

Carbon Bed Fires and the Use of Carbon Canisters for Air Emissions Control on Fixed-Roof Tanks

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ABSTRACT

Fixed-roof tanks are used extensively at manufacturing, waste management, and other facilities to store or process liquids containing volatile organic compounds. Federal and state air standards require the control of organic air emissions from many of these tanks. A common practice used for some fixed-roof tanks that are required to use controls is to vent the tank through an activated carbon canister. When organic vapors are adsorbed on activated carbon, heat is released. Under certain conditions, the temperature of the carbon bed can increase to a level at which the carbon or organic vapors spontaneously ignite, starting a fire in the carbon bed. Bed fires in carbon canisters are not uncommon and can present a significant safety hazard at facilities if proper safety measures are not implemented. This article discusses how carbon adsorber bed fires occur and presents general guidance on safety measures for carbon canisters installed on fixed-roof tanks to reduce the likelihood of a carbon bed fire and to minimize the impact in the event of a fire.

IMPLICATIONS

A number of U.S. Environmental Protection Agency (EPA) regulations require control of organic air emissions from tanks and containers that store hazardous waste and other volatile organics. Carbon canisters are commonly used as a control device to comply with these air standards. This paper examines spontaneous ignition of activated carbon when used as an adsorbent and the conditions that contribute to bed fires in carbon adsorption systems. It provides practical guidance on reducing the incidence of bed fires and minimizing their impact when they occur. With some basic safety measures incorporated into their design and operation, these inexpensive emission controls can be safely and effectively used to comply with air pollution regulations.

INTRODUCTION

Tanks are used at many manufacturing facilities for storing and processing liquid materials that contain volatile organics (e.g., raw materials, feedstocks, finished products, or process wastewaters). Waste management facilities also use tanks extensively for accumulating, storing, and treating hazardous and nonhazardous liquid wastes that contain volatile organics (e.g., spent solvents, used oil, process wastewaters, or sludges). The volatilization and subsequent release of organics from these tanks can be a significant source of air pollutant emissions. Under the Clean Air Act, the U.S. Environmental Protection Agency (EPA) has established New Source Performance Standards (NSPS) and National Emission Standards for Hazardous Air Pollutants (NESHAP) to control organic air emissions from a wide variety of tank applications. Under the Resource Conservation and Recovery Act (RCRA), EPA has established air standards for tanks used to manage hazardous wastes at large-quantity generator sites and at hazardous waste treatment, storage, and disposal facilities (see subpart CC in 40 CFR parts 264 and 265).¹ Many states also have adopted air standards with tank emission control requirements similar to those required under federal air standards.

The NSPS, NESHAP, and RCRA air standards for tanks share an approach that specifies the air emission control level required for a given tank based on the tank's design capacity and the properties of the organic material managed in the tank (e.g., maximum organic vapor pressure and organic concentration). For those fixed-roof tanks required to use controls, the tank owner or operator must use controls that either suppress volatilization of the organics contained in the material managed in the tank (e.g., use an internal floating roof) or capture or destroy organic vapors vented from the tank (e.g., vent the tank through a carbon adsorption system, condenser, or vapor incinerator). Venting a fixed-roof tank through a carbon canister is

an air emission control practice used at many facilities to comply with the applicable federal and state air standards.

Carbon canisters are a simplified type of activated carbon adsorption system. The adsorption of organic vapors on activated carbon releases heat. Under certain conditions, the temperature of the carbon bed can increase to the point at which spontaneous ignition of the carbon or organic vapors occurs and starts a fire in the bed. A carbon bed fire can present a significant safety hazard at facilities if proper precautions are not implemented. Without appropriate safety devices, the flame from a carbon bed fire can propagate back to the tank's vapor space and cause an explosion.

This article discusses activated carbon bed fires as related to the use of carbon canisters for air emission control on fixed-roof tanks. A literature review is presented summarizing the results of studies investigating the ignition and combustion of activated carbon when used as an adsorbent. The experiences with bed fires that have occurred in the carbon adsorption systems used at three facilities are discussed. Finally, general guidance is presented on design, equipment, and work practice measures that can be implemented to reduce the incidence of bed fires and minimize the impact of these fires for carbon canisters used to control air emissions from fixed-roof tanks. The collection and analysis of the information used to prepare this article was funded by EPA, Region 4, RCRA Programs Branch.

USING CARBON CANISTERS FOR FIXED-ROOF TANK AIR EMISSION CONTROL

EPA literature² notes that organic air emissions from a fixed-roof tank primarily occur by two emission mechanisms: working losses and, to a lesser extent, breathing losses. When liquids (or other materials managed in a tank) containing volatile and semi-volatile organics are placed in a fixed-roof tank, some fraction of the organics will volatilize. These vapors collect in the internal volume between the liquid surface and the tank roof (i.e., the tank "vapor space"). Working losses result when liquid is pumped into the tank and the rising liquid level pushes the vapors out of the tank vapor space through open vents on the tank roof. Breathing losses occur when the volume of vapor in the tank vapor space increases due to changes in ambient temperature or pressure, and the vapors flow out through the open vents. The quantity of organic emissions from a given tank varies with the concentrations and volatilities of the individual organic constituents composing the liquid managed in the tank.

The typical adsorption process used for controlling air emissions involves passing an organic vapor-laden gas stream through a packed bed of activated carbon particles. Adsorption takes place when the organic molecules come in contact with the surface of the carbon particles and are selectively held there by attractive forces between the molecules and

the carbon particles. A given mass of carbon adsorbs a finite amount of organic molecules. Once the carbon reaches its capacity, the saturated carbon must be desorbed (i.e., regenerated) or replaced with fresh carbon before organic emissions control can resume. Two common types of carbon adsorption systems used for air emission control are carbon canisters and regenerable fixed-bed systems.

Carbon canisters are compact, relatively low-cost units used to control intermittent gas streams with low-volume flows (typically less than 100 ft³/min). The intermittent, low-vent flows associated with working and breathing losses from a fixed-roof tank make the carbon canister a particularly suitable and practical control option for tank owners and operators. Figure 1 shows the basic carbon canister installation for a fixed-roof tank. For many tank applications, the size of the carbon canister is similar to a drum-type container. Carbon canisters in significantly larger sizes also are available and may be used at some tank facilities. The vent stream from the tank enters at the base of the canister and flows upward through a packed bed of activated carbon particles. The treated gas stream is exhausted through an open pipe on the top of the canister.

A carbon canister cannot be desorbed or regenerated on-site once the carbon becomes saturated. When the carbon reaches a certain saturation level, the canister must be replaced with a new canister containing fresh activated carbon. This saturation level is typically determined by an engineering calculation of useful carbon life, from past operating experience, or sometimes by direct monitoring of the organics in the canister exhaust gas stream. The spent carbon canister is either disposed of or returned to the vendor (where spent carbon is removed from the canister for regeneration and the canister is repacked with fresh carbon).

ACTIVATED CARBON IGNITION AND COMBUSTION

Heat is released when a gas stream containing organic compounds is treated with activated carbon. This heat release (or exotherm) is generated from the adsorption of

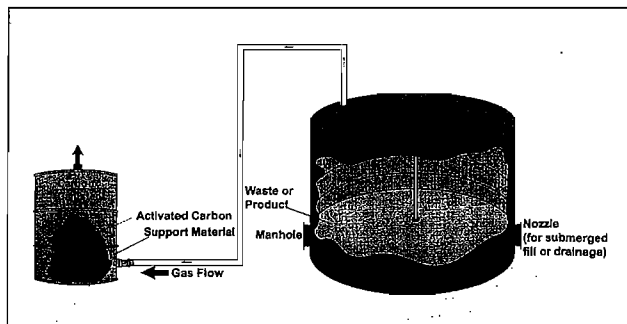


Figure 1. Basic carbon canister installation on a fixed-roof tank without safety devices.

the organic compounds and the water vapor contained in the untreated gas stream. In addition, certain reactive chemical compounds, once adsorbed onto activated carbon, undergo chemical oxidation or polymerization on the carbon surface. These reactions are also exothermic. In cases where the rate of heat removal is slower than the rate of heat generation, temperatures in the carbon bed increase. Depending on the carbon bed conditions, this temperature increase can potentially reach the ignition temperature of the carbon or the organic compounds adsorbed on the carbon.

A literature search of carbon adsorption systems used for air pollution control applications found very limited information that directly addresses carbon bed fires in carbon canisters. Much of the available information focuses on carbon bed fires in regenerable fixed-bed carbon adsorbers used for organic solvent recovery. Regenerable fixed-bed carbon adsorbers are large, multiple-component systems used to treat continuous gas streams with flows ranging from several 100 to several 1000 ft³/min. The activated carbon bed is regenerated on-site without removing the carbon from the unit. These systems commonly are used not only for air pollution control but also for industrial applications such as organic solvent recovery. Notwithstanding the design differences between a carbon canister and a regenerable fixed-bed carbon adsorber, both carbon adsorption systems are prone to bed fires when used to treat gas streams containing certain organic compounds. The reactive chemical compounds that compose many organic solvents (e.g., ketones or aldehydes) are also often found in spent solvents, wastewaters, and other waste materials managed in fixed-roof tanks vented through carbon canisters for air emission control. Therefore, information from studies of carbon bed fires in carbon adsorption systems used for solvent recovery is relevant and applicable to carbon canisters used for air emission control. The findings of studies investigating the spontaneous ignition and combustion of activated carbon used in carbon adsorption systems are presented in the next sections.

Experiments Investigating Activated Carbon Combustion

Naujokas³ conducted a series of laboratory experiments to evaluate the adsorption of various industrial organic compounds in carbon beds. The first set of experiments tested individual organic compounds in beds of fresh activated carbon. The carbon bed was heated to a starting temperature of 125 °C. Bed temperatures were maintained by thermally insulating the bed's encasement and equipping it with wall heating elements. A stream of nitrogen containing a fixed concentration of the organic compound being tested was then passed through the bed. When exit gas temperature and composition changes were no longer observed (i.e.,

when the bed was saturated), the carrier gas was changed from nitrogen to air. By saturating the bed and then maintaining the same inlet concentration to the bed, heat effects due to adsorption were eliminated.

Bed temperature changes and the concentrations of the reaction products CO and CO₂ were monitored. Depending on the organic compound tested, switching the carrier gas from nitrogen to air resulted in either an increase in bed temperature with CO production, indicating that the adsorbed compound was oxidizing, or no change in either bed temperature or CO production, indicating that the adsorbed compound was not oxidizing. The results of the oxidation behavior of 22 organic compounds at a starting temperature of 125 °C are reported. At this temperature, aldehydes, ketones, and organic acids all show high reaction/oxidation rates when the carrier gas is switched from nitrogen to air. The experiment was repeated for 10 organic compounds using a starting temperature of 100 °C. At this lower starting temperature, the oxidation reaction rates of ketones and organic acids decrease markedly, while the reaction rates of aldehydes remain high (i.e., they were unchanged relative to the values measured at 125 °C).

In the second set of experiments, a bed of activated carbon was saturated with air containing methyl ethyl ketone at a temperature of 40 °C. Once the bed was saturated, the gas flow was stopped. A small air bleed was then introduced upstream of the carbon to supply oxygen for oxidation. Bed temperature changes and reaction product emissions were monitored. At an air bleed velocity of 0.2 cm/sec, hot spots in the carbon were observed, and CO and CO₂ emissions substantially increased (from 0 to 8000 and 6000 ppm, respectively). At an air bleed velocity greater than 0.35 cm/sec, hot spots were not observed, indicating that convective heat transport exceeded the heat generation rate. When no air bleed was used, hot spots did not develop, indicating insufficient air/oxygen was available for oxidation. When natural convection (i.e., air flow) was allowed, hot spots and CO and CO₂ emissions were produced at levels similar to those produced with forced convection. In experiments using humidified air (60–65% relative humidity), hot spots developed several hours later than they did when using dry air.

In a third set of experiments, the investigator found that increasing air velocity across an existing hot spot can lead to bed combustion if the temperature of the hot spot is high enough. In one experiment, the air velocity was increased from 0.2 to 10 cm/sec across a hot spot at 200 °C (the bed was saturated with methyl ethyl ketone). Within 6 min, the hot spot temperature was at 376 °C and rising and, ultimately, resulted in bed combustion. Similar results were obtained when the temperature of the hot spot was between 160 and 300 °C and the air velocity was increased to 50 cm/sec.

Testing different activated carbon types, the investigator found that oxidation reactions vary, depending on the type of carbon used. In particular, reactive compounds oxidize more readily on coconut-based carbon compared with coal- or petroleum-based carbon. Carbon that had been in service for some time was also found to be more conducive to oxidation. Under identical experimental conditions, oxidation rates of acetone were greater on previously used carbon than on fresh carbon. Similar results were observed with methyl ethyl ketone and other compounds.

Characteristics of Carbon Combustion in Carbon Adsorption Systems Used for Solvent Recovery

Smisek and Cerny⁴ studied the characteristics of carbon fires that had occurred in regenerable fixed-bed carbon adsorbers used for recovery of ketones, aldehydes, or similar compounds. They found that prior to a carbon bed fire occurring, the carbon adsorber usually had been shut down for a few days due to production schedules, mechanical failures, or other circumstances. The bed fires occurred when the adsorption cycle was restarted (i.e., when the air/vapor stream was reintroduced to the bed). The investigators attribute these fires to the spontaneous oxidation of carbon, which occurs when an insufficiently dried and cooled carbon adsorber is shut off. During shutdown, air can be drawn into the carbon bed through the imperfectly sealed walls of the carbon adsorber vessel. The airflow is sufficient to maintain the oxidation process. Since the heat generated by this oxidation process is removed slowly, localized areas in the carbon bed may be heated to the carbon's self-ignition temperature. Self-ignition can also be aided by oxidation of incompletely desorbed solvent residues (e.g., the oxidation of acetone to acetic acid). If hot spots exist when the carbon adsorber is restarted, the sudden increase in air/oxygen can start a fire. The investigators concluded that the hazard of self-ignition can be avoided by thoroughly drying the carbon adsorber and cooling it to -40°C before it is shut down.

The investigators, in addition, noted that during the adsorption cycle, the temperature of the activated carbon is increased somewhat by the heat of adsorption. However, this increase is not considered significant and under normal conditions would not lead to self-ignition. Also, they state that desorption at temperatures less than 120°C does not cause fires; however, desorption at higher temperatures (up to 200°C), which is done to increase system capacity, is of concern because localized heating may occur that can lead to ignition during drying with hot air.

Acetone Oxidation in Activated Carbon

Boiston⁵ conducted a study that investigated the oxidation of acetone, a ketone, adsorbed on activated carbon, and the effect of its oxidation on carbon

combustion. The activated carbon used for the study was a commercially available, coconut-based carbon. The investigator found that adsorbed acetone begins to oxidize rapidly at 80°C . When the heat released by acetone oxidation did not dissipate from the carbon bed, the reaction manifested itself by increasing the bed temperatures. Eventually, the bed temperature attained the ignition temperature of the carbon (determined to be 240°C by the investigator). The investigator observed that bed fires ignite in regions of the bed with low airflow, then spread to other areas of the carbon bed with greater air (oxygen) availability. In low airflow applications, the heat released from oxidation can exceed the heat dissipated by the flow. The resulting heat imbalance creates a temperature rise in the bed that in turn accelerates oxidation rates.

The study results also emphasize that, even in applications where sufficient gas stream flow occurs to cool the bed, a localized heat imbalance can arise if dead spots are present in the carbon bed. A dead spot is a pocket of carbon through which little or no airflow passes. Dead spots can result from channeling of the gas flow or from carbon breakdown. (Carbon breakdown is more common in regenerable fixed-bed carbon adsorbers where the repeated adsorption-regeneration cycle causes the carbon to physically break down into regions of tightly packed carbon granules and dust.) Since little gas flow passes through a dead spot, the heat generated from adsorption or oxidation is not adequately dissipated. As a result, the dead spot can increase in temperature until it reaches the ignition point of the adsorbed organics or the carbon.

Prevention of Activated Carbon Bed Ignition and Degradation during the Recovery of Cyclohexanone

Takeuchi et al.⁶ investigated oxidation of cyclohexanone, a ketone, adsorbed on activated carbon and the effect of its oxidation on carbon combustion. The investigators found that oxidation of adsorbed cyclohexanone was largely responsible for carbon bed ignition. Based on the study, effective measures identified for preventing bed fires included weathering or aging of the carbon (oxidation rates were higher on fresh carbon versus carbon aged for 2 years, the opposite of Naujokas's findings³) and removing ash from the carbon and adding a small amount of moisture to the incoming gas stream (i.e., the moisture in the carrier gas helps prevent the carbon bed from overheating; moisture of only $\sim 5\%$ relative humidity was found to be effective in avoiding ignition). The investigators also recommended that the contact of activated carbon with oxygen be avoided after drying and that a supply of inert gas, such as nitrogen, be used to cool the bed.

Self-Heating and Ignition of Chemically Activated Carbon

Bowes and Cameron⁷ found that newly manufactured activated carbon undergoes appreciable exothermic reactions upon initial exposure to air at ambient temperatures. The exothermic reactions, which are due to rapid adsorption of oxygen and moisture, are largely completed in a period of a few minutes to a few hours. In contrast, the investigators found that long-term self-heating of activated carbon is mainly due to oxidation of the carbon. The oxidation is relatively slow and can continue for weeks following manufacture. The self-heating process is sensitive to carbon activation conditions and exposure to air at high temperatures (e.g., 100 °C). The investigators also observed that the increase in carbon temperature associated with self-heating depends on the balance between the rate at which heat is generated by adsorption/oxidation reactions and the rate at which heat is lost to the surroundings.

Oxidation of Methyl Ethyl Ketone and Cyclohexanone on Activated Carbon

Henning et al.⁸ investigated the surface oxidation of methyl ethyl ketone and cyclohexanone on three types of activated carbon (lignin-based, peat-based, and hard coal-based carbons). The investigators found that both ketones, even in the adsorbed state, oxidize on the surface of activated carbon due to the presence of oxygen. The effects of temperature, carbon type, and ash content on oxidation were also investigated. Selected findings from the study are (1) to minimize surface reactions, a low adsorption temperature is more important than the type of activated carbon used; (2) the adsorption temperature should not exceed 30 °C for methyl ethyl ketone and cyclohexanone because surface reactions with these ketones increase exponentially above this temperature; (3) a flow velocity of at least 0.2 m/sec should be used to dissipate the heat of adsorption; and (4) oxidation reaction rates are higher on carbons treated to remove ash content than on untreated carbons.

Conclusions Regarding Activated Carbon Ignition and Combustion

Based on the information presented in the studies reviewed, the following conclusions are made regarding the ignition and combustion of activated carbon in carbon adsorption systems.

- *Activated carbon adsorption is an exothermic process.* The quantity of heat release from activated carbon adsorption is a function of the following properties of the gas stream being treated: gas flow rate, concentration of the gaseous contaminants, relative humidity of the gas stream, and presence

of certain reactive compounds.

- *Adsorption and oxidation of organics can release significant quantities of heat.* For certain classes of chemical compounds, adsorption and oxidation on the activated carbon surface can release a significant quantity of heat, particularly if the chemicals are present at high concentrations in the gas stream. Bed fires in carbon adsorption systems reported in the literature frequently occurred in those systems treating gas streams that contained oxygenated hydrocarbons. However, other types of chemical compounds also can burn on activated carbon. Chemical compounds of concern include ketones, aldehydes, certain organic acids (e.g., propanoic acid and butyric acid), and organic sulfur compounds (e.g., mercaptans).
- *Bed temperatures can reach the carbon self-ignition point.* Under certain conditions, carbon adsorption reactions can release sufficient quantities of heat to increase the temperatures in a carbon bed to the carbon's ignition temperature, resulting in spontaneous combustion of the activated carbon.
- *The carbon self-ignition point is a function of carbon type and condition.* Reported ignition temperatures for activated carbons range from less than 300 °C to more than 600 °C.⁹ The type and condition of activated carbon are important factors contributing to the ignition temperature for a given carbon.
- *Heat is removed from the carbon bed primarily by convective heat transfer.* For most carbon adsorption systems, conductive heat transfer through the carbon bed vessel walls is small. Consequently, the primary heat transfer mechanism for removing heat released by adsorption and oxidation reactions from the carbon bed is convective heat transfer by the gas stream flowing through the bed. The typical vent stream flow from a fixed-roof tank is intermittent and at relatively low flow rates. Under these conditions, gas stream flow through a carbon canister may be insufficient to dissipate heat adequately when the gas is composed of highly reactive organic compounds or high concentrations of organics.
- *Localized hot spots can occur in the carbon bed.* Hot spots occur when the heat generated by adsorption and oxidation reactions exceeds the heat removed by convection. Channeling of the gas flow around pockets of carbon can also contribute to a heat imbalance in the carbon bed.

- *Fires originate in hot spots in the carbon bed.* Carbon bed fires occur when hot spots in the carbon reach the ignition temperature of the adsorbed vapors or activated carbon itself and sufficient oxygen is present to sustain combustion of the carbon and adsorbed compounds.

CARBON BED FIRES IN CARBON ADSORPTION SYSTEMS

Bed fires in carbon adsorption systems occur and can lead to serious consequences, including a tank explosion. The following sections summarize experiences at three facilities in addressing carbon bed fires in their carbon adsorption systems.

Bed Fires in Carbon Canisters Used for Air Emission Control

Harrell et al.¹⁰ described an organic chemical manufacturing facility that experienced several bed fires in carbon canisters used to control air emissions from fixed-roof tanks containing crude sulfate turpentine. The facility's operators installed the carbon canisters as shown in Figure 1. A single vent on the tank roof was connected to a carbon canister using a hose with no check valve to prevent back flow. When the tank was emptied or when the liquid in the tank cooled, negative pressure conditions (i.e., a vacuum) developed in the tank vapor space, which pulled in ambient air through the carbon canister. It was reported that fires frequently occurred at night following a hot day. In one case, the daytime temperature was 35 °C (95 °F) or more, and the tank was exposed to full sunlight. The temperature within the tank increased to 57 °C (135 °F), causing the liquid to expand and vaporize and forcing the vapor-laden air out of the tank and to the carbon canister. In the evening, when the tank had cooled, the vapor in the tank's headspace condensed, creating a pressure gradient or slight vacuum in the tank. As the ambient air was drawn into the tank through the carbon canister, the hot organic molecules adsorbed on the carbon oxidized (due to the presence of oxygen), resulting in the bed fire.

To address the problem with carbon bed fires, the company installed a check valve in the vapor line between the tank and the carbon canister. This valve prevented back flow of ambient air through the carbon bed. A vacuum-breaker was installed upstream of the check valve to allow ambient air to flow directly into the tank vapor space when necessary to maintain the internal tank pressure within the tank design pressure range. These modifications removed the path by which ambient air could be drawn into the tank through the carbon canister and reduced the exposure of the bed carbon to an oxygen source. Although these modifications did not completely eliminate

the carbon bed fires, they significantly reduced the incidence of the fires at the facility.

Bed Fires in a Carbon Adsorption System Used for Solvent Recovery

Chapman and Field¹¹ described a graphics company that experienced three serious bed fires in a regenerable, fixed-bed carbon adsorber used for solvent recovery of ketones. To address the bed fires, the company consulted with equipment vendors, carbon suppliers, consultants, insurance carriers, and other users of carbon bed adsorption equipment. Most people contacted believed that the bed fires were a result of a heat imbalance due to the high heat of adsorption of the ketones. The recommended measure to correct this heat imbalance was to keep the carbon beds moist. Adding moisture to the carbon beds allowed the latent heat of vaporization of water to dissipate the heat of adsorption of the ketones. To keep the beds moist, various "fixes" were recommended, including extension of steaming cycles, increased steam flow rates, increased steaming times at startup and shutdown, desuperheating the steam, and humidification of vapor inlet streams. The company followed these recommendations but still encountered bed fires.

Facility personnel noted that the fires never took place during an extended adsorption cycle but only occurred during startup following a weekend shutdown. They believed that the fires resulted from a heat imbalance during the shutdown when there was insufficient gas stream flow to cool the bed. This allowed the oxidation of adsorbed ketones to accelerate and form localized hot spots. Bed combustion occurred when the adsorption cycle was restarted (i.e., when the gas stream of solvent-laden air was reintroduced to the bed).

Based on the facility's experience with carbon bed fires, the facility personnel prepared a list of minimum safety requirements for any carbon bed adsorption system in ketone service. Foremost among the recommendations for safe operation of the carbon bed adsorber is to monitor the adsorption process and its propensity for ignition. They concluded that the best parameters to provide this information are on-line, real-time monitoring of CO and CO₂ concentrations in the exhaust gas stream from the carbon bed when the system is operating in the adsorb mode and monitoring the concentrations in the bed at all other times. For large-scale carbon adsorption systems, safe operation requires that the monitoring equipment operate continuously, whether the unit is on-line or off-line.

Explosion of a Fixed-Roof Tank Vented to a Carbon Canister

On January 15, 1998, a fixed-roof tank vented to a carbon canister exploded at a facility in Sumter, SC.¹² The tank was used to store a mixture of lacquers and thinners

that contained acetone, methyl ethyl ketone, and toluene. At the time of the incident, the tank was using a carbon canister as shown in Figure 1. A single vent on the tank roof was connected to the carbon canister by a pipe with no check valve. The facility personnel concluded that the most plausible explanation for the tank explosion was that localized heat of adsorption and reaction in the carbon canister provided sufficient thermal energy to reach the ignition temperature of the flammable vapor in the piping. Because no safety devices were in place to prevent backflow to the tank, the fire in the carbon bed flashed back through the piping to the vapor space in the tank.

The facility had never experienced a tank explosion prior to the installation of the carbon canisters. Following the incident, facility personnel measured the bed temperature in the carbon canisters used on other tanks and recorded readings in the range of 49–66 °C (120–150 °F). While these temperatures were well below the self-ignition temperature of the organic vapors, according to the canister manufacturer, it is possible to have localized hot spots in the carbon bed with temperatures significantly higher than those measured. These hot spots could have ignited the vapor. Given the fact that the tank was used to store solvents containing ketones and other highly reactive compounds, and considering the tank configuration, the carbon canister manufacturer agreed with facility personnel that it was feasible that hot spots in the carbon bed ignited the vapor in the gas stream, which flashed back through the vent piping to the tank.

To prevent recurrence of another tank explosion, the following safety measures were implemented at the facility for each tank vented through a carbon canister. A check valve was installed in the vapor line to prevent vapor or liquid back-flow from the carbon canister into the tank. A vacuum-breaker valve was also installed upstream of each check valve to prevent collapsing the tank when pumping liquid out of it. An inline flame arrester was installed in the vapor line between the tank and the check valve. Metered nitrogen gas was used as an inert blanket for the atmosphere in the tank and in the vapor line. The facility reports that, since making these changes to carbon canister systems, no tank explosions have occurred.

SAFETY MEASURES FOR CARBON CANISTER SYSTEMS

Carbon canisters can safely be used to control organic air emissions from fixed-roof tanks.¹³⁻¹⁷ A variety of equipment and work practice safety measures have been implemented at facilities to reduce the risk of carbon bed fires and to prevent an explosion or other large-scale damage to the tank system should a bed fire occur. Each of these safety measures is described in this section. Not all of the

safety measures described are implemented at a given tank site. The combination of safety measures used for a specific fixed-roof tank application will depend on site-specific conditions, the safety measures selected, and the preferences of the tank owner or operator.

Install Check Valve with Vacuum-Breaker Relief Valve

A check valve automatically limits gas (or liquid) flow in a pipe to one direction. Installing a check valve in the carbon canister system line prevents the reverse flow of ambient air through the canister outlet into the carbon bed when negative pressure develops in the tank vapor space due to cooling at night or when liquid is withdrawn from the tank. With the installation of a check valve in the carbon canister system, a vacuum-breaker valve (sometimes referred to as a vacuum relief valve) must also be installed upstream of the carbon canister. A vacuum-breaker valve is a one-way valve that opens automatically at a preset pressure, allowing ambient air to flow into the tank to maintain the tank system's internal pressure within design specifications. When the internal pressure of the tank adjusts to a prescribed pressure setting, the valve automatically closes and air no longer flows into the tank. The vacuum-breaker valve is needed to prevent the tank from collapsing inwardly when negative pressure develops in the tank vapor space due to cooling at night or when liquid is withdrawn from the tank. The vacuum-breaker valve opens only in situations when vacuum relief is required to protect the tank or canister. Organic vapors from the tank cannot flow out through the valve. In some applications, the vacuum-breaker valve is connected to a nitrogen tank to provide additional fire protection (described later in this section).

Install Flame Arrester

A flame arrester is a device that prevents the propagation and transmission of a flame or flame front in locations where flammable vapor/air or gas mixtures are present. Flame arresters are available in several different configurations (e.g., parallel rectangular metal plate, wound crimped metal, parallel round metal plate). One common feature of all flame arresters is that the flammable vapor mixture is forced to pass through a series of small openings as it flows through the arrester. The size of the openings and their length of passage can vary, depending on the arrester style. If a flammable vapor should ignite, the flame burns toward the arrester/element. As the flame attempts to pass through the element, it is slowed and cooled by contact with the metal walls of the small passages. Heat is transferred to the element until combustion no longer can be sustained, extinguishing the flame front. The flame arrester prevents flashbacks from a carbon canister to a tank in the event of a bed fire.

Install Emergency Pressure Relief Valve

A pressure relief valve is a device that opens automatically at a preset pressure allowing vapors to flow out of the tank. When the internal pressure of the tank adjusts to a prescribed pressure setting, the valve automatically closes, and vapors are no longer vented from the tank. An emergency pressure relief valve is a safety device that vents the tank vapor space directly to the atmosphere when it is necessary to prevent physical damage or permanent deformation to the tank due to unsafe conditions resulting from an unplanned, accidental, or emergency event. This valve is not used for venting of gases or vapors from the tank during normal operations. An emergency pressure relief valve protects the tank should vapor flow through the carbon canister bed become partially or completely restricted because the bed becomes blocked or plugged. In such an emergency situation, the pressure-relief valve will open and, thereby, relieve the tank's internal pressure until a safe level is attained.

Use Nitrogen Gas Blanket

An inert gas (in this case nitrogen) can be used in place of ambient air as the source of makeup gas for a vacuum-breaker valve. Using nitrogen gas in place of ambient air provides a nonflammable atmosphere in the vapor space and vapor line of a fixed-roof tank. Being an inert gas, nitrogen is nonflammable and usually chemically nonreactive when mixed with the organic vapors in the tank. The nitrogen gas eliminates or reduces the oxygen available for combustion. Nitrogen can be used as the primary makeup gas for the vacuum-breaker (in which no ambient air enters the system), or it can be used with ambient air. In the latter case, the amount of nitrogen gas added is such that the concentration of oxygen in the air is too low to sustain combustion.

Prewet Carbon Bed

Two carbon manufacturers recommend prewetting the carbon as a means to avoid bed fires. According to Calgon,¹³ prewetting the carbon helps dissipate excessive heat. Carbtrol¹⁴ recommends prewetting the carbon when the organic composition of the tank vent stream is uncertain (e.g., a tank used to manage wastes that contain volatile organics and are received from off-site generators). The Carbtrol literature describes how the carbon should be wetted.¹⁴

Use an Activated Carbon Type with Higher Ignition Temperatures

Activated carbon is made from a variety of carbon sources, including coconut shells, wood, bituminous coal, and other organic materials. A coconut-based activated carbon is the most common type of carbon used

for air pollution control applications. Different types of activated carbon have different ignition temperatures and ash contents (in some cases, a high percentage of ash content promotes carbon bed ignition). For applications where the tank vent stream to be controlled contains reactive organics, selection of an activated carbon with a high ignition temperature and a low ash content may help avoid carbon bed fires. The ignition temperatures of coal-derived activated carbons are generally ~450 °C.¹⁵ Lignin-based carbon generally has an ash content of ~15% ash, whereas bituminous-based carbon has an ash content from 5 to 10%.¹⁶ Ash contents can be lowered by washing the carbon with acid during the manufacturing process.

In contrast, the ignition temperatures of coconut-derived activated carbons generally range from 280 to 300 °C¹⁵ and generally have ash contents less than 2%.¹⁶ The Naujokas study³ found that reactive compounds oxidized more readily on coconut-based carbon compared with coal-based or petroleum-based carbons. In addition, the Hassler study⁹ observed that comparisons of ignition temperatures for different activated carbons are of significance only when determined under identical experimental conditions. The various methods used to establish the ignition temperature may not obtain identical ignition points for a given activated carbon type because the temperature at which the carbon ignites in air is influenced by the test method and experimental conditions used.

Monitor Exhaust Gas Parameters

Large carbon bed systems, such as those used for solvent recovery, are often equipped with sensors for monitoring temperatures in different parts of the carbon bed as well as in the exhaust gas. Some systems also have instruments for detecting the oxidation products CO and CO₂ in the exhaust gas. These built-in monitoring devices are less likely to be used on carbon canister systems, because the beds are frequently replaced due to their small size. One carbon manufacturer, Carbtrol,¹⁴ recommends monitoring the exhaust temperature during the first 24 hr of operation of a canister. According to Carbtrol, a rise in the gas temperature of greater than 10 °C (50 °F) indicates excess heat generation. Under these conditions, the unit should be removed from service and the cause of the excessive heat generation determined.

Carbon Canister Location

The carbon canister should be located where it can be easily accessed for removal or replacement. Preferably, the carbon canister should be placed at ground level where it is readily visible to facility personnel and in a location that is physically isolated from the tank that vents to it. The carbon canister should be situated with open space between it and major pieces of equipment or tanks.

Work Practices

At initial startup of a new carbon canister, facility personnel should closely monitor the first hours of operation by periodically measuring the temperature and CO/CO₂ levels in the gas stream exhausted from the canister. Increasing temperature and CO/CO₂ levels in the gas stream provide early warnings of excessive heat buildup or combustion problems in the unit. Air leaks in valves, fittings, and other carbon canister system components can provide additional sources of oxygen to the carbon bed and help promote oxidation reactions. Facility personnel should periodically inspect and maintain valves and other system components to minimize openings by which air can be pulled into the carbon bed.

Facility personnel should be trained to respond rapidly to a carbon bed fire. They should know how to disconnect the canister quickly from the vapor line and how to extinguish the fire. Once the canister is disconnected, the unit can be moved to an open area away from the tank. Overhead deluging of the carbon bed with water has been reported to be an effective means for extinguishing the fire.

IMPLEMENTATION OF SAFETY MEASURES TO FIXED-ROOF TANKS

This section presents general guidance on how to implement the available carbon canister safety measures to a specific fixed-roof tank application. Tank owners and operators should always discuss their site-specific conditions with the carbon canister manufacturer or vendor prior to installation of a carbon canister to ensure that adequate safety measures are implemented. Safe operation of carbon canisters begins with eliminating or minimizing, to the extent practical, the incidence of bed fires in carbon canisters. Because of the wide variety of tank applications that potentially can be controlled using carbon canisters, a definitive list of the specific organic constituents, concentrations, temperatures, and other properties associated with activated carbon bed fires cannot be provided in this article. Therefore, the first step in selecting the combination of safety measures appropriate for a given tank application is to gather site-specific information to characterize the tank vent stream to be controlled by the carbon canister. Useful vent stream information includes the organic chemical constituent composition and concentrations, flow rates, temperature, and relative humidity. Using this information, an assessment can be made of the likelihood of any potential heat buildup problems occurring in the carbon bed because of the presence of reactive compounds, high organic concentration loadings, or an inadequate gas stream flow.

For tank applications where the nature of the tank vent stream to be controlled is such that the likelihood of

a bed fire is reasonable, appropriate precautionary safety measures can be incorporated into the carbon adsorption system design. Examples of such safety measures include (1) selecting an activated carbon with a high ignition temperature to help prevent fires, (2) installing an exhaust gas temperature monitor with an audible alarm to detect and alert facility personnel of a bed fire, or (3) equipping the carbon canister with a fire suppressant system (such as water flood or spray systems) to promptly extinguish bed fires. For tank applications where sufficient information to characterize the vent stream is unavailable, appropriate precautions should be followed at initial startup of the carbon canister system. For example, the temperature of the exhaust gas from the carbon canister can be monitored while maintaining a continuous gas flow through the canister for the first few hours of operation. An increase in the gas temperature indicates excessive heat generation or heat buildup. Prewetting the carbon will reduce the likelihood of a bed fire should a problem be indicated.

Safety measures should also be implemented to prevent large-scale collateral damage to the tank in the event of a fire or canister malfunction. The risk of a tank explosion can be reduced significantly by installing appropriate safety devices to confine the fire to the carbon bed and prevent flashback to the tank. In a situation where openings in the canister become blocked or plugged, restricting vent stream flow and increasing internal tank pressures, rupture of the canister, vent line, or tank can be prevented by installing emergency pressure relief devices.

Four basic safety components are recommended for all carbon canister systems used to control fixed-roof tank air emissions. Use of one or more additional safety measures may be prudent to address site-specific tank conditions. The four basic components are (1) a *backflow check valve* to prevent reverse flow of ambient air through the carbon bed to the tank when negative pressure develops in the tank vapor space due to cooling at night or when liquid is withdrawn from the tank, (2) a *vacuum-breaker relief valve* installed upstream of the carbon canister to allow ambient air into the tank vapor space as needed to maintain the tank system's internal pressure within design specifications, (3) a *flame arrester* to prevent flashbacks from the carbon canister to the tank in the event of a bed fire, and (4) an *emergency pressure relief valve* to prevent physical damage to the tank in the event the carbon canister becomes plugged.

The set of basic safety components can be installed on a fixed-roof tank carbon canister system using a number of different configurations. Figures 2 and 3 show two of the possible installation configurations. The backflow check valve can be installed in the exhaust outlet for the carbon canister (see Figure 2) or in the

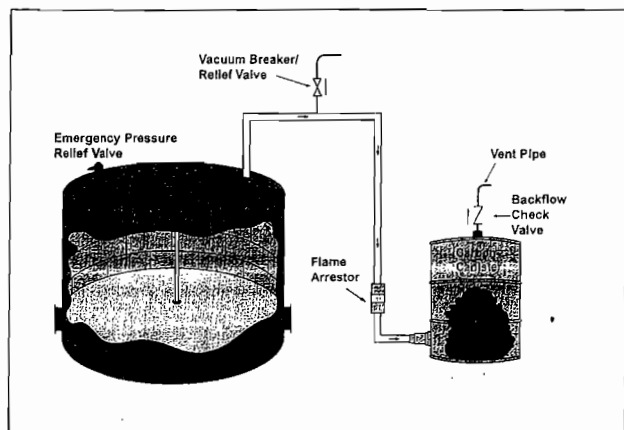


Figure 2. Carbon canister safety device installation Configuration A.

vent line between the tank and the carbon canister (see Figure 3), depending on preference. For a check valve installed on the outlet to the carbon canister to be effective, it is important to ensure that there are no air leaks in the carbon canister vessel or its connections. If the backflow check valve is mounted on the canister exhaust, the vacuum-breaker must be set at a pressure that takes into consideration both the tank's and the canister's structural design. This prevents situations where the canister could collapse if the vacuum-breaker is set for the tank rather than for the canister (assuming the tank is stronger than the canister).

The vacuum-breaker relief valve can be installed in the vent line between the tank and the carbon canister (as shown in Figures 2 and 3) or installed directly on the tank. The flame arrester is installed in the vent line between the tank and the carbon canister. Care should be taken in determining the type and location of the flame arrester. The flame arrester should be mounted as near as is practical to the canister (i.e., the potential point of ignition). If placed too far from the canister, the flame can accelerate sufficiently through the vent pipe to cause the arrester to fail.¹⁸ For fixed-roof tank applications, emergency pressure relief valves are normally installed on the tank roof but can be located in the vent line.

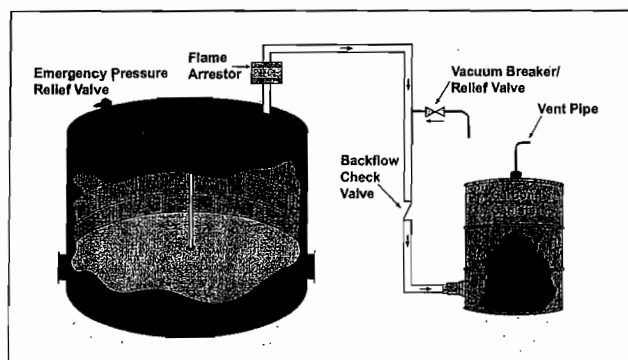


Figure 3. Carbon canister safety device installation Configuration B.

Table 1. Summary of conditions contributing to bed fires in carbon canisters used for fixed-roof tank air emission control.

- Adsorption and oxidation of high heat-generating organic compounds (e.g., ketones, aldehydes, organic acids, organic sulfur)
- Use of activated carbons with low ignition temperatures
- Backflow of ambient air through carbon canister (i.e., tank breathing through the canister)
- Low and intermittent gas stream flows from the tank through the carbon canister insufficient to remove heat generated by activated carbon adsorption and oxidation reactions
- Air leaks in valves and other system components allow oxygen to enter carbon bed

SUMMARY AND CONCLUSIONS

Carbon canisters can safely (and effectively) be used to control organic air emissions from fixed-roof tanks. Safe operation of carbon canisters begins with eliminating or minimizing conditions conducive to starting a bed fire. Table 1 summarizes conditions that may contribute to carbon bed combustion. Should a carbon fire occur, large-scale collateral damage can be prevented by using appropriate safety measures that will confine the fire to the carbon bed and will result in the fire being extinguished promptly. The basic set of safety components for a carbon canister system consists of installing a backflow check valve, a vacuum-breaker relief valve, a flame arrester, and an emergency pressure relief valve. Implementation of other safety measures may be advisable depending on the organic characteristics of the tank vent stream and other site-specific conditions. Table 2 summarizes safety measures that can reduce the incidence of carbon canister bed fires and minimize the impacts in the event that a bed fire occurs.

Table 2. Summary of safety measures for carbon canisters used for fixed-roof tank air emission control.

- Install check valve to prevent backflow of ambient air through carbon bed (e.g., due to nighttime cooling or when liquid is pumped out of the tank). Also must install vacuum-breaker relief valve upstream of carbon canister to allow airflow into tank when needed to maintain the tank internal pressure within design limits
- Install flame arrester upstream of carbon canister to prevent flashback to the tank vapor space in the event of a bed fire
- Install emergency pressure relief valve upstream of carbon canister to prevent tank rupture due to a plugged carbon bed
- Use nitrogen gas blanket to eliminate oxygen needed for combustion
- Prewet activated carbon bed to remove excess heat
- Use activated carbon having high ignition temperature and low ash characteristics
- Locate carbon canister where it is easily accessed for removal but physically isolated from the tank being controlled
- Monitor temperature, CO, and CO₂ levels and closely supervise carbon canister during initial startup for early warning signs of bed oxidation
- Inspect and maintain valves and carbon canister system components to minimize air leaks into the carbon bed that promote oxidation reactions
- Train facility personnel on how to rapidly respond to and extinguish a carbon bed fire

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