Section III: Ethanol Manufacturing Health and Safety Hazards

The principal hazards in ethanol manufacturing are associated with processing dry feedstocks and handling ethanol; therefore, ethanol manufacturing facilities combine some of the attributes of grain handling facilities and chemical processing facilities. Individually, these two types of facilities are accompanied by distinct hazards, but when they are combined, hazards associated with both grain handling and flammable liquid processing, storage, and transport come into play (RFA, 2007). Sources of information on past incidents in the ethanol industry include: OSHA IMIS accident investigation summaries, the media, and trade association publications (e.g., Jessen, 2011a).

While individual ethanol manufacturing facilities vary in terms of layout and their sequence of operations, safety and health hazards at these facilities typically occur in various production areas common to most facilities, such as the feedstock receiving area, process buildings where feedstocks are prepared for processing, the ethanol bulk storage area, and the ethanol load-out area (IAFC, 2008).

The remainder of this section provides an overview of some of the common types of hazards found at ethanol manufacturing facilities. Section IV discusses some of the preventive measures that may be implemented to assure workers' safety. Preventive measures in OSHA's PSM standard (29 CFR 1910.119) apply when a process involves a chemical at or above the specified threshold quantities, listed in Appendix A of the PSM standard and/or involves 10,000 pounds or more of a flammable gas or liquid, if the exemption discussed in Section I does not apply.

A. Flammable Liquids

(Controls: IV.A and IV.B)

Large ethanol manufacturing facilities produce more than 100 million gallons of ethanol each year and store large quantities of the chemical on site at any given time; because ethanol is flammable, the production and storage quantities have the potential to cause catastrophic fires and explosions. Ethanol manufacturing facilities typically take numerous precautions to prevent ethanol fires (IV.A; IV.B), which are perhaps the most well-known occupational hazard for this industry. They must also ensure compliance with emergency planning requirements (V).

> **Two Employees are Burned in Distillery Explosion**
>
> On September 13, 2002, Employees #1 and #2 were working in the vicinity of the A-still [where initial distillation took place] when it was started. One of the manhole covers in the absorption column was apparently open and flammable alcohol vapors escaped and exploded. Employees #1 and #2 both sustained burns and were hospitalized. The absorption column had been previously opened to inspect the corn grits process and apparently one of the manholes had not been closed. No lockout and tagout procedures (IV.U) were used when the absorption column was opened, and there was no verification process in place to ensure that all the manhole covers were closed before the still was activated.
> (Modified for clarity)
>
> (OSHA IMIS Inspection #305030181 and #305030207)

In addition to ethanol, these facilities process and handle many other hazardous chemicals (III.F), but usually in much lower quantities. Table III.1. below lists some chemicals that are commonly found at ethanol manufacturing facilities. One example is the gasoline (which also contains benzene, 29 CFR 1910.1028; 29 CFR 1926.1128) that is added to ethanol as a denaturant. While gasoline and many other substances in the table exhibit their own hazardous properties, the total amount of gasoline used at these facilities is minimal in comparison to the quantities of ethanol.

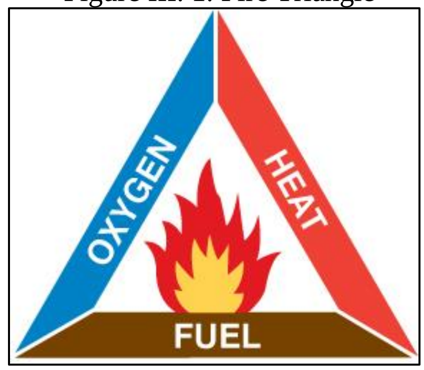
Table III.1. Examples of Hazardous Chemicals Found at Ethanol Manufacturing Facilities

Chemical	Associated Type of Production				Associated Process at Facility
	Corn Dry-Milling	**Corn Wet-Milling**	**Biochemical Conversion**	**Thermochemical Conversion**	
Alcohols other than ethanol				√	May be found at all kinds of facilities, but primarily produced during catalysis of syngas at thermochemical conversion facilities.
Ammonia	√	√	√	√	Used for various purposes, such as to adjust solution pH, as a nutrient for yeast and other beneficial microorganisms, and for pretreatment in thermochemical conversion.
Carbon dioxide	√	√	√		Formed as a by-product in all fermentation processes and either captured for further processing or vented to the atmosphere. Used in some pretreatment processes for biochemical conversion of cellulose.
Ethanol	√	√	√	√	Formed in fermentation tanks and thermochemical conversion reactors, separated from water and other chemicals in multiple unit operations, and kept in storage tanks.
Gasoline	√	√	√	√	Added to ethanol product in storage tanks. Benzene is an important hazardous constituent of gasoline (29 CFR 1910.1028; 29 CFR 1926.1128).
Hydrochloric acid		√			Used to treat starch suspension to produce modified starches and sweeteners.
Sodium hydroxide	√	√			Used in fermentation tanks for pH control and as a yeast nutrient
Sulfur dioxide	√	√			Added to large tanks of water for steeping corn kernels, and used to treat starch suspension to produce modified sweeteners.
Sulfuric acid	√	√	√		Used to control bacteria; added to slurry mixtures to separate corn into starch, germ, fiber, and protein; and used during steam explosion or acid hydrolysis.
Syngas				√	Primary product from process in gasification reactor and used to form ethanol in catalytic reactors.

Note: This table presents a partial list of raw materials, intermediates, and products that may be encountered at ethanol manufacturing facilities. However, individual facilities are different, and they can use different chemicals and chemical combinations in their production processes. The table was adapted from Weston Solutions, Inc., 2008 and Section A; and the table does not consider typical process emissions.

Both OSHA and the National Fire Protection Association (NFPA) have classified ethanol as a flammable liquid (29 CFR 1910.106; NFPA 30). Ethanol meets the criteria for a Category 2 flammable liquid, according to OSHA's Flammable Liquids standard and the HCS (29 CFR 1910.106; 29 CFR 1910.1200 Appendix B). This is because ethanol ignites at normal room temperatures, has a flash point of 55°F, and has a boiling point of 173°F (OSHA/EPA, 2011).

Figure III. 1. Fire Triangle



When ethanol vapor combines with air in the presence of ignition sources, fires and explosions can result. The lower and upper explosive limits of ethanol are 3.3 percent and 19 percent, respectively, by volume in air. This range spans air concentrations of ethanol that can ignite and burn in the presence of an ignition source (OSHA/EPA, 2011). As the ethanol is blended or denatured (e.g., using gasoline) the explosive limits of the product mixture change slightly. As an example, a blend of 85 percent ethanol and 15 percent gasoline has lower and upper explosive limits of 1.4 percent and 19 percent, respectively (Shaw, 2011). Another key factor is that high-ethanol fuels can form flammable mixtures in the headspace of storage tanks at ordinary temperatures. Gasoline, by way of contrast is usually too rich (above its upper flammable limit) to support combustion in gasoline storage tank headspaces (ullage). Another important physical property of ethanol is that its vapors are heavier than air, this is apparent from ethanol's vapor density (approximately 1.6). Thus, ethanol vapors do not rise in air and tend to accumulate at ground level until dispersed by wind or ventilation (if inside a structure).

At ethanol manufacturing facilities, fire and explosion hazards are present from the time ethanol is first formed through product purification, storage, and transport. As shown in the fire triangle in Figure III. 1., three components must be present for a fire to occur: fuel, oxygen (oxidizing agent), and heat (All About Fire, NFPA, 2011b). For ethanol fires, the ethanol vapor represents the "fuel" in the fire triangle; oxygen is the "oxidizing agent;" and, the "heat" component comes from ignition sources that cause the ethanol vapor to first burn.

Several factors can contribute to the release of ethanol, thus providing the fuel for an ethanol fire. These factors include improper storage, accidental releases (e.g., spills, containment failures), undetected leaks, inadequate venting of gases, equipment malfunctions, human error, and transportation accidents. Ethanol spills must be carefully addressed, because flammable vapors will form above all areas where the liquid ethanol travels. Examples of typical ignition sources in areas where ethanol is handled include electric arcs, human activities (e.g., smoking), heating equipment (e.g., furnaces and ovens), open flames, static electricity, and frictional heat. One of the most common ignition sources encountered at these facilities is "hot work" activities, such as welding, cutting, and grinding.

Fires fueled by pure ethanol generate no visible smoke and have a blue flame that may be difficult to see. Fires fueled by denatured ethanol produce no smoke or minimal smoke, but have a faint orange flame that may be noticeable. Fires fueled by ethanol are particularly challenging because they are not easily extinguished by traditional firefighting methods. Some commonly used fire suppression foams (e.g., those used to extinguish gasoline fires) are ineffective on ethanol fires, so special alcohol-resistant foams must be used.

The following are some common areas at ethanol manufacturing facilities that present flammability hazards (Gardiner et al., 2008, 2010).

> **Saccharification Tank Explodes**
>
> A contractor was killed and a worker suffered acid burns when an ethanol manufacturing facility's saccharification tank exploded. The 50-foot tall tank contained 40,000 gallons of corn mash. A welding contractor was cutting a hole in the top of the tank so workers could remove and load material from the top. Reportedly, atmospheric conditions had not been checked before the worker began welding, and flammable ethanol vapors had built up inside the tank. The welding ignited the vapors, and the resulting explosion threw the entire tank 75 feet. This event ruptured several interconnecting pipes, which in turn discharged an estimated 1,700 gallons of sulfuric acid. In addition, the saccharification tank landed on an empty railcar and an ethanol-containing tanker truck, causing the ethanol to catch fire. The facility's saccharification tank and fuel load-out area were destroyed during the incident, and other equipment was heavily damaged.
>
> (Powell, 2003)

- *Distillation process area.* Ethanol is initially formed at manufacturing facilities prior to distillation. However, the distillation process area is typically where the liquid contains high concentrations of ethanol and becomes flammable. This part of the facility, therefore, has significant flammability hazards due to the presence of highly concentrated ethanol vapors and heat. Overpressure or mechanical damage in the distillation columns can cause ethanol vapors to leak, which presents a hazardous situation due to the various ignition sources present and the potential for workers to be exposed beyond OSHA's permissible exposure limit (PEL) for ethanol (1,000ppm for a time-weighted average, 29 CFR 1910.1000 Table Z1). This hazard also exists for other equipment (e.g., piping, molecular sieve) typically found in the distillation process area.

- *Fuel storage tank area.* Ethanol manufacturing facilities usually store their finished products—both ethanol and denatured ethanol— in large storage tanks before the product is distributed into commerce. Proper handling of the ethanol is critical to avoid leaks in tanks and interconnecting equipment and to prevent more catastrophic ruptures. Some important concerns include pipe ruptures, tank ruptures, and lightning strikes.

- *Storage tank headspace.* The headspace is the gas-phase area above liquids inside a tank or other vessel. Recent research found the headspace vapors of denatured ethanol to be flammable at room temperature (64^{o}F) and all temperatures down to approximately 22^{o}F (NREL, 2008). No upper flammability limit was established for the denatured ethanol evaluated in the study and no tests were conducted at elevated temperatures. Instead, the denatured ethanol approached its lower (lean) flammability limit as the ambient temperature was lowered and eventually would not ignite if it was too cold (NREL, 2008).

  Fire occurs when there is an ignitable vapor-air mixture and a source of ignition, such as a static discharge (for some examples of previous incidents refer to the United States Chemical Safety and Hazard Investigation Board (USCSB) reports for: Barton Flammable Liquid Explosion and Fire (9/18/2008) and Barton Solvents Explosions and Fire (6/26/2008)). Static electricity may be generated as liquid flows through ungrounded pipes, valves, and filters while being transferred. It can also be produced by entrained water or air, splashing or agitation, and when sediment in the bottom of the tank becomes suspended.

At normal handling temperatures, flammable storage tanks, like those containing materials such as gasoline, may contain vapor-air mixtures that typically cannot be ignited because the vapor-air mixture is too "rich" (i.e., contains too much fuel and not enough oxygen or is above the gasoline's upper flammability limit) to burn. However, other flammable liquids, including ethanol and high ethanol content fuels, may form ignitable vapor-air mixtures inside tanks at normal handling temperatures.

- *Heated storage tanks.* There are specific hazards related to storing flammable liquids in heated tanks. For example, draining flammable liquids below high temperature tank heating elements can result in the ignition of the flammable headspace vapors, as the liquid is pumped out of the tank and oxygen flows into the tank, if the maximum temperature of the heating element can exceed the ignition temperature of the mixture.

  Also, excessive tank heating in general (with the heating elements submerged or with the use of heating jackets) can cause boiling and release large quantities of flammable vapor, which is unsafe if the vapors are venting inside a building or close to ignition sources.

  Examples of incidents involving deflagrations inside buildings are the Universal Form Clamp Company Explosion and Fire (6/14/2006), Synthron Explosion and Fire (1/31/2006), and CAI/Arnel Chemical Plant Explosion (11/22/2006), all of which involved flammable vapors venting from heated tanks inside structures. All of these incidents were investigated by the USCSB.

- *Ethanol loading areas.* Ethanol manufacturing facilities usually have loading docks or loading zones where flammable chemicals are transferred to the facility (e.g., the facility receives gasoline for use as a denaturant) and where the denatured ethanol is loaded into trucks or railcars for distribution into commerce. Overfilling, leaking equipment, and other unanticipated releases in the loading areas are extremely hazardous, especially when ignition sources are present (e.g., idling vehicles).

B. Equipment Ruptures

(Controls: IV.C and IV.D)

Ruptures can occur in fermentation vessels, product storage tanks, or pipes for various reasons. For example, due to the lack of safety systems or improperly functioning safety systems (e.g., failure of a rupture disk or pressure relief device on a fire protection line, failure of a safety valve to open when a heated storage tank is overheated). Ruptures may also be the result of fires; age deterioration; cracks (e.g., at the bottom and welding edges of storage tanks); corrosion (e.g., of a defective weld); or a lack of proper maintenance (Chang and Lin, 2005; Nolan, 1996).

Leaking Valve Causes Fire

Workers at an ethanol manufacturing facility suffered first- and second-degree burns after a leaking valve caused a stream of pure ethanol to pour from process equipment onto a floor, out an open door, and into a separate production area where hot work operations were taking place. A spark from nearby cutting and welding activities ignited ethanol vapor from the accidental release and caused the fire, which rapidly spread over a large area.

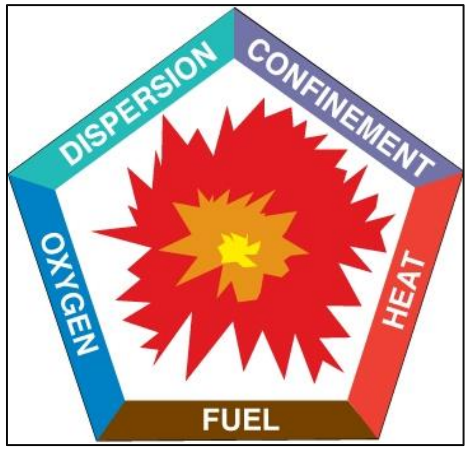
(Cahill, 2000)

If hazardous substances (e.g., anhydrous ammonia, ethanol, gasoline, sulfuric acid) released during ruptures are not controlled and contained this may result in fires, explosions, and workers' exposure to hazardous air contaminants.

C. Combustible Dusts

(Controls: IV.E and IV.F)

Figure III. 2 Combustible Dust Explosion Pentagon



Handling and size reduction of feedstock materials can generate combustible dusts. Combustible dusts are fine dust particles that when present in air at certain amounts and under the right conditions, can cause dangerous flash fires[1], deflagrations[2], and explosions[3] (OSHA Fact Sheet: Combustible Dust Explosions [OSHA, 2008a]; Combustible Dust National Emphasis Program (NEP), CPL 03-00-008 [OSHA 2008b]). Although some exceptions occur, the hazard potential of a given dust material increases as particle size decreases and as moisture content decreases. NFPA has published standards that present far more detailed information on the hazards associated with combustible dusts (e.g., Standard for the Prevention of Fires and Dust Explosions in Agricultural and Food Processing Facilities, NFPA 61; Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids, NFPA 654).

Flash fires, deflagrations, and explosions are the primary hazards related to combustible dusts at ethanol manufacturing facilities and can result in death, injury, and substantial property damage. As shown in the combustible dust explosion pentagon above, five elements must be present for a combustible dust explosion to occur: fuel (i.e., combustible dust), an ignition source (e.g., heat), confinement (e.g., a building, a room, vessel, or process equipment), oxygen, and dispersion in sufficient quantity and concentration (OSHA, 2008a). Removing any of these elements prevents an explosion from occurring.

The initial flash fire, deflagration, or explosion which occurs during a combustible dust incident is known as a primary event. A **primary explosion** has the potential to launch even more severe **secondary explosions**. Secondary explosions may occur when additional dust gets lofted into the air following an initial incident, providing the fuel necessary for multiple additional explosions throughout a facility. The dust fueling a secondary explosion may be dust released as a result of damage to a containment structure by the primary event; or, the release of dust that had previously settled, for example, on the floor, on top of equipment, on overhead structures, and on other visible and hidden surfaces. The secondary explosion may cause more damage than the primary explosion because they may be fueled by larger amounts and higher concentrations of dispersed dusts (OSHA, 2008a). Dust incidents may also lead to other hazardous

[1] Flash fire – A fire that spreads by means of a flame front rapidly through a diffuse fuel, such as dust, gas or the vapors of an ignitable liquid without the production of damaging pressure (NFPA 654).

[2] Deflagration – Is the propagation of a combustion zone at a velocity that is less than the speed of sound in the unreacted medium (NFPA 654).

[3] Explosion – Is the bursting or rupture of an enclosure or container due to the development of an internal pressure from a deflagration (NFPA 654).

events in other operating or storage areas of the facility, for example, the release of flammable liquids from storage areas due to fires or explosions spreading to those areas.

Many different types of combustible dusts can be found at ethanol manufacturing facilities. The largest quantities and accumulations of combustible dusts are expected to occur at facility locations that handle dry materials or processes that dry wet materials, such as in areas where feedstocks are received and processed and co-products are dried and loaded into trucks and railcars. Several different materials are expected to present combustible dust hazards at ethanol manufacturing facilities:

- Grain dusts (e.g., from corn, wheat, sorghum), which are present in every load of grain received at typical dry and wet milling operations. Grain dusts are also released from unit operations that transfer, crush, grind, and otherwise handle the agricultural feedstocks.
- Dusts from various co-products produced at dry and wet milling operations. These dusts are typically first formed in dryers and are present at all downstream process locations through eventual product load-out.
- Wood dusts from cellulosic materials, as well as other dusts from cellulosic operations (e.g., agricultural residue, municipal solid waste) that may be combustible.

Corn Dust Explosion Injures Three Workers

Three workers at an ethanol manufacturing facility endured serious first- and second-degree burns following a corn dust explosion. The explosion resulted from welding activities near a grain elevator, which caused hot metal to come into contact with corn dust near the base of the elevator. Following the initial explosion, a secondary explosion emitted smoke and dust into the atmosphere. Nearly 50 firefighters responded to the explosion, which was so powerful it raised a semi-truck hauling 80,000 pounds of grain.

(Galvan, 2008)

The list below identifies some typical unit operations and production areas that most commonly present combustible dust hazards at ethanol manufacturing facilities:

- *Cleaning area.* Screeners and scalpers are designed to remove oversized objects and finer material (e.g., dusts) from shelled corn. When operating properly, these devices should collect and control dusts. However, older, leaking, and malfunctioning devices can release significant quantities of dust into the workplace.

- *Bulk storage.* Dust clouds can form when loading materials into silos, bins, hoppers, and other bulk storage locations, including large storage piles. If fine dust in these areas contact an ignition source (e.g., nearby welding, or electrical equipment not rated for combustible dust environments), fires and explosions are possible.

- *Transfer points.* Transfer points, such as enclosed belt conveyors, which are dust ignition-proof (Figure III.3.) and bucket elevators, move large quantities of solid materials and dusts. Ordinarily, these devices effectively move material from one production area to the next. However, blockages, leakages, and other operational conditions can cause large quantities of solids to fall to the ground and high concentrations of dust particles to enter the air. Dust clouds can ignite at transfer points if an ignition source is present, such as a hot bearing along a belt conveyor or use of a conventional vacuum cleaner that is not dust ignition-proof.

Figure III. 3. Enclosed Belt Conveyor

Failure to Protect Workers' from Fire and Explosion Hazards

(a) General Duty Clause Violation at a Grain Handling Facility: There were multiple locations where dust collectors, cyclones, hoppers, heat exchangers, bag houses, and other equipment did not have adequate fire protection or meet the venting requirements. There were also storage bins that did not have an explosion suppression system.

(b) Abatement note: Among other methods, one feasible and acceptable abatement method to correct these hazards is to comply with NFPA 61 (Prevention of Fires and Dust Explosions in Agricultural and Food Processing Facilities) and NFPA 69 (Standard on Explosion Prevention Systems). Equip dust collectors with deflagration venting (vented to the outside). Install deflagration suppression system and deflagration pressure containment system for the Soymeal, Wheat and Dry Soy Powder locations in accordance with NFPA 69. Install spark detection devices inside pneumatic conveyor systems. Install proper fans and blowers in accordance with NFPA 61 chapter 10. Install proper explosion panels and explosion suppression system in wheat storage bins in accordance with NFPA 61 chapter 6.

(OSHA IMIS Inspection # 310768262)

- *Dryers*. Ethanol manufacturing facilities use dryers primarily to prepare co-products, for example, dried distillers' grain with solubles (DDGS), which is high in protein and sold as animal feed (II.B.1.viii). Facilities use dryers to reduce the moisture content of solid streams to the desired levels to meet product quality standards.

  Dryers can lead to fires through various means. For example, if the moisture content of the inlet stream unexpectedly drops, the material inside the dryer can become excessively dry producing conditions that can lead to smoldering and fires inside the dryer itself. Fires may also be caused by dead spots in fluidized bed dryers, which usually occur when material stops flowing, accumulates, or fluidization is lost in some or all of the beds, resulting in heat buildup and combustion.

- *Dust collectors*. Dust collectors remove and collect dust particles from air streams before venting "clean" air for recirculation or exhausting it to the atmosphere. Air material separators are designed to separate the conveying air from the material being conveyed (NFPA 654), they may be used for dust collection and removal (Figure III. 4.). Fires and explosions can result from dust collectors that are not well maintained; malfunctioning; or poorly designed, for example, not complying with design requirements in applicable standards, such as NFPA 654.

  Dust collector problems should be suspected when there is a sustained dust cloud in the workplace. A common cause of dust collector incidents occurs when smoldering material is inadvertently conveyed to the dust collector, where it can ignite the accumulated dust.

Figure III. 4. Air Material Separator (Cyclone)

- *Grinding or milling area*. Grinding and milling reduces feedstock materials into smaller particle sizes (corn flour). The inherent nature of these unit operations causes high levels of combustible dust to form inside the equipment and also generates heat. The key to avoid fires and explosions is to prevent ignition sources from entering the equipment, for example, tramp metal that might be inadvertently conveyed inside the mill along with the feedstock.

- *Load-out and cooling areas.* Facilities transfer dried co-products to interim storage areas and eventually to railcars or trucks for distribution into commerce. The transfer and loading of the dried product leads to dust formation. Fires and explosions may result if dust clouds are not adequately controlled and ignition sources are present.

D. Engulfment

(Controls: IV.G, IV.H, IV.I, and IV.U)

In addition to receiving, handling, and processing grain, ethanol manufacturing facilities also store grain on site in very large silos, and some facilities temporarily keep much smaller quantities of dry co-products in large storage piles that might reach heights of 20 feet or more. A significant safety issue associated with grain storage and large storage piles is the possibility of workers becoming **engulfed** and **entrapped** by the materials (Inspection of Grain Handling Facilities, 29 CFR 1910.272, CPL-02-01-004, OSHA 1996). Although sometimes used interchangeably, these terms do have subtle differences in meaning (Anku, 1993; Purdue University, 2011):

- **Engulfment** describes situations in which a worker is entirely buried and submerged below the grain surface.
- **Entrapment** describes situations in which a worker is physically stuck in grain or co-products, but still has his or her head above the surface.

Figure III.5 Image of a Grain Engulfment Hazard

Source: OSHA, 2011b

For the purposes of this document, the term engulfment will be used to encompass both engulfment and entrapment hazards. Engulfment hazards (Figure III.5.) may be present when grain is stored in silos, bins, and other large vessels. Grain engulfment presents a suffocation risk for workers and is a leading cause of deaths and injuries in the grain handling industry. Once a worker is engulfed in grain, suffocation quickly follows as the grain fills the mouth, nose, and throat of the submerged individual (Danger of Engulfment and Suffocation in Grain Bins, Hazard Alert, OSHA 20011f). This hazard also applies to large storage piles of co-products that can collapse without warning, especially in instances when workers use heavy-duty equipment (e.g., front-end loaders) to scoop up and move material from around the base of a storage pile. Specific examples of hazardous activities involving workers include (OSHA, 2010):

Workers Engulfed in Storage Bin

Two teenage workers suffocated and died and another young worker was seriously injured when they were engulfed in corn in a storage bin at a grain elevator facility. Reportedly, the storage bin's unloading system was operating as the three workers stood in corn that was more than 30 feet deep. While a conveyor system underneath the bin was removing corn, the workers were trying to make the corn flow by *walking down the grai*n, a practice in which workers enter storage bins and other structures and literally walk on top of encrusted grain to break it up and facilitate the transfer. *(Note: OSHA standards specifically prohibit this practice (*29 CFR 1910.272(g)(1)(*iv).)* Upon doing this, one worker began to sink in the corn, and the other two workers attempted to rescue him. Two of the workers became entirely engulfed in corn, while one worker was able to keep his head above the surface and survive until he was rescued.

(OSHA, 2011b, OSHA, 2011c)

- *Standing on flowing or moving grain in silos.* Grain flows downward when unloaded, which results in a funnel-type effect. This moving or flowing grain is like quicksand, and can cover and suffocate a worker within seconds. It is for this reason that workers must never enter silos and large storage vessels that contain moving grain (29 CFR 1910.272(g)(1)(iv)).

- *Standing on a grain bridge in silos* (OSHA, 2011f). A grain bridge forms when mold or moisture causes grain to stick together. As a result, the grain surface in a silo might appear to be stable, but an empty space below the grain surface can form as bin unloading occurs. The grain bridge will readily collapse under the weight of a worker and instantly bury the individual.

- *Standing on or next to a grain mass in a storage pile.* Facilities can have piles of grain along the side of a storage bin and poorly conditioned grain inside a storage bin. If a worker tries to dislodge the grain in the pile or in a bin, the grain pile can quickly fall and cover the worker.

The aforementioned scenarios are extremely dangerous because workers simply cannot extricate themselves after being engulfed in grain. Engulfment typically has fatal results.

E. Hazardous Noise Levels

(Controls: IV.J, IV.K, and IV.L)

Noise is a prevalent potential hazard throughout many grain handling and processing operations. However, noise levels may not translate into high exposure levels because of workers' mobility between operations and tasks, and equipment not being operated continuously. Excessive noise can hinder communication between workers. It can also damage workers hearing due to long-term repeated exposure. Varying levels of exposure to noise may occur during grain unloading operations; in grain elevators; and grain processing areas, where the most significant exposure to noise is possible (excerpt from Cralley, 1985 (continues below)).

- *Grain unloading.* Sources of noise include grain dumping, pneumatic blowers or internal combustion–powered vehicles. Sometimes, during the unloading of powdery grain-related products, vibrators may be attached to the metal hoppers of vehicles to facilitate complete dumping of the product which may adhere to the inside surfaces of the vehicle. Noise levels vary depending on the type of vibrator, amount of grain in the vehicle, and its location. As the vehicle empties, noise levels immediately adjacent could easily increase to more than 115 decibels on the A scale (dBA), even for outdoor operations.

- *Grain elevators.* Noise levels typically exceed 90dBA on the gallery and basement floors of elevators, although full-shift exposures may not reflect these high levels because of worker mobility and the intermittent nature of equipment operation. The primary noise sources include conveying equipment, dust collection equipment, and compressed air used for housekeeping.

- *Grain processing.* Noise occurs at almost every processing stage and seems to be an inherent, undesirable side effect associated with the operation of most grain processing machinery (e.g., hammer mill). Other major sources of noise include exhaust ventilation equipment, blowers for pneumatic transport, and compressed air usage and generation.

F. Exposure to Hazardous Substances

(Controls: IV.M, IV.N, IV.O)

OSHA standards address employers responsibilities when there is a potential for workers to be exposed to harmful concentrations of toxic and other hazardous substances in the workplace (e.g., 29 CFR 1910.1200; 29 CFR 1910.119; 29 CFR 1910.119 Appendix A; Section I). OSHA standards specifying permissible exposure limits (PELs) for air contaminants include: 29 CFR 1910 Subpart Z; 29 CFR 1926 subpart Z; 29 CFR 1926 Subpart D (e.g., 29 CFR 1926.55, 29 CFR 1926.60, and 29 CFR 1926.62). Although OSHA's standards are the regulatory requirements, employers are encouraged to adopt stricter measures to ensure the maximum protection for workers (Permissible Exposure Limits Annotated Tables, OSHA 2014).

Chemicals, feedstocks, catalysts, enzymes, intermediates, products, and other substances (Table III.1) involved in ethanol manufacturing may be hazardous to workers. If appropriate preventive measures are not implemented exposure can occur during handling, storing, processing, and transporting activities. Some of the safety precautions that can be implemented to protect workers from exposure to hazardous chemicals are discussed in IV.M. Examples of hazardous substances likely to be found at ethanol manufacturing facilities include, but are not limited to the following (Brisman et al., 2004; Grisso et al., 2005; LaPrade, 2008; NIOSH, 2010b; Pahwa et al., 2006):

- *Enzymes.* As noted in II.B.1.iv iv, facilities add the enzyme **alpha-amylase** to the solution/slurry during liquefaction to convert corn starch into **dextrins**. Exposure to alpha-amylase is associated with increased risk for respiratory illnesses, such as occupational asthma, in exposed workers. Also reported are exposure-related symptoms in the eyes (e.g., itchiness) and nose (e.g., sneezing), as well as allergic reactions in those who are more sensitized to its effects (Houba, 1996; HSE, 2010). At this time, OSHA has no permissible exposure limit (PEL) for alpha-amylase.

- *Gases.* For example, carbon dioxide (CO_2) may build up in stored grain, CO_2 is also produced during the fermentation process, and other gases can be produced from decomposing and fermenting grain, for example, hydrogen sulfide, ammonia, sulfuric acid, and methane.

- *Combustion by-products.* For example, carbon monoxide can be generated when workers use machinery within or close to confined spaces.

- *PSM covered chemicals.* Some hazardous chemicals that may be used in ethanol processing facilities in quantities that necessitate compliance with OSHA's PSM standard include: sulfur dioxide, ammonia, and anhydrous hydrochloric acid (29 CFR 1910.119, 29 CFR 1910.119 Appendix A, Section I).

- *Fumigants.* Fumigants, for example, phosphine, used for pest control can be present in stored grains. Many of the fumigants used in grain handling and processing facilities are hazardous chemicals. Workers exposed to fumigants can develop serious chronic health effects, such as heart disease and cancer.

- *Molds in stored grain.* Mold spores can form in spoiled stored grain. Exposure to molds can cause adverse effects.

- *Grain dusts.* Workers exposed to grain dusts generated throughout ethanol manufacturing unit operations can experience respiratory effects.

- *Metallic catalysts.* Metallic catalysts are used at facilities that thermochemically convert syngas into ethanol. Potential worker exposures to the metal constituents will depend on the physical state of the catalyst, the extent of catalyst handling, and other parameters.

G. Confined Spaces

(Controls: IV.P, IV.Q and IV.R)

Some examples of confined spaces at ethanol manufacturing facilities include silos, process vessels, storage tanks, grain storage bins, and feed hoppers. The safety and health of workers entering confined spaces in grain handling facilities is addressed by both the Grain Handling Facilities standard, 29 CFR 1910.272, and the Permit-Required Confined Spaces standard, 29 CFR 1910.146. However, confined space work, such as grain bin entry, that is regulated by 29 CFR 1910.272, is not subject to the provisions of 29 CFR 1910.146, as long as the provisions of 29 CFR 1910.272 protect workers against all the hazards within the grain bins (OSHA Letter of Interpretation: Questions regarding the PRCS standard, 1910.146, and the Grain Handling standard, 1910.272. [02/08/2005]). CSHOs should also refer to OSHA's directive, Application of the Permit-Required Confined Spaces standard, CPL-02-00-100, for additional information.

Adverse health effects are possible if workers enter confined spaces containing toxic atmospheres. These are atmospheres containing gases, vapors, or fumes known to have poisonous physiological effects (OSHA, 1993). Examples of some, but not all, of the potential hazards in confined spaces at ethanol manufacturing facilities include the following (OSHA, 1998, 2011b; Porter, 2010):

- *Hazardous chemicals.* Employers must prevent workers exposure to concentrations of toxic and other hazardous substances (III.F.; 29 CFR 1910 Subpart Z; 29 CFR 1910 Subpart Z; 29 CFR 1910.119, 29 CFR 1910.119 Appendix A, Section I) capable of causing acute health effects (e.g. within seconds or minutes) that can prevent workers from effecting self-rescue or being able to request help when working in a confined space.

- *Oxygen-deficiency.* Some confined spaces can be oxygen-deficient, especially when oxygen is displaced by other gases (e.g., CO_2) formed by the decomposition of stored grain or other processes in the confined space.

- *Fire and explosion hazards.* For example, combustible dusts (e.g., in bucket elevators (III.C) and flammable gas or vapor in excess of 10% of its lower flammable limit (III.A).

Employee Dies after Falling into a Fermentation Tank

On November 20, 2011, Employee #1 opened an access door on the top of a fermentation tank to perform tank prewash activities utilizing a high-pressure water hose to presoak the sides and agitators inside of the tank. The tank was **energized** and the agitators were turning (III.I). The tank was approximately 18 ft. deep and contained approximately 4 ft. of finished liquid product the employer described as "13 percent beer". Sometime during the presoaking activity, Employee #1 **fell** into the tank for an unknown reason. There were no witnesses to his activities. Coworkers found Employee #1 unresponsive on the bottom of the tank. He was pronounced dead at the scene by a local physician.
(OSHA IMIS Inspection #316034545)

- *Physical hazards.* These include: falls from heights; drowning; pipes that could cause workers to trip and fall; crushing or laceration injuries from moving mechanical parts, for example, sweep augers capable of causing severe laceration or crushing injuries or death; and, exposure to hazardous energy (III.I., IV.U.).

H. Motor Vehicles

(Controls: (IV.S and IV.T)

Heavy-duty trucks and railcars have a ubiquitous presence at ethanol manufacturing facilities. At larger facilities, a nearly constant stream of truck traffic delivers corn to receiving areas, and a separate set of trucks and railcars are routinely filled with denatured ethanol at product load-out areas. Hazards that could affect safe transportation and safe loading and unloading of motor vehicles include: a flammable atmosphere; static electricity which could act as a source of ignition during loading and unloading of flammable substances or combustible dust; poorly maintained roads (e.g., pot holes, uneven road surfaces); severe weather conditions (e.g., lightning, snow storm); unsafe driving; and, operating motor vehicles in poor working condition. Unsafe driving habits and/or improperly planned routes may also result in motor vehicle collisions with pedestrians, equipment, pipes, etc. Safety measures must be implemented to preclude motor vehicle incidents.

I. Exposure to Hazardous Energy

(Control: IV.U.)

Sources of hazardous energy include mechanical, electrical, hydraulic, and pneumatic equipment, which present a danger to workers if the energy isolating source (e.g., circuit breaker, disconnect switch) is not properly shut down and if appropriate measures are not taken to prevent the equipment from starting up unexpectedly while employees are still working (IV.U; 29 CFR 1910.147).

J. Other Hazards

Ethanol manufacturing facilities, like many chemical manufacturing and processing operations, have numerous additional potentially hazardous situations. To name a few, hazards can be associated with the boiler operation; use of hand tools; electrical fixtures; walking and working surfaces; elevated platforms; and, brazing, cutting and welding operations. For example, employers are required to protect workers from exposure to hexavalent chromium (above the PEL) that may be produced from the welding or torch cutting of piping and vessels made of steel (29 CFR 1910.1026; 29 CFR 1926.1126; OSHA 2013b).

Some ethanol manufacturing facilities will have specific hazards that are not common across the industry. For instance, the small number of facilities that operate coal-fired boilers may have hazards associated with coal dust, while wood dust may be an issue at facilities that process certain cellulosic feedstocks. It is, therefore, necessary to identify the complete set of site specific hazards when developing and implementing worker safety and health programs at ethanol manufacturing facilities.