Unusual Reformer Events and Modeling

As a basis for examining reformer and heater safeguards, the potential hazards of reformers, reformer damage and explosion events were compiled, including both better-known and lesser-known events. A number of significant consequence events had unusual causes that could be missed in a normal hazard analysis.

A study was then developed to examine certain reformer events where potential blast impacts were identified. The events were modeled to evaluate their impact and the associated frequencies. The model provides a method to evaluate the risk and consequences during these critical periods of operation for site considerations and so that proper controls can be considered.

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Introduction

An ammonia reformer is ‘primary’ to the site in several ways—not only in providing a main source of hydrogen for ammonia production, but also a primary operating practice, safety, and engineering concern. A study of primary reformer events characterizes the consequences of reformer incidents and modeling of potential blast events. While some events result in minor incidents, others cause significant costs and production losses. Reformer events can also cause Significant Injury or Fatalities (SIF), including the risk of catastrophic explosions. The results of this study serve as a resource for reformer operation, plant production, and plant safety.

Understanding Explosions--Beyond the Fire Triangle

A vapor cloud explosion (VCE) results if flammable vapors and oxygen are mixed with concentrations in the flammable range, and ignition occurs. In order for the flammable mixture to develop, the flammable vapor must be above the lower flammable limit (LFL) but below the upper flammable limit (UFL), which are values established for many flammable chemicals, such as methane. Having a flammable gas concentration between LFL and UFL is a necessary but insufficient condition for an explosion to occur, however. Oxygen concentration must also be above the minimum oxygen for combustion (MOC). Once the flammable gases are between LFL and UFL, and oxygen concentration is above MOC, ignition is all that is required to cause an explosion.

The strength of the blast wave associated with a VCE depends on both the flame speed and total energy of the explosion. Confinement and/or congestion are generally required, in order for the VCE to create a significant blast wave. A reformer represents a large confined volume with significant congestion, so if the flammable cloud forms inside the reformer, ignition of those gases will result in an explosion. The question is the order of magnitude of the explosion. If the cloud is very small (moments of plume formation), it would not be detected and would just be considered a fire. As the size of a flammable cloud increases, the potential impacts become more significant. However, even moderate flammable clouds within the reformer would be contained within the reformer volume, causing what is called a “woof” or “poof” event.

Larger flammable plumes, if ignited, would catastrophically fail the reformer boundary and generate a significant blast wave that could damage equipment and buildings in the vicinity, as well as cause potentially lethal injuries to personnel in the area. Filling the entire reformer firebox volume with a flammable mixture, followed by ignition is predicted to cause a very large blast wave with potential to cause severe blast loads to nearby buildings.

Because the consequences of a reformer firebox explosion is a function of the size of flammable cloud that forms, it is important for the firebox design to minimize the likelihood of ever creating a large flammable cloud within the firebox.

During initial startup of a reformer, it is standard practice to purge the reformer and convection volume prior to initiating fuel gas flow or attempting to ignite any burners. The purpose of purging the volume is to ensure that flammable gases are not present in sufficient concentration to allow an explosion to occur. The flammable sources may be from the fuel gas or from leaks in the convection coils and tubes. Failing to sufficiently purge the reformer during initial startup could result in a large flammable volume to be present during the initial light-off procedures, and an explosion and/or large fire could result.

Reformer Incidents

As a basis for examining reformer safeguards, potential reformer hazards, reformer damage, and explosion events from the past 30 years were compiled, including both better-known and lesser-known events. A number of events resulting in significant consequence had unusual causes that could be missed in a normal hazard analysis; these are highlighted.

Process Side Events:

Coking Events

A coking event (carbon buildup on the primary reformer catalyst) occurs on partial or total loss of steam, with continued process gas flow to the reformer. Except where multiple tube failures occur, coking most often occurs without loss of process containment, thus an associated SIF event is unlikely. For that reason, these less serious events will not be detailed here. However, the lack of control leading to a significant coking event may be an indicator of poor controls that could result in SIF events and/or extensive furnace damage. These scenarios will be discussed under multiple tube failure events.

Failure incidents, from coking to furnace explosions, are routinely associated with a plant upset or startup conditions when systems are changing or operators are distracted by other events. Steam to Gas ratio (S/G) trips are often in place that trip the process feed gas upon a low value. Varying conditions in an upset may also lead to trips during these periods, some of which may be considered nuisance trips. Operators may avoid installing S/G or other protective trips altogether, or bypass trips during abnormal conditions—but these are the conditions where trips are most needed! The S/G control that is excellent under normal conditions may create a false sense of security; the assumptions inherent in key controls, including human factors, must be tested for unexpected conditions. A "What If" or perhaps more aptly put, a "How can this fail? / What can go wrong?" analysis may better account for abnormalities and measures to prevent loss of control. Questions to address could include: Does the steam flow meter only measure steam to the primary, or does it include steam to the air coil? Does the control rely heavily on operator actions during abnormal conditions? If so, experience teaches us that a failure will occur at some point. If there is an electronic or physical minimum stop on the steam control valve, ***is it in place***? Is there an S/G trip in place with a voting system? Will the S/G trip be bypassed, or is the trip system robust—avoiding coking conditions AND reducing spurious trips?

Staged S/G trips can be easily programmed in the electronic system, in which a very low S/G value trips the system with minimal delay, while a marginal S/G value provides more time for corrections, thus avoiding an unnecessary shutdown.

Tube Failure Events

Single Tube Ruptures/Failures due to creep during operation typically cause an upset and plant shutdown, followed by pinching of tubes where this is allowed. Such failures are not normal, but these are not viewed as a particular hazard, as the resulting fire is contained within the firebox.

Unlike single tube failures, multiple tube ruptures can result in reduced draft or loss of draft, especially in a downdraft furnace with significant additional fuel availability. A single tube failure can affect nearby additional tube losses through impingement. A number of multiple tube failure incidents have been reported, and for most of the incidents, the root causes seem obvious in hindsight. However, in all the events, the site was not expecting the incident to occur, and we should seek out the potential unexpected events. A short summary of factors involved is included here, along with a reference for more information where available.

Multiple Tube Failures, Overheat on Startup[1] The plant was in controlled startup and the reformer had reached the temperatures for adding steam to the process. The control board operator did not monitor the flue gas temperature but instead monitored the feed gas transfer header temperature, which read low due to the startup conditions. Consequently, the panel board operator instructed the outside operator to continue to light burners. As steam was never introduced to carry the heat away, the tubes were overheated to failure.

Loss of Draft, Multiple Tube Failures, Loss of Process Containment on Startup[2] The reformer draft fans lost power. The fans and furnace were restarted quickly (hot restart); there were indications of low/no steam flow during the upset conditions. The tubes overheated, with one or more initial tube failures suspected. The startup attempt continued with startup process steam and then some process gas was introduced, but at that point the draft on the furnace could not be controlled as the feed streams flowed into the firebox and overwhelmed the draft system. No explosion resulted, but heavy reformer tube damage was incurred.

Loss of draft triggers a host of upset conditions due to loss of firing and temperature control and typically loss of process gas and air flow, which in turn decreases steam generation from the secondary reformer outlet. A quick recovery may be possible, but as multiple abnormal conditions are occurring, the risk of overheating coils, multiple tube failures, and major furnace damage is increased.

Failure of multiple tubes can result in enough process gases flowing into the reformer that the vacuum condition is either significantly reduced or lost altogether. The addition of flammable process gases and reduction or loss of combustion air creates a fuel-rich, unstable configuration. If the reformer pressurizes due to process gas flow from failed tubes, the entire reformer may become oxygen deficient. Where forced draft is not part of the design or is lost and the reformer box pressure goes positive, burners could be extinguished from air starvation.

A reformer pressurized with flammable gases creates an external VCE hazard in which the flammable gases flow out of the reformer, as well as the potential for explosion downstream of the reformer after air is added to effluent gases. As is the case within the reformer, flammable gases outside of the reformer or in the ventilation ducts downstream of the reformer can create a VCE hazard when the rich gasses mix with enough air to raise the oxygen concentration above the MOC.

Depending on how the reformer volume is returned to a safe condition, it may pose a severe blast hazard as it evolves. For example, if fuel sources are all isolated, and draft fans draw air into the reformer, mixing the fuel-rich atmosphere within the reformer with the air can create a large mixture of vapors with enough fuel and oxygen to explode.

<u>Multiple Tube Failures, Process Loss of Containment During Operation</u>[3]

A false high steam flow indication to the controller led to loss of actual steam while process gas continued. The subsequent tube ruptures resulted in a firebox process fire. Fourteen tube failures resulted; some failures were from thermal shock when steam was reintroduced.

Figure 1. Tube failure from thermal shock

<u>Reformer Pigtail Failure Results in Major Fire</u> [4]

A pigtail failed at the bottom of a tube inside the firebox. The plant went into shutdown mode, but the process feed gas flow continued (though the process steam was stopped). The process gas flow fed a fire resulting in 56 tube failures. There is no comment on loss of draft in this report (Selas-designed furnace).

Earlier in the year, a similar pigtail failure with proper shutdown techniques resulted in no tube failures.

<u>Factors involved with Multiple Tube Failure Events</u>: Multiple tube failures typically result in losses in the range of $10 million to $70 million, or perhaps more at current ammonia prices. SIF events are less common, but they may occur with positive pressure on the box or if the tube failures continue until a conflagration (very large uncontrolled fire) occurs. Conflagrations may develop at a slower rate with more time for personnel to protect themselves than is available with VCEs.

A number of the incidents may have been either prevented or reduced in consequence by the good practice of simply observing the tubes in the box on a regular basis, particularly during startups. However, a loss of draft will cause flames to shoot from observation ports and into the face of an unsuspecting operator. Some sites are placing low draft beacon alarms and sirens in the reformer structure to warn operators of low draft dangers and to evacuate the reformer area.

Most factors contributing to these major events are clearly evident, and a proper Layer of Protection Analysis (LOPA) can assist in evaluating the controls in place to prevent them. Other similar but less documented events have occurred. Some of these reports document steam thermal shock, including a total loss of a newly re-tubed furnace at startup when the tubes were overheated by over-firing, and just a "whisper of steam" was added to cool them down. The events demonstrate how poor S/G protections can result in not just minor coking, but also a major failure of the furnace, so that a coking event may point to a near miss of a major event.

Events also occurred when an operator depended on a safety system that was not in place. In one, a stop on a steam controller was missing, and in another, it was assumed that loss of process gas and steam would trip the reformer burners. While these errors may seem obvious in hindsight, we as operations managers and engineers should be careful to protect our processes and our operators with robust controls and quality refresher training.

Many reformers struggle with tube overheat trips, as the tube temperature may be unreliable. Electronic controls ease voting systems with multiple inputs. However, a loss of flow can coincide with an incident that leads to inaccurate temperature readings; for those cases, temperature trips may be insufficient.

Steam Explosion Tube Failure Events

Reformer Tube Steam Explosion on Startup[5] The Canadian plant was shut down during the winter to remove pinched tubes, and steam was kept in system to avoid freezing. Condensation occurred in a steam circuit, and "when the steam flow was increased it picked up some remnant water and carried it into the furnace" resulting in a phase change explosion with catastrophic failure inside the firebox near the top of five tube assemblies.

Debris from the top assemblies for the five tubes was launched both inside and outside of the reformer box. Flying shrapnel resulted in one serious injury and six more "close calls" for other maintenance and operations personnel in the area. Forty-one other tubes were damaged, and the flue gas tunnels were damaged due to the impulse and shrapnel.

Per the paper, calculations indicated only a small amount of water would have caused the incident.

Discussion of Steam Explosion Tube Failures: The frequency of steam explosion tube failures may be underestimated, and phase change explosions are not well appreciated. However, these may be powerful.[6] Other unpublished events have occurred with a root cause of a steam explosion in a few tubes leading to other tube failures. It is also probable that other multiple tube failure events have occurred but a steam explosion was not recognized as the root cause. While the known events have been in colder regions, the typical process steam saturation temperature is ~480 F (249 C) so the potential is ever present. While the steam flow typically is heated in the mixed feed coil before entering the reformer, a slug of condensation as cited in the paper above may still reach the tubes. Where low or no flow on startup leads to condensation, steam condensation may pose a SIF hazard and can lead to serious reformer damage. Drying out the steam system is a necessary step and knowing the consequences will reinforce its importance.

Fire Side Events:

While the consequences of process side events may be severe, incidents involving the fuel side are often more serious. A summary of incidents for review follows.

Reformer Startup Fuel Leak Explosions

Reformer fire box explosions are not common, but when they occur there is a high probability of a SIF event and total furnace destruction. These events often occur upon startup, when operators or others are near or on the reformer, and can occur without warning with potentially catastrophic results. While trip and safety systems (including fuel system pressure checks prior to startup) avoid most fuel gas explosions, some events demonstrate the importance of procedural discipline and evaluating for unusual circumstances.

<u>Explosion on Startup:</u> Recapping a US government investigation report[7] for a 1985 incident: "*Six employees were preparing a large Lummus reformer furnace for startup. The furnace had been shut down for about five months due to another incident at the plant. "Because there was a lack of communication between the workers, and because some of the employees were not familiar with the furnace operator's manual, the furnace was lit while 10 manually operated gas valves were open. The flame ignited the gas which had built up in the furnace, causing an explosion. The proper procedure is to open the valve on each burner, and light each burner, separately. Also, a 5 minute pressure test is called for to detect any leaks in the system. The explosion probably would have been prevented if the pressure test had been run."* One employee was killed and another seriously injured.

Two other explosion incidents that occurred during the initial lighting of the reformer furnaces are similar.[8,9] A review of these indicates that while details are somewhat different, they are variations in the theme that the procedures, checklists, and/or checks thought to be in place to prevent accumulation of fuel in the firebox were not followed. In one case, there was no fuel system pressure system in place to verify valves were closed. In others, including the incident above, the check systems were not used.

A number of papers and resources that outline measures for safeguards on the reformer are available, including the Mossgas[10] and Yara[11] incident papers, and FM Global also provides resources for reformer practices. While extensive control systems can be installed, there is no substitute for a proper training and a disciplined approach in verifying that procedures and checklists are being followed.

Composition Changes in the Gas Supply

A variety of unplanned gas supply changes can trigger incidents and also have the potential for a catastrophic result.

<u>Reformer Explosion on Startup</u>[12] The plant reformer had fairly extensive safeguards. During normal operations, the reformers commonly burned low-BTU value syngas and ran at burner pressures higher than 7 psig (48 kPa). The paper identified that on this night shift startup, high-BTU value gas was used, where the appropriate pressure would be a very low pressure of 1.5 psig (10 kPa). The excessive fuel pressure used led to excessive gas and an explosion. The site stated that "miraculously", no one was hurt but it was a SIF potential event and extensive damage was incurred.

In that event, the BTU content of the supply gas was sharply higher than expected, which posed a hazard of overheat and/or explosion. Other events have occurred when low flow or dead-legs in fuel lines are cool and pressurized, which condenses the higher hydrocarbon liquids present in the gas. A slug of these ultra-rich gas distillates entering the fuel system results in a complete loss of control of air/fuel ratio. Reports are that the burners will look like "flamethrowers". The overly rich mixture can lead to overheating of the tubes (and damage to catalysts as well), or the potential for explosions[13] if a more efficient air to fuel ratio returns too quickly. Supply gas issues have also resulted in low temperature shift catalyst runaways during a reduction.

The gas supply BTU content dipping sharply threatens equal or greater hazards, as a reformer loss of flame may occur. Return of fuel gas would almost immediately lead to a potentially explosive condition. Inert liquids may be present, from hydrotests or contamination by solvents or oils from mis-operation of a pipeline supply. The potential for a local or single supplier to charge the line with a nitrogen or CO_2 supply that is inappropriately discharged to the gas supply system should be considered, as it will result in a reformer flameout. Since liquids in the fuel supply are unpredictable and can have significant consequences, some sites have installed adequately sized separators.

Primary Reformer VCE Modeling and Fault Tree Analysis:

BakerRisk has a long history of analyzing explosions through detailed modeling that is verified by extensive testing programs and observations from actual incidents.

In addition, BakerRisk has supported the fertilizer industry and has a decades-long background in addressing ammonia plant hazards. This background serves as a foundation for developing a fault tree analysis and modeling of potential VCE conditions that tests reformer explosion hazard assumptions, so that the effectiveness of mitigation systems can be quantified.

Figure 2. Flammability and explosion testing at BakerRisk test facilities

Certain scenarios of interest to clients have been modeled for their potential to create a catastrophic explosion event. The likelihood of a reformer firebox explosion to occur is calculated using fault tree analysis, which is a means of identifying scenarios that could lead to the explosion and quantifying the frequency of each of those scenarios. The sum of all scenarios identified is the predicted frequency of explosion.

The following reformer explosion scenarios have been identified as events to model, based on a review of startup operations, normal operations, and incidents with potential to cause an explosion that have occurred in the industry.

- **Flame-out / ignition failure**

This scenario involves the loss of flame for one or more burners having continued fuel flow. It is primarily an issue during initial startup, as normal operations involve fire at many burners, so re-ignition of flow from a single burner would not be an issue. However, it was identified that it is possible for a slug of "bad fuel" to lead to this type of event, should all of the burners simultaneously lose flame, which could lead to the event of interest.

- **Lack / Loss of Combustion Air**

This scenario involves the presence of fuel without combustion air. This condition causes a high concentration of flammable gases and could result in an explosion downstream of the combustion section of the reformer. Subsequent recovery of combustion air could produce a large flammable volume in the combustion section which could then cause a severe explosion.

Loss of combustion air can be the result of fan failure, damper closure, or excessive fuel flow. One potential cause of excessive fuel flow is tube failure within the reformer. Flow from a single failed tube is insufficient to overwhelm combustion air, and thus does not create an explosion hazard unless other failures occur. However, failure of multiple tubes can result in more fuel flow into the reformer than normal combustion air flow and draft is designed to accommodate. In addition, flow from the tubes reduces the vacuum in the reformer, which further reduces the combustion air flow, exacerbating the issue.

- **Improper Shutdown**

This scenario involves improper isolation of fuel sources to the reformer during shutdown conditions or during startup operations (prior to draft air flow being initiated). Once draft fans are shut down, a relatively small amount of fuel flow into the reformer may accumulate over time, thus causing potential for a large explosion.

Discussion of modeling and fault tree event analysis: Results of the modeling quantify the potential consequences of different reformer scenarios, and the fault tree analysis identifies the risk for a set of circumstances that lead to the event. A short discussion of some interesting results follows. A caveat is that while two different types of typical reformers were modeled, the modeling inputs and results may not apply to all sites.

Scenarios: A typical reformer with many burners provides different scenarios than a startup heater, boiler fireboxes, or other heater with a single or limited number of burners would provide. Fireboxes with a single or a limited number of burners often match airflow closely to the available fuel, and the loss of flame for a single burner can quickly lead to a VCE.

For a typical primary reformer at startup (for example, when personnel are lighting burners), the modeling indicates that the typical airflow to the box is many times more than what would allow a significant VCE when a single burner loses flame. If the airflow is maintained, the actual number of burners open without flame may be significant before the VCE potential rises to a catastrophic event, particularly if the burners are distributed through the furnace. Conversely, if airflow is lost or partially lost, the danger associated with multiple burners and the configuration of a reformer box can quickly lead to a catastrophic failure event that has the potential for severe injuries and fatalities for personnel in the area and even in nearby un-reinforced buildings. A catastrophic VCE can also be caused by a loss of fuel pressure that results in loss of flame, or a slug of inerts in the fuel system that can cause a flame-out long enough to build-up an explosive mixture in the furnace.

Lesser “woof” or “poof” events can also be categorized either as events that will pressurize the box and produce a hazard to personnel at the furnace, or those that will not over-pressurize the draft system when in operation.

Fault Tree Analysis: The fault tree analysis approach provides a tabulation of paths that may lead to a catastrophic event, and the resulting quantified risk based on assigned probabilities. While the results can be useful in a quantitative risk analysis for determining facility siting decisions, fault tree analysis also identifies the relative key risk factors to be further evaluated. For example, there may be a path that depends heavily on operator actions, which have a higher risk of failure, or an event path may be found for which the site has not considered a protective measure—such as a problem with the gas supply or a trip typically in bypass. If the path leads to a relatively catastrophic event rather than a benign event, the site can examine how to supplement its protective measures in order to avoid the serious VCE.

Summary

A number of incidents involving reformer failures have been summarized for reference by those who may be unfamiliar with the events, the potential hazards, and unusual reformer failure causes. These summaries of lessons learned and their source documents can serve as valuable training and planning tools for evaluation of reformer hazards and site vulnerabilities.

Additional incidents related to pigtail or outlet header failures outside the reformer furnace, or issues within the convection section or with auxiliary boilers, startup, and other heaters have occurred as well. Many of these incidents are available through previous AIChE Ammonia Safety Symposium readings.

Process Hazard Analyses, LOPAs, and properly designed and maintained safety instrumented systems can go far in reducing the risk. However, it can be important to take a second look at reformer incidents and analyses, as reformers are very complex systems. Anticipated conditions for HAZOPs and LOPAs may not all be considered, especially for startup, upset, or shutdown when multiple unusual conditions are present.

Fault tree and reformer VCE modeling analyses provide additional tools for characterizing reformer hazards for a particular site, for both the consequence and the risk factors involved. While a few results of fault tree and VCE modeling are discussed, the particular conditions are specific to a site design, site operation, what trips are in place, and the specific risk factors present at that site. These tools can provide methods for evaluating the mitigation systems in place, and the risks of a serious VCE event.

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