



Property Risk Consulting Guidelines

A Publication of AXA XL Risk Consulting

PRC.9.6.1.1

DIRECT HALOGENATION

INTRODUCTION

Halogenation is a chemical reaction that adds halogens to an element or molecule to form a new halogenated molecule. The halogens are fluorine, chlorine, bromine, iodine and astatine. Chlorine is the most commonly used halogen in industry, while astatine is not used at all in industrial processes.

These elements are located on the far electronegative side of the periodic table. This strong electronegativity makes them highly reactive, particularly with strongly electropositive elements, such as alkali metals. Because of this high reactivity, direct halogenation is usually an exothermic reaction; that is, the reaction generates heat. For example, reacting hydrogen with chlorine produces 75% of the amount of heat liberated when hydrogen burns in oxygen.

Halogens react with most organic chemicals and metals. Halogenation, particularly with a hydrocarbon, can produce an explosion if heat production is uncontrolled. The amount of heat depends upon the type and concentration of the reacting materials. Control of the reaction depends on an adequate cooling system and process controls that regulate temperature, and flow rates and concentration of reactants.

POSITION

Management Programs

Implement management programs as described in *OVERVIEW* (PRC.1.0.1), AXA XL Risk Consulting's total management program for loss prevention and control. In developing a program for direct halogenation processes, pay particular attention to the following important areas:

Process Hazards Evaluation Program

Determine the characteristics of the specific reaction. Relevant characteristics include: the amount of heat available from the desired reaction; any side reactions; any possible unintended reactions; and the rate at which the heat can be released for various reactant concentrations, temperatures and pressures. Additionally, determine physical constants, such as specific heat, density and viscosity, for the appropriate temperature and pressure ranges.

Establish routine procedures for testing physical and chemical properties of all incoming raw materials, intermediates and final products to confirm properties required for safe operating conditions.

Select construction materials for vessels and piping that are compatible with the reactants, intermediates, products and catalysts.

When designing the process, minimize material hold-up to reduce the amount that can be spilled by equipment failure or operator error. Computer controlled processes often require a smaller material inventory.

Provide redundant instrumentation and transmission loops for all critical controls. Place the primary and redundant loops in different conduits, and run conduits on different routes. In each loop, include separate signal transmitters and signal receivers for each sensor or control. Install a comparator to notify operators when the redundant signals differ by more than the design tolerances of the system.

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 operating instructions.

Design instrumentation to prevent uncontrolled reactions during steady state operations, startups and shutdowns. Design and construct instrumentation systems to:

- Maintain reactants at a temperature that allows the reaction to start and proceed smoothly.
- Introduce reactants at a limited rate.
- Add reactants when instruments measuring the reactant ratio will be most effective.
- Detect any deviation in the reaction zone temperature as early as possible and control it by individually regulating the flow of reactants or cooling system(s).
- Measure temperature with thermocouples located to detect any temperature stratification.

Design necessary safety instrumentation to include both diversity and redundancy, and to detect hazardous situations as directly and as quickly as possible. For example, measure pressure directly rather than inferring it from temperature and volume data.

Interlock the temperature sensing system with one or more fail-closed control valves to prevent reactant flow if the temperature is too low or too high. The same thermocouples may also regulate the addition of the reactants. Base the upper safe temperature limit on the normal (not emergency) capacity of the heat removal system. Include excess cooling capacity in the process design to allow for future design changes. Design cooling system valves to fail open.

For reactions where cooling systems are especially important, consider the use of backup cooling system power, backup cooling system pumps or even an entire backup cooling system.

Limit the maximum rate of halogen addition by limiting the size of the halogen inlet pipe, the maximum solubility of the halogen in the reactant or carrier, or the halogen feed concentration. If thermal currents set up by the heat of reaction give inadequate agitation, provide mechanical agitation or gas sparging at the reactor bottom to assure prompt and complete mixing and reaction. Use an inert gas rather than a gaseous halogen for gas agitation. Make the reacting system as homogeneous as possible. Monitor agitator drive motor current to prevent nonhomogeneous zones from developing in the event of an undetected agitation failure.

For gaseous systems, measure the halogen temperature in the discharge line of the vaporizer or gas heater and at the liquid level in the bottom of any knockout drum. If temperatures are low enough to permit a liquid halogen to be present are indicated, arrange the halogen flow to shut off automatically.

Install direct pressure measurement on all reactor systems. Promptly depressurize the reactor and shut off reactant flows upon detection of an unusual pressure rise.

Design equipment to vent or contain runaway reactions. Design emergency venting according to the DIERS venting technology or in accordance with NFPA 68. Detonations and product decompositions are not covered by either of these venting guides.

To contain the overpressure created by a runaway reaction or a deflagration, design the reactor to withstand the maximum pressure that can be generated.

Investigate the possibility of automatically injecting a reaction inhibitor to slow or stop reactions before they reach dangerous temperatures and pressures.

If a process hazard evaluation finds a possible incident that cannot be contained or vented, such as a fast product decomposition or detonation, isolate the process by blast walls and distance from all other equipment and buildings.

Operator Training Program

Educate all operators about the hazards involved and in the functions of the safety control equipment. Forbid operators to run the process when any of this equipment is out of service. Train operators in manual emergency shutdown procedures. Issue written operating procedures and forbid any deviations.

Schedule periodic re-education and re-training at least annually. Include testing to assure proper performance of all assigned duties with particular emphasis on emergency shutdowns. Use process simulators where possible.

Pre-Emergency Planning

PRC.1.7, the pre-emergency plan from *OVERVIEW*, may be used as a reference to develop a customized plan. This customized plan should include programs to:

- Monitor and respond to the fire and disaster alarm system.
- Employ an emergency communications system, including radio, where needed.
- Train, staff and equip an organization of employees for firefighting and other emergency duties.
- Cooperate with neighboring plants and with public firefighting and disaster control organizations.
- Analyze the interruption of business that may result from potential incidents.
- Develop plans for minimizing loss of production during rebuilding.

Inspection, Testing and Preventive Maintenance Program

Inspect and maintain process equipment, piping, instrumentation, electrical equipment and pressure relief devices according to a schedule established with proper consideration of design and service conditions. Include all appropriate types of modern nondestructive testing, IR scanning and vibration analysis in the inspection techniques. Establish a detailed record-keeping system that includes equipment retirement forecasts.

Management of Change

Apply all management programs to any changes that are made to the facility's physical arrangements or procedures. Pay particular attention to the following areas:

- Repeat the process hazards evaluations program for all new processes or for any modification to an existing process. Determine the need for new or different safety equipment or measures.
- Whenever equipment is changed from one service to another, or when process 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 management of change to all new construction, especially to the activities of outside contractors.
- Update operating procedure manuals after each process unit modification that results in a change in operating procedure.
- Review and follow through expeditiously on all inspection recommendations from insurance, code enforcement and regulatory agencies.
- Update P&IDs after each modification. Perform on-site inspections to confirm that P&IDs agree with the work done.

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 of fire protection equipment using AXA XL Risk Consulting’s “RSVP” program, PRC.1.1.0.
- Smoking regulations.
- Plant security and surveillance.

DISCUSSION

At room temperature fluorine and chlorine are gases, bromine is a liquid, and iodine and astatine are solids. However, by varying the temperature or using various solvents, the different halogenation processes may be carried out in solid, liquid or gas phases. Typical of the industrial processes are:

- Solids with gaseous halogens;
- Liquids with gaseous halogens;
- Liquids with liquid halogens;
- Gases with gaseous halogens.

Solids with Gaseous Halogens

Reacting gaseous halogens with solids is a technique used mostly in the metallurgical field, such as in refining titanium. When a solid ore is halogenated by gaseous halogens, the ore in oxide form is mixed with coke and heated to make it susceptible to halogenation. The reaction produces a metal halide, carbon monoxide, carbon dioxide and heat.

In addition to the normal hazards of the fired equipment used for heating the solid to reaction temperature, the overheating of metallic equipment to its ignition temperature in a halogen atmosphere must be avoided. The separation of metallic halide vapors from gaseous oxides of carbon must be carried out in equipment designed to prevent air entry because the metal halide vapors will burn to oxides in the presence of oxygen. Additionally, carbon monoxide is flammable and can mix with air to form flammable and explosive mixtures.

Some metallic halides are liquid and may be purified by filtration and distillation. When chlorine reacts with the tin on scrap and recycled tin plate, liquid tin chloride forms at a low temperature. The low temperature prevents chlorine from reacting with the iron in the equipment. In this reaction, the lack of metallic chloride vapors and the low temperature make explosion hazards negligible.

Liquids with Gaseous or Liquid Halogens

When a halogen enters a liquid reaction system, it will either dissolve in the liquid or immediately react. Dissolved halogens have the potential for uncontrolled reaction or explosion when heat or some other stimulus initiates the reaction. Higher reactant concentrations can cause an accelerating reaction rate, which generates enough heat to overpower the cooling system. Alternatively, two liquid layers may form and react only at the interface until thermal currents or other mechanisms cause mixing and a consequent, sometimes uncontrollable, reaction. This is one reason why mixing should be designed to speed the reaction as much as possible.

Some liquid phase halogenations may use a catalyst. A number of reactions are stimulated by light as a catalyst and are known as photohalogenations. The light dissociates the reactive halogen molecule into even more reactive halogen ions or radicals. Because of the ever present danger of glass breakage, it is safer to have the light source inside a metal reactor than outside a glass reactor or to have a reactor with many sight glasses to allow light to enter.

Many organic materials are halogenated in the liquid phase. Chlorination of benzene and benzene derivatives is an important source of intermediates and finished products for the dye and

pharmaceutical industries. Many industrially important halogenated hydrocarbons originate from the liquid phase halogenation of ethylene to produce ethylene dihalide (1,2 dihaloethane), which is a basic building block for other compounds.

Gases with Gaseous Halogens

Producing hydrogen halide by burning hydrogen with a halogen parallels burning hydrogen with air. Similarly, vapor phase halogenation of hydrocarbons or partially substituted hydrocarbons resembles partial oxidation processes, such as burning methanol to formaldehyde or producing phthalic anhydride from orthoxylene. The reactions may take place spontaneously if temperatures are high enough. It may also be necessary to catalyze the reactions with either fixed or fluidized bed catalyst systems.

Direct halogenation of light hydrocarbons in a gas phase reactor can produce halomethanes, carbon tetrahalides, perhaloethylene or methyl halide. Some undesirable side reactions can form carbon and may take place explosively. Diluent gases or inerts are generally used for better temperature control.

The production of aluminum chloride involves bubbling chlorine gas through molten aluminum. When aluminum wire burns in oxygen, combustion, as opposed to surface oxidation, takes place only when the aluminum is vaporized. Therefore, this chlorination is similarly a reaction of gas with gas. As is the case with ore halogenations, however, the hazard involves the heating equipment for melting aluminum and the combustible product vapors.

Selection of the materials of construction and their interaction with the reactants are important factors in reaction control. Fluorine reacts violently with most metals at room temperature, depending upon how finely divided the metal is. Dry chlorine reacts with gold and most other metals at elevated temperatures. Iron, steel, copper and nickel react with dry chlorine above 250°F (121°C). Carbon steel ignites when in contact with chlorine at 483°F (251°C). Bromine reacts with most metals, although usually only at elevated temperatures. Iodine reacts with most metals but only slowly. It does corrode most metals, including stainless steel at room temperature in the presence of water. Unlike the other halogens, iodine will react with hydrocarbons only endothermically; that is, the reaction absorbs heat which must be supplied externally. Additionally, some metals can act as a catalyst in some halogenation reactions, increasing the danger of a runaway reaction. Astatine is radioactive and therefore requires additional precautions beyond those required by the halogenation hazards. Its uses are usually limited to research facilities.

Temperature control is a key to having reactions proceed quickly and smoothly, preventing runaway reactions. Deviation from normal temperatures indicates the reaction zone is not homogeneous or the reaction is not proceeding to completion. In either case, a hazardous mixture could be developing.

Removal of the heat of reaction will normally be accomplished by vaporizing products or byproducts, with additional cooling provided by an external cooling system. Instruments that measure the flow and temperature of product vapor can be used to check the reaction rate.

Hazardous situations may arise from dissolving a halogen rather than reacting it. A dissolved halogen may react at a later stage to create a runaway reaction. This is why it is desirable to use temperature or catalysts to initiate the reaction as the halogen is being introduced to the reactor.

Adding a liquid halogen to a system designed to handle a gas is also hazardous, because a much larger amount of the halogen is introduced at the same pressure. Since chlorine at 32°F (0°C) becomes liquid at pressures above about 45 psig (3.1 bar), it is the halogen most likely to have this problem. In fact, it is often transported as a liquid to the reactor site and vaporized there.

Since considerable heat is required for vaporization, failure of the heat source would cause a liquid halogen to be fed into the reactor. Temperature in the halogen gas feed should always show some degree of superheat with respect to liquefaction temperature at recorded pressure involved.

Pressure is usually the most sensitive variable and responds more rapidly than temperature. Increasing pressure may be due to rising temperature or increasing reaction rate. In the early stages of a sudden pressure rise, vents or a blowdown system can be operated to depressurize the system. The sudden release of the pressure can slow the reaction because some of the contents vaporize

and produce a cooling effect. Depressurizing is effective only in reactions normally operating under pressure and not those that normally run at atmospheric pressure.

Additional information on chlorination hazards (the most common halogenation process) is available in AIChE's "Chlorination Hazards."