DISTILLATION OF FLAMMABLE OR COMBUSTIBLE LIQUIDS

INTRODUCTION

Fires and explosions originating in distilling equipment are rare, considering the number of units in use. However, since distillation requires that any liquid being processed must be heated above its boiling point, most liquids in question are in their flammable range. The only exceptions involve vacuum distillation or heat transfer fluids for process heating. As a consequence, accidental releases in distillation units have resulted in serious fires and explosions.

This section addresses distillation units that handle flammable/combustible liquids and recommends actions to reduce accidents in them.

POSITION

Management Programs

Implement management programs as described in *OVERVIEW*, AXA XL Risk Consulting's total management program for loss prevention and control. In developing a program, pay particular attention to the following important areas:

Hazardous Materials Evaluation

Develop a program to determine the pertinent physical and chemical properties of the materials to be distilled. Choose test conditions that best represent all possible operating conditions.

Establish routine procedures for testing physical and chemical properties of all materials to be distilled to confirm properties required for safe operating conditions.

Process Hazards Evaluation

When designing processes, reduce the flammable and combustible material hold-up so the amount that may be spilled by equipment failure or operator error will be less. Use modern computer control systems to keep the flammable or combustible liquids inventory to a minimum.

Determine the safe operating and potential upset conditions of all new or existing distillation processes used by the plant. Include scaling factors (bench, pilot, semi-works or full scale) in establishing the safety parameters.

Design all distillation systems to be safe by using proper instrumentation and adhering to written operating procedures. Provide adequate pressure relieving devices. Interlock equipment to shut down automatically and safely in event of operator error or equipment failure. Provide intermediate alarms to allow operators time to take corrective action.

Provide redundant instrumentation loops for all critical controls. In redundant loops, include **both** separate signal transmitters and signal receivers. Install a comparator to notify operators when control and redundant signals differ significantly. Do not expose both loops to the same loss potential; i.e., run them in the same conduit, or close to the same exposure.

To limit the amount of materials released by equipment failure, include the following measures:

- Accessible block valves (see PRC.8.0.1.3);
- Venting to flare stacks or to incinerators;
- Liquid dumping to adequately sized blowdown systems;
- Purging or flooding of equipment with a nonhazardous fluid.

Actuate these shutdown measures with combustible vapor detectors where appropriate.

When designing safety features, assume a minimum of two consecutive errors, one of which may be misinformation because of a faulty instrument or a misunderstanding of instructions.

Design and specify equipment considering all possible operating conditions, both normal and abnormal. Give particular attention to suitability of the equipment to handle the process materials and to withstand external environmental influences.

Operator Training

Develop safe operating procedure for the distillation unit. Document these procedures thoroughly and provide copies to all relevant personnel. Educate all operators in the hazards involved and in the functions of the safety control equipment. Forbid operators to run the process when any safety equipment is out of service. Train operators in:

- Normal operating procedures;
- Handling upset conditions;
- Emergency shut-down procedures;
- Emergency operations;
- Safety procedures;
- Routine and nonroutine work authorizations.
- Forbid deviations from the written procedures.

At least annually, schedule re-education and training. Include testing to assure proper performance of all assigned duties with particular emphasis on emergency shutdowns.

Pre-Emergency Planning

Develop a customized pre-emergency plan. PRC.1.7.0, the pre-emergency planning section from *OVERVIEW*, may be used as a reference. Include the following features:

- A fire and disaster alarm system;
- An emergency communications system, including radio, where needed;
- An adequately trained, staffed and equipped organization of employees for firefighting and other emergency duties;
- A planned program of cooperation with neighboring plants and with public firefighting and disaster control organizations;
- A program to analyze the interruption of business that may result from potential incidents and to develop plans for minimizing loss of production during rebuilding;
- A business continuity plan to assure that operations are unaffected;
- Procedures specific to loss scenarios located in the distillation process area.

Preventive Maintenance and Inspection

Inspect and maintain distillation system equipment, piping, rotating machinery, instrumentation, electrical equipment, pressure relief devices, and fire protection and detection equipment according to a schedule that accounts for design and service conditions. Include all appropriate types of modern nondestructive testing, IR scanning, lubrication oil and vibration analysis in the inspection techniques. Establish a detailed record keeping system that includes equipment useful life forecasts and appropriate "benchmarks."

Management of Change

Apply all management programs to any changes that are made to the facility's physical arrangement or procedures. Include the following actions:

- Repeat the process hazards evaluation program for all new distillation systems or for any modification to an existing system, including component replacements. Determine the need for new or different safety equipment or measures.
- Whenever equipment is changed from one service to another, or when distillation system changes are made, examine the inspection and maintenance program and modify as necessary. Monitor daily operating changes.
- Verify that new construction materials and all maintenance parts and supplies conform to original (or modified) design specifications.
- Apply the program for handling new construction, including the control of outside contractors.
- Update operations procedure manuals after each modification that results in a change in operating procedure.
- Do a field review and update all piping and instrumentation diagrams (P&IDs) with a computer aided design (CAD) system.
- Review and follow through expeditiously on all inspection recommendations from insurance, code enforcement and regulatory agencies.

Other Management Programs

Incorporate these features into the comprehensive management program for loss prevention and control:

- Welding, cutting and other "hot work" permit programs;
- A program for supervision of impairments to fire protection equipment using AXA XL Risk Consulting's "RSVP" program or an equivalent;
- Smoking regulations;
- Plant security and surveillance.

Duplication of Facilities

Duplicate, with installed spares, distillation equipment highly susceptible to loss or very important for continued operations. If this is not possible, keep readily available spare parts and maintain them ready for use. Physically separate or compartmentalize duplicate equipment.

For smaller scale or batch type plants, install distillation systems important to production in the form of multiple small-scale units rather than a single unit. Design a single unit to facilitate prompt repair using readily obtainable or pre-purchased parts. Where neither is feasible, store the distilled product in question in sufficient quantity to permit normal sales until repair or replacement is complete.

For large-scale chemical and petrochemical plants, provide multiple distillation systems. Also, maintain spare parts for critical equipment.

Spacing

When choosing locations for distillation equipment, do the following:

- Locate distillation systems in accordance with PRC.2.5.2.
- Segregate and barricade distillation systems for unstable materials.
- Locate any recirculating pumps handling flammable or combustible liquids so as to minimize exposure to other equipment.

Design

When designing distillation facilities, include the following:

- Maintain the smallest practical inventory of flammable liquids.
- Operate at conditions that will limit the severity of a release. E.G. operating under a vacuum will lower the temperature at which the liquid boils.
- Limit the number of flanges in the piping system to reduce the potential for leaks.
- Use corrosion resistant materials to reduce the frequency of leaks.
- Use canned pumps, magnetic drive pumps, or pumps with double mechanical seals to reduce the potential for pump seal leaks.
- Insulate the piping system so that the surface temperatures are below the lowest autoignition temperature of the materials being handled.
- Size the heat source for the reboiler so that the condenser system always has more capacity to remove heat than the reboiler has to put it in.
- Avoid the use of heat transfer mediums that are reactive with the contents of the reboiler.
- Avoid the use of electrical resistance or induction heaters.
- Establish a reliable condenser coolant supply.
- Avoid the use of flammable brines, such as alcohol and acetone.
- Avoid the use of coolants that are reactive with the material being distilled, as ammonia would with an acid, or with the residue in the still.
- Install ceramic or stainless steel packing. Avoid plastic packing due to its fire hazard when the column is open for maintenance.

Pressure Relief

Provide pressure relief systems in accordance with ASME “Boiler and Pressure Vessel Code,” or API RP 520 and API RP 521 where permitted. When sizing relief valves, take into account the maximum vapor overhead, tower flooding, reboiler and condenser capacity, and other factors discussed by Bradford and Durrett in *Avoiding Common Mistakes In Sizing Distillation Safety Valves* and by Walker in *Sizing Relief Valves For Distillation Columns*.

Discharge each vent to a safe location preferably through a pressure relief valve, conservation vent, seal pot or rupture disc. Use rupture discs, only in series with a relief valve. Where the potential for a runaway chemical reaction exists, size vents according to the DIERS protocol.

Install controls that, upon detection of a pressure increase in the system, will shut off the heat source and open valves to drain out the heat transfer medium (if any). Arrange the control system to sound an alarm when an overpressure is detected, thus permitting an orderly shutdown of the equipment. Provide an automatic second supply of coolant to the condenser.

Operations

In distillation systems with high reflux ratios, continuously purge and regularly sample and test material.

Protection

Provide 2-½ h fireproofing per UL 1709 on all major load-bearing structural supports of the distillation unit. See PRC.2.5.1 for details.

Provide drainage around and beneath the distillation unit in accordance with PRC.2.5.3.

Provide automatic water spray or foam-water spray for the distillation unit in accordance with PRC.12.2.1.2. If organic heat transfer fluids are involved, see also PRC.7.1.5 and various publications.[1] If a fired heater is used, see PRC.4.3.2 for additional details.

DISCUSSION

Distillation separates different components of a mixture according to their boiling points. Distillation usually includes three components: a still, or reboiler; a distillation, or fractionation column; and a condenser. The fractionation column recovers low boiling point products at the top and high boiling point products at the bottom.

The reboiler is the part of the equipment that vaporizes liquid. In the fractionation column, vapors become richer in one component as they rise up the column. In the condenser, rich vapors are liquefied and either run out of the unit or flow back down the column as reflux to re-evaporate on column trays or packing and help enrich the rising vapors. The fractionation column can be divided in two sections if the feed is introduced at one point along the column. The upper section is the rectifying section and the lower section is the stripping section.

Usually, a system for distillation involves all three components. However, under certain conditions, one component can be omitted.

- The reboiler may be omitted when hot vapors from a process are run directly to the fractionation column.
- The column may be omitted when the process involves boiling off all but one component of a mixture.
- The condenser may be omitted if the distilled material is to be discarded or further processed and no reflux is required.

Industry widely uses both continuous and batch distillation units. Typically, designers chose between the two based on whether the rest of the process is continuous or batch.

Reboilers

A reboiler connects to the bottom of a fractionating column and provides the heat necessary for distillation. A reboiler consists of a metal shell with tube bundles inside and is similar to a vaporizing heat exchanger. The heating medium can either be steam, gas or hot thermal fluids. Small scale and batch distillations sometimes use internal or external electric resistance or induction heaters.

Reboiler Types

The four types of reboiler designs are:

- Internal type: reboiler is located inside the column bottom.
- Thermal siphon type: reboiler is a horizontal or vertical heat exchanger where the density difference between liquid entering and liquid-vapor leaving moves the liquid through the reboiler.
- Kettle type: reboiler is a separate externally heated unit that heats the product inside a vessel.
- Fired heater: reboiler is a separate fired unit that heats the product inside tube bundles.

Liquids in reboilers circulate either by natural or forced circulation. A pump feeds the column bottom liquids through the reboiler. Fully flooded reboilers (as opposed to thermosiphon reboilers) handle heat sensitive materials.

Heat Exchange Media

Steam, thermal oil, hot water, high temperature (molten) salts and electricity are typical heat exchange media in the internal, kettle and thermosiphon reboilers.

Steam or hot water is generally a safe heating medium. Process applications requiring temperatures above 450°F (232°C) make steam an inadequate heating medium. Direct firing, high temperature (molten) salts, or thermal oil heat transfer systems produce these higher temperatures.

Low temperature distillations, particularly in the petrochemical industry, use an LP gas, such as propane, propylene or ethylene. As it liquefies under pressure, it gives up heat just as steam does when it liquefies to water. Similarly, in oxygen plants, the liquefaction of air under pressure gives up the heat needed to distill the liquid oxygen.

Operating Problems

Common operating problems of reboilers are:

- Fouling;
- Steam condensate flooding;
- Steam condensate seal blowing;
- Film boiling;
- Heating medium inadequacy;
- Boiling point elevating;
- Foaming;
- Leaking;
- Undersizing.

Distillation Column

Columns are equipped with internal trays or packed beds. Operational problems of columns are generally due to flooding, excessive pressure drop or inefficient liquid vapor contact. Such problems are well described in *Trouble-Shooting Distillation Columns* by Harrison and France.

Pressure Relief

Distillations usually run at near atmospheric pressure but may run under vacuum or pressure. The following conditions can overpressure distillation columns:

- Loss of condenser coolant due to:
    - Power failure resulting in coolant pump or air fan shutdown;
    - Mechanical failure of fan or pump.
- Excessive heating in reboiler due to:
    - Temperature controls failure;
    - Heating tube failure.
- Chemical reactions due to contamination, excess temperature or decomposition;
- Fire exposure.

Depending on the materials involved, residual vapors go to atmosphere, a scrubber or some other process. Flammable products generally go to a flare.

Designers favor relief valves over rupture discs because the sudden reduction in pressure accompanying rupture disc operation will result in flash boiling of the hot liquid, and release of more vapor than is the case with any other device. If a column is involved, the sudden rush of evolution of foam accompanying rupture disc operation may cause major disarrangement of the column internals.

Proper instrumentation prevents over- or under-pressure from developing in the distillation system but does not replace a pressure or vacuum relief system.

Operations

In distillations with high reflux ratios, unstable or undesirable materials can accumulate and create an explosion hazard. A regular material sampling and continuous purge will avoid such buildups.

An example is the distillation of ethers, where ether peroxide sometimes builds up in the still and explodes spontaneously. Other materials subject to peroxide formation are tetrahydrofuran, aldehydes, and unsaturated compounds, such as styrene, butadiene, vinyl acetate, vinyl chloride, dicyclopentadiene and similar raw materials for plastics. Most nitrated materials, such as nitrochlorobenzene, dinitrophenol, dinitrotoluene, and other similar dye and plastics intermediates, explode if heated too much or too rapidly.

Other materials that react violently when distilled are those with triple bonds, such as propargyl alcohol; unsaturated aldehydes, such as acrolein; and unsaturated materials with inorganic groups and one or more hydrogen atoms loosely attached to carbon atoms due to the presence of double or triple bonds.

Condensers

Typically, water is the heat exchange medium in condensers, but sometimes a brine or direct refrigerant expansion is used where lower temperatures are needed. On the other hand, air cooling is adequate with some high boiling materials.

For very low temperatures, particularly in the petrochemical industry, direct expansion of liquefied petroleum gas is used. Similarly, in oxygen plants, vaporization of liquid oxygen or nitrogen is used to condense one of the gas streams. Brine-type coolants use low flammability solutions, such as methyl chloride, glycol or glycerine.

REFERENCES

1. *Health, Environmental And Safety Considerations In High Temperature Heat Transfer Fluid Systems*, Dow Chemical Company, Midland MI.

   Heat Transfer Fluid Fires And Their Prevention In Vapor Thermal Liquid Systems, R.L. Green, D.E. Dressel, Loss Prevention Symposium, April 1989, American Institute of Chemical Engineers, New York, NY.