to the TO during an ignition attempt.*

Is tail gas allowed to be flowing to thermal oxidizer during light off?		
Answer Choices	**% Responses**	**Summary of Comments**
Yes, with safety verification (please explain in comment)	64%	• 6 of 7 yes respondents indicated either LEL <25% or proven to non-flammable to allow for ignition attempt. • 5 of 7 respondents indicated diverting tail gas or acid gas to an alternative location for TO ignition is recommended prior to relying on LEL and flammability. • 2 of 7 respondents indicated different responses for forced vs natural draft.
No	36%	
Is pit off-gas allowed to be flowing to thermal oxidizer during light off?		
Answer Choices	**% Responses**	**Summary of Comments**
Yes, with safety verification (please explain in comment)	45%	• 3 of 4 yes respondents indicated LEL <25% is required to be routed to TO and that if pit sweep is meeting design requirements to keep the pit below 25% LEL then the off gas is assumed to be safe to be routed to the TO.
No	55%	

While several operating companies allow the use of LEL or flammability to prove a safe ignition state, it can be difficult to meet those targets. Reducing hydrogen concentration in tail gas to meet an LEL requirement can be difficult with units running high CO_2 acid gas or cofiring. It can also be challenging to prove the flammability using reliable sampling and testing techniques available.

Other considerations that operating companies have used to form their thermal oxidizer guidelines include whether they have continuous pilots installed and if they deflagration panels on the thermal oxidizer. Some operating companies have installed a caustic scrubber to handle short operation of acid gas to allow for thermal oxidizer reignition, while others operate with enough spare SRU capacity that a SRU trip is a small impact to refinery production or emissions.

Managing Toxicity

Managing the emission of SO_2 and uncombusted H_2S is the most pressing concern with the loss of the thermal oxidizer. With a tail gas unit online and stable operations on the front end of the Claus plant, emissions can be of minimal concern at the outlet of an unlit thermal oxidizer stack. However, off-ratio Claus operation during a process upset or with a bypassed tail gas unit can very quickly increase the load of toxics to the thermal oxidizer.

Initially on a trip of the thermal oxidizer burner, H_2S combustion may continue when the thermal oxidizer is still hot. However, as time passes and the thermal oxidizer cools off, H_2S destruction efficiency decreases. With the gradual cooling, the exhaust gas also becomes less dispersed upon exit of the thermal oxidizer stack. Units with relatively short stacks are disadvantaged compared to units with stacks approaching 300 feet. Dispersion modeling can aid in evaluating the risk at grade near the thermal oxidizer stack across a variety of operating and ambient conditions.

Natural draft thermal oxidizers can be even worse in comparison to their forced draft counterparts as they rely on temperature to generate sufficient draft to exhaust gases at elevation. Available draft is reduced as the thermal oxidizer cools off and can result in backflow of toxic process gas through the air intake near grade and in close proximity to operating personnel. This can lead to increased exposure potential.

As the thermal oxidizer cools with process gases still flowing through it, sulfur vapor can also be condensed or solidified along the walls of the thermal oxidizer chamber and stack. Once the thermal oxidizer is relit, this sulfur will combust, leading to a local sulfur fire and high SO_2 emissions.

Managing Deflagration

Claus section tail gas can contain significant concentrations of H_2S, CO, and H_2. Industry standards such as NFPA 86 Standard for Ovens and Furnaces target lower than 25% LEL in the thermal oxidizer and associated ducting prior to the burner ignition sequence (section 8.5.1.5.2) to ensure a controlled ignition. While there are exclusions for not requiring a purge on systems where the combustion chamber temperature is proved to be above 1400^{o}F (section 8.5.1.9.1), this is not always possible to achieve or prove. The low lower flammability limits of hydrogen (4.1% vol at 20^{o}C/68^{o}F) and H_2S (4.3% vol at 20^{o}C/68^{o}F) can make this a challenge, as LEL concentrations are reduced at elevated temperatures.

Temperature impacts to LEL can be estimated using the following relationship (1):

$$LEL_t = LEL_{20°C} \cdot [1 - 0{,}0011 \cdot (t - 20)]$$

$$UEL_t = UEL_{20°C} \cdot [1 + 0{,}00214 \cdot (t - 20)]$$

where:

- LEL_t lower explosive limit by the temperature of t in vol. %,
- UEL_t upper explosive limit by the temperature of t in vol. %,
- $LEL_{20°C}$ lower explosive limit by the temperature of 20°C in vol. %,
- $UEL_{20°C}$ upper explosive limit by the temperature of 20°C in vol. %,
- t operating temperature in °C.

At 482°C/900°F, the LEL for H_2 is reduced from 4.1% vol to 2.0% vol. Similarly, H_2S LEL is reduced from 4.3% vol to 2.1% vol.

As the % LEL of a gas mixture is the summation of the % LEL for each component, it can become challenging to meet the 25% LEL or lower preignition target with process gas flowing through the thermal oxidizer. It is true that with stable upstream Claus plant and tail gas unit operation that there can be a limited fuel concentration during a purge cycle in the thermal oxidizer. However, abnormal conditions on upstream units can skew the H_2S content well above normal levels. The uncertainty in guaranteeing upstream operational stability prior to an air purge and relight attempt can add an additional complexity to ensuring relight attempts maintain safe conditions in all circumstances.

Given the difference in site configuration, there is not a simple solution for all plant layouts regarding the loss of a thermal oxidizer on a sulfur complex. There are risks associated with uncombusted toxic emissions and the potential for a deflagration, that need to be evaluated before a thermal oxidizer is relit without removing the sources of process gas to the thermal oxidizer. Temporarily reducing refinery sulfnvur loads and tripping the Claus plant or routing the feed gases to a properly designed acid gas flare (or less directly to refinery furnaces and hydrocarbon flare through upstream absorbers) may be the preferred operation to remove fuel sources from the thermal oxidizer to allow relight.

Several operating companies indicated that they utilize continuous pilots to verify safe conditions exist for reignition of the main burner. If pilot is confirmed to be running after a trip of the main flame then any combustibles will not accumulate in the firebox. The continuous pilot also provides a means for reigniting the main burner and no deflagration will occur on relight of the main flame. Even with the use of a continuous pilot a natural draft thermal oxidizer still holds the risk of loss of draft and H_2S toxicity at grade. A maximum time limit on the time from main burner trip to reignition is one option to accommodate for this risk.

Conclusions

Each operating company has been faced with the question, “How should I respond to a SRU thermal oxidizer trip?” It has historically been difficult to come to a consensus on the topic. The survey sent to the Amine Best Practices Group did reveal that the industry is still not in agreement on the topic. There is agreement on which hazards need to be considered during upsets and reignition of the thermal oxidizer, but how those hazards are mitigated varies between operating companies and often within those operating companies. This topic will continue to be discussed as the industry strives towards safe, environmentally friendly, and reliable operation of SRU thermal oxidizers.

References

(1) Lepik, P.; Serafin, J.; Mynarz, M.; Dragacova, J., “*Effect of Temperature on the Concentration Explosion Limits of Combustible Liquids*,” Safety and Security Engineering V (WIT Press, 2014) p.597.