Minimize the Risk of Fire During Column Maintenance

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Understand the causes of fires in distillation columns equipped with structured packing and how to prevent them.

RECENTLY, THERE HAS BEEN INCREASED awareness of the potential for internal fires in distillation equipment, especially in columns equipped with structured packing. An investigation of 56 incidents (involving columns with various suppliers' products) found that, indeed, the large majority of the fires involved columns packed with wire-gauze and sheet-metal structured packing (Figure 1). This article discusses the findings of that study (conducted by Koch-Glitsch) and provides guidance on how to prevent fires.

Wire-gauze structured packing was introduced in 1964, with the initial applications limited to the fine chemical and pharmaceutical industries. In the first ten years, only a few hundred columns were equipped with structured packing. The introduction of sheet-metal structured packing in 1977 extended the use of structured packing to the chemical and petrochemical industries, as well as to petroleum refineries (in 1983). Since then, the installed base of structured packing has increased significantly. Currently, there are a few thousand columns in operation using structured packing in a wide variety of materials of construction. With this increase in use has come an increase in the number of fires (Figure 2).

Known causes of fire

Structured packing is very popular because of its high efficiency, due to its high specific surface area, and its low pressure drop. For the separation of temperature-sensitive products, the small liquid hold-up is also an advantage. Unfortunately, these benefits are also possible sources of problems during shutdown and maintenance.

Any hydrocarbon product residues that remain in the column after shutdown may coat the packing with a very thin film that has a surface area similar to that of the packing. It is very difficult to remove all of the residue. Small quantities of hydrocarbons have the potential to self-ignite at elevated temperatures upon exposure to the atmosphere.

Increased pressure drop is usually the first indication of the formation of coke or polymers inside the packing. However, by the time this increase is measurable, the coke already occupies a large portion of the packed bed. Cooling such a lump of coke may create several problems. Due to the low liquid (or cooling water) hold-up in the packing, a limited amount of heat can be removed. Cooling water cannot penetrate the coke formation and will only act on the upper surface, leaving the center and the bottom of the coke at elevated temperatures. Finally, the temperature gage on the column measures the temperature in the vapor phase close to the vessel wall (not the temperature inside the coke formation), so it may incorrectly appear that ambient temperature is reached inside the column, even though the majority of the coke may remain at a high temperature.

Pyrophoric substances, such as iron sulfide (FeS) formed by sulfur corrosion of carbon steel components, can settle on the packing during operation. Conventional cleaning methods cannot remove the iron sulfide. Once exposed to the atmosphere, iron sulfide will autoignite at ambient temperature.

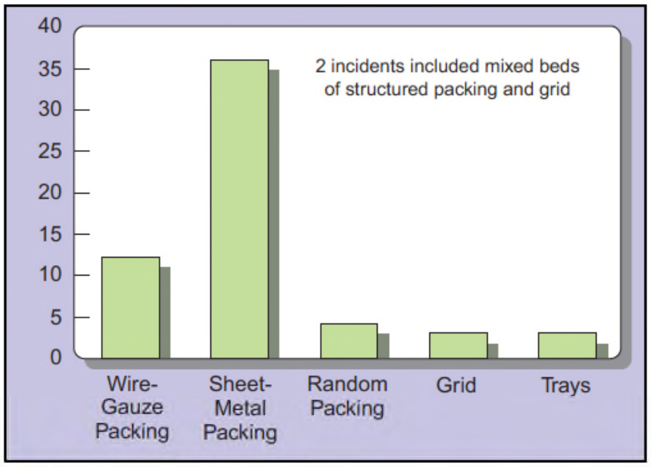
New packing is coated with a thin film of lubricating oil from the manufacturing process. In one incident, new packing caught fire after hot work was performed above the packing.

Once ignited by a hydrocarbon or pyrophoric fire, the thin sheet of the packing (0.1 to 0.2 mm) can support a metal fire. In some columns, temperatures up to 1,500°C (2,700°F) have been reported.

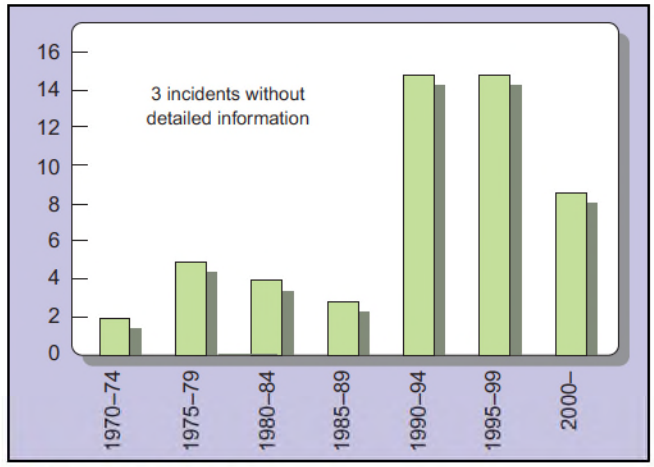
Some metals — *e.g.,* titanium, aluminum, zirconium — are highly reactive and more susceptible to ignition than others, and require special caution. For example, replacement with a less-sensitive material of construction should be considered.

Ignition sources typically follow one of two patterns:

• *spontaneous ignition* — either of pyrophoric material, or of hydrocarbons if the column temperature is above the hydrocarbon's autoignition temperature



■ Figure 1. Incidents by equipment type.



■ Figure 2. Incidents over time.

• *hot work inside the column* — generally performed in close proximity to the structured packing; welding, cutting, grinding or other operations that may generate heat or sparks.

Since most incidents are caused by pyrophoric ignition, the rest of this article focuses on that type of fire.

Pyrophoric ignition of structured packing in a crude vacuum column

Case 1. An Eastern European refinery installed sheet-metal structured packing in August 1993 in a crude vacuum column. All column internals were made of Type 410-S stainless steel. Structured packing was used in all sections to reduce pressure drop and minimize flash zone pressure in order to maximize the yield of vacuum gas oil. The column was designed for a crude with a sulfur content of 1.5–1.7%. However, due to problems with crude supply in 1994, the refinery switched to a higher-sulfur-content crude (2.8–3.0%). The unit was shut down in April 1995 for the first time after being in continuous service for 19 months.

The shutdown was performed as follows: After two days of steaming and cooling the column, the manways were opened, starting from the bottom. After opening the manway second from the top, the maintenance crew noticed smoke coming out of the manway and glowing inside the packed bed. The manways were closed and the steaming process continued. The top pump-around return was used to feed water into the column after the steaming was concluded. The next day, the column was opened again. Inspection revealed that the packing in Bed 2 was destroyed by fire. The packing was removed from the column and the column was put back into operation without any packing in Bed 2. (During the next shutdown, in April 1996, new packing was installed in Bed 2.)

Although the packing was completely destroyed, major damage to the structure of the column vessel and casualties were avoided by the fast reaction of the maintenance crew to close the manways.

Case 2. The same refinery installed structured packing in a different vacuum unit in July 1994. This packing was made of Type 316-L stainless steel because of the high sulfur content of the crude oil being handled.

When the highly sulfurous feed was processed, pyrophoric compounds were formed as a result of corrosion of external equipment (heat exchanger, coolers, etc.), and they were reintroduced into the column by the reflux and pump-around return. The liquid distributed over the cross-section of the column carried the pyrophoric components into the packed bed, where they coated the packing. The large surface area of the packing provided a large iron sulfide surface area, and the iron sulfide ignited when the column was open during the April 1995 shutdown.

Lessons learned

These and the other incidents studied provided some valuable lessons:

• The fractionation bed below the top pump-around is more sensitive to iron sulfide deposits because of the lower specific liquid load.

• Steaming of the column and water wash are not sufficient to remove the iron sulfide deposits from the packing surface.

• Iron sulfide can form anywhere from iron oxide and hydrogen sulfide (H_2S). Iron sulfide in contact with oxygen (or air) will self-ignite. Consider material selection not only for the packing and vessel, but also for piping and heat exchangers, since iron sulfide formed in carbon-steel heat exchangers and piping is reintroduced into the column via reflux.

Prevention

Frequently review the shutdown and maintenance procedures, and make sure they include the latest safety considerations. Consult the procedures before any shutdown, especially when revamping a trayed column with structured or random packing. In addition to many other plant-specific isues, the following points should be addressed in the procedures.

Shutdown procedures:

• Cool the column to ambient temperature before opening.

• Wash the column extensively and remove any product residue and other deposits.

• Employ chemical neutralization (discussed below), for example, use a permanganate or percarbonate wash to remove pyrophoric material.

• Purging the column with inert gases is recommended. Make sure you follow confined-spaces entry procedures to ensure the safety of the personnel entering the column!

• Open the column carefully and continuously monitor the temperatures of the packing as well as the column.

• Minimize the number of open manways to reduce air circulation and to enable the column to be sealed quickly.

Maintenance procedures:

• Monitor air quality and temperature inside the column and the packed bed continuously during shutdown. Install additional temperature gages and utilize continuous air monitoring with multiple gas analyzers to detect combustion products.

• Be careful when working above or in close proximity to structured packing. Do not cut, grind or weld the packing. Remove the packing before hot work. If hot work is absolutely required above the packing, take extensive measures to protect the packing.

• Do not force air circulation inside column.

• Watch for smoke, fire and temperature increases inside the column.

• Utilize a knowledgeable, experienced and trained contractor.

Safety considerations:

• Be careful when using water to extinguish packing fire. Temperatures can be very high, and water can evaporate instantly. If hydrogen is formed (in the case of a metal fire at extremely high temperatures), an explosion may result. Furthermore, liquid hold-up in packing is very low, so the use of water may not be as effective as expected.

• Cut off the supply of oxygen by: sealing the column (do not obstruct entry to column via manways during shutdown); purging the column with inert gases; and filling the column with steam.

• Prepare staff and position equipment to extinguish a fire at any time during a shutdown.

Chemical wash to remove pyrophoric substances

Several vendors offer chemical neutralization of pyrophoric compounds prior to vessel entry. This typically consists of rinsing the tower with a potassium permanganate solution, either in vapor or liquid phase. The permanganate chemically oxidizes the iron sulfide. A final water rinse is conducted prior to vessel entry.

Unfortunately, permanganate leaves a manganese dioxide (MnO_2) residue on the packing and vessel surfaces that is virtually impossible to completely rinse off. This residue is an oxidizer that may initiate or support combustion under the right circumstances. Potassium permanganate also interferes with the degreasers typically used for chemical cleaning. It must therefore be used in a two-step process, which extends the time required for cleaning the vessel. Finally, the manganese dioxide sludge generated by the permanganate must be properly disposed of.

Sodium percarbonate (sodium carbonate peroxyhydrate) is an alternative to permanganate washes that has none of the latter's major disadvantages. It can be used in a single-step process, leaves no residue, and has no special disposal requirements. As with permanganate, it can be applied in either vapor or liquid phase. Unfortunately, few vendors have experience with its use. Due to the nature of the oxidizer, it is imperative that it be applied only by experienced personnel.

Chemical neutralization procedures should always be used if there is reason to suspect the presence of pyrophoric substances in a packed tower. However, no neutralization procedure is perfect. This is especially true in a heavily fouled tower. In one incident, a packed bed ignited after vapor-phase neutralization with potassium permanganate — the iron sulfide was not completely neutralized, and it ignited the packing during tower ventilation. The vessel was closed and the fire was extinguished without significant damage to the internals or the vessel shell due to proper monitoring during ventilation and quick response by operations and maintenance personnel.

Closing thoughts

There can be no substitute for careful evaluation of ventilation, entry and emergency response procedures. Operations and maintenance people must be properly trained and ready to respond at the first sign of problems to prevent major equipment damage or potential injury to plant personnel. CEP

Further Reading

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