Technical Dialogue

Fires: What's in That Smoke?

by John S. Nordin, Ph.D.

A fire threatens a place where chemicals are stored. The firemen or emergency responders know what chemicals are present, but is there any way of predicting what might be in that smoke if the chemicals catch fire or vaporize because of the heat?

This is not an easy question to answer, but let us start with some basic chemistry.

Basic Chemistry

1. Burning of Natural Gas

Natural gas is almost entirely made up of methane, which has the chemical formula CH_4 . There is also a very small amount of ethane (chemical formula CH_3CH_3), ethylene (chemical formula CH_2CH_2), perhaps a very small amount of propane, and a few other components. The "C" in the chemical formula stands for the element carbon. The "H" in the chemical formula stands for hydrogen. When natural gas is burned, the carbon components react with the oxygen in the air producing carbon dioxide. The hydrogen components react with oxygen in the air producing water vapor. A great deal of heat is given off as the natural gas is burned. The chemical reaction for methane is

$$CH_4 + (3/2)\ O_2 \longrightarrow CO_2 + 2H_2O$$

For ethane, the chemical reaction is

$$CH_3CH_3 + (7/2)\ O_2 \longrightarrow 2CO_2 + 3H_2O$$

Natural gas is a clean-burning fuel, meaning that the fuel burns producing carbon dioxide (CO_2) and water giving off heat without producing a lot of soot.

Notice that oxygen (air is made up of approximately 21% oxygen by volume) is required for this burning to take place. If there is nothing to restrict the airflow to the flame, the natural gas burns clean producing carbon dioxide and water. But suppose the airflow is restricted, that is, not enough oxygen gets to the flame. The flame might turn yellow in color. Some of the carbon "burns" producing carbon monoxide (CO) instead of carbon dioxide. Carbon monoxide is a very poisonous gas. The National

Institute for Occupational Safety and Health (NIOSH) and OSHA both recommend as an 8-hour exposure limit for carbon monoxide of 35 parts per million (ppm) on a time weighted average (TWA) basis, or a ceiling limit of 200 ppm. The Immediate Dangerous to Life and Health (IDLH) limit is 1200 ppm in air. It does not take much carbon monoxide to kill. The reaction might be written (without balancing the elements on each side of the equation) >

$CH_4 + O_2 \longrightarrow CO_2 + CO + 2H_2O$

Of course, if air prevented entirely from reaching the flame, the flame will go out (the burning stops). How much carbon monoxide is produced per unit of methane? It depends upon how efficient the burning, that is, can enough oxygen reach the flame for the methane to convert entirely to carbon dioxide. Even with the best burners and unrestricted air supply, the burning is not 100% efficient; there could be few parts per million (ppm) of carbon monoxide in the exhaust gases above the flame. This is not enough to be of concern in a residence using natural gas for heating and cooking. But if something is wrong, e.g. the burning is constrained, concentrations of carbon monoxide in the house could build up to several hundred parts per million and even higher.

The production of carbon monoxide is not limited to burning of natural gas with an insufficient air supply. Anything that has carbon as part of the fuel source can produce carbon monoxide during the burning process.

2. Burning of ethanol

Ethanol, like natural gas, is another clean-burning fuel. But there is one important difference. Ethanol is a liquid at room temperature. The ethanol must vaporize before the burning takes place. The vaporization occurs right at the surface of the liquid. The liquid may be a pool or fine droplets or an aerosol that vaporizes. When ethanol vaporizes, the oxygen from the air can get at the individual ethanol molecules. The chemical reaction for the burning of ethanol (also called ethyl alcohol) is

$CH_3CH_2OH + 3O_2 \longrightarrow 3H_2O + 2CO_2$

Ethanol has a flash point of 55^oF, meaning that if the temperature of ethanol is 55^oF or higher, enough vapors are given off to start the burning process if there is an ignition source. At 55^oF, the vapor pressure of ethanol is about 25 mm Hg [25 millimeters of mercury], which is equivalent to a 3.3% concentration of ethanol in air (25/760 x 100% = 3.3%). The Lower Explosive Limit (LEL) of ethanol in air is 3.3%. At 68^oF, the vapor pressure of ethanol is 44 mm Hg, which calculates to (44/760 x 100% = 5.79%) about a 5.8% concentration in air. Once ethanol starts burning, heat is given off resulting in more ethanol vaporizing. We now have fire using ethanol as fuel. Remember that it is the ethanol vapor that is burning.

Can some carbon monoxide form? Yes, if not enough air can get to the flame to completely combust the burning ethanol.

3. Burning of Ethylene dichloride

Let’s consider the situation where a chemical containing chlorine is burned. Ethylene dichloride has the chemical formula $ClCH_2CH_2Cl$, sometimes written as $C_2H_4Cl_2$. This chemical has a flash point of 56^oF, a LEL of 6.2%, and a vapor pressure at 68^oF of 64 mm Hg. It will ignite at room temperature. With ample air, the following combustion reaction takes place:

$C_2H_4Cl_2 + (5/2)\ O_2 \longrightarrow 2CO_2 + H_2O + 2\ HCl.$

Hydrogen chloride (HCl) gas is produced. Hydrogen chloride readily dissolves in water producing hydrochloric acid. This is an irritating, noxious gas if inhaled. It is corrosive to the linings of the respiratory tract and to the skin. Both OSHA and NIOSH have a ceiling limit of 5 ppm in air for an 8-hour exposure. The IDLH limit for HCl is 50 ppm.

Any material containing chlorine (Cl) as part of its chemical structure will most likely produce hydrogen chloride if burned.

In the example given, there could be other chemicals produced depending upon how the burning of ethylene dichloride takes place. There could be some carbon monoxide. There could be some soot. There could also be some carbonyl dichloride, also known as phosgene ($COCl_2$). Phosgene is a very poisonous gas. Both NIOSH and OSHA publish an 8-hour TWA exposure limit of 0.1 ppm. The IDLH limit for phosgene is 2 ppm.

Minute amounts of other toxic chemicals can be produced whenever materials containing chlorine are combusted. Some of the worst ones are in the chemical group called dioxins and furans. This group of chemicals has the potential to cause cancer if inhaled or otherwise absorbed into the body. Some dioxins and furans are more toxic than others, the worst actor being 2,3,7,8-TCDD, also called 2,3,7,8-tetrachlorodibenzo-p-dioxin. The concentrations of dioxins and furans emitted from a fire might be very low, on the order of several hundred nanograms per cubic meter in the gases emitted from the fire. The concentration of 2,3,7,8-TCDD in this gas might be less than one nanogram per cubic meter. The occasional breathing during normal firefighting operations probably is not enough to result in cancer later in life, but repeated inhaling of soot and tars which contain trace dioxins and furans and other chemicals is of concern.

Burning of Plastics and Tires

Let’s talk about something more complicated. What happens when plastics burn? We are taking about the solid materials made from polymers found in homes and industry. Plastics are not clean burning fuels, that is, they produce a lot of smoke and soot when they burn.

The solid plastic material of itself does not burn. It is the vapors given off from the plastic material which burns. There are exceptions to this. If there is an oxidizing material mixed in with the plastic or if the plastic is a fine dust in the air, burning can take place, often with explosive violence, without the plastic first vaporizing. We are assuming in this example that we are dealing with the plastics making up the materials commonly found in the home or commercial businesses. Therefore the material must first vaporize before burning takes place.

The ignition source could be a spark or a smoldering cigarette butt. Perhaps some paper catches fire. Enough heat is given off to vaporize plastic material nearby. Once the vapors ignite, more heat is given off and more plastic material vaporizes. The vapors give off a lot of heat as they burn. A very hot fire can result.

The fire can become very turbulent. A lot of the vaporizing material gets shoved out of the way of the flame before it gets a chance to burn completely. The vapors condense forming soot and tars. We see a thick black or gray-black smoke coming from the fire.

The author of this paper (John Nordin) set up a series of test burns at Western Research Institute north of Laramie, Wyoming, where various plastics and tires were burned. A private company interested in incinerator design sponsored the tests during the 1989-1991 time period. Various materials (plastics, whole tires, municipal solid waste, etc.), were placed on a grate inside an enclosed large steel box with openings without any shredding or other preparation. These materials were burned. The box was the size of a small room with openings, which might represent vents or doors. All the gases given off including the volatiles which escaped the burning were routed to a second steel chamber (an “afterburner”) which was equipped with a natural gas or propane pilot light which provided an ignition source for the volatiles which escaped the burning. The steel box was designed is such a way that the burning could take place under excess air or air-starved conditions (like opening and closing doors and windows of a room containing burning materials). During the burns, the gases and volatiles given off were captured and measured. From these measurements, the emissions expressed in parts per million or in pounds of emissions per ton of material being burned were calculated for various materials, under excess air and air starved conditions. While the objective of the tests was to design a better incineration system, a lot of data was obtained on what pollutants might be in the gases given off when there is a large fire inside an enclosed structure.

One of the surprises of the tests is that when whole tires or plastics were burned in the steel box, sometimes more than half of the total fuel heat content was in the form of volatiles which escaped the burning. The volatiles could be captured and condensed as a black tarry, sooty mess. They were a complex mixture of many chemicals. Under air-starved conditions, concentrations of carbon monoxide reached up to about 3% of the total gas volume or about 30,000 parts per million (sometimes peaking even higher). Also given off were hydrogen sulfide, sulfur-containing organic compounds, sulfur dioxide, hydrogen chloride, a small amount of methane and ethylene, and other gases. Under excess air conditions, the oxygen might be 4 to 10% in the gas, but there would be still a lot of volatiles given off, and carbon monoxide concentrations might be still several hundred parts per million. Carbon dioxide might vary from about 6% to maybe 16% depending upon the test. The balance was nitrogen from the combustion air. A lot of water vapor was given off. These are the kind of emissions that might be expected in a large fire when plastics or tires are burned.

In the Laramie tests, the gases (including the carbon monoxide and volatiles) were captured by the second chamber, ignited, and burned. Gas temperatures entering the secondary chamber were typically 700 ^{o}F. Gases leaving the secondary chamber might be 2200^{o}F. The natural draft of the system pulled the gases through the secondary chamber. The secondary chamber was designed such that the burning was complete with no visible emissions. Extensive measurements were taken leaving the secondary chamber (particulates, metals, hydrogen chloride, organics, dioxins, sulfur dioxide, NOx, carbon monoxide, water vapor, etc.). The measurements showed that combustion was essentially complete.

The burning of tires produced some sulfur acid gases, mostly sulfur dioxide. The NIOSH recommended limit for 8-hour exposure to sulfur dioxide is 2 ppm; the OSHA limit is 3 ppm. The IDLH limit for sulfur dioxide is 100 ppm. If there is insufficient air, some hydrogen sulfide is produced. Another possible chemical produced is sulfur chloride (S_2Cl_2). Sulfur chloride has a

NIOSH and OSHA recommended 8-hour exposure limit of 1 ppm, and an IDLH limit of 5 ppm.

If burning temperatures exceeded 2400°F, some of the air nitrogen and oxygen reacted producing NOx. The reactions are

$N_2 + O_2 \longrightarrow 2\ NO$

$2\ NO + O_2 \longrightarrow 2\ NO_2$

Some NOx (e.g. NO and NO_2) is also produced when fuel containing nitrogen is burned, such as burning plant waste.

Dioxins and furan concentrations were on the order of several hundred nanograms per standard cubic meter (dry basis) when plastics containing chlorine were burned, or about 4 nanograms per standard cubic meter (dry basis) when plastics that did not contain chlorine as part of the chemical structure were burned.

A real-world fire that a responder might deal with produces pollutants similar to the burning that took place in the steel box in the Laramie tests.

Pesticide Fires

Pesticide fires are particularly nasty because of the many pollutants that can be given off. There are many kinds of pesticides. They may contain sulfur, chlorine, bromine, phosphorous, nitrogen, and/or fluorine as part of the chemical structure. Some pesticides may contain the toxic elements mercury or arsenic. There is good potential for some dioxins and furans to form whenever pesticides containing chlorine are burned and be incorporated as part of the soot and particulates given off. Some pesticides are incorporated with inorganic fertilizers, which may result in oxides of phosphorous, potassium, NOx, and metal oxides given off in a fire.

About 14 years ago, a large pesticide fire occurred near Minot ND. The fire produced a smoke cloud about 50 miles long requiring the evacuation of people in the cloud path. Fortunately, that part of the country is sparsely populated.

For example the pesticide dieldrin has a chemical formula $C_{12}H_8Cl_6O$. In a chemical fire, hydrogen chloride (HCl) can be expected in the smoke cloud. The smoke cloud will contain partly combusted dieldrin including small amounts of dioxins and furans.

Fipronil is a recently developed pesticide (introduced in 1996) with the chemical formula $C_{12}H_4Cl_2F_6N_4OS$. In a fire, combustion of this pesticide is expected to produce hydrogen chloride (HCl), hydrogen fluoride (HF), some NOx, and sulfur dioxide. The NIOSH and OSHA 8-hour exposure limit for HF is 3 ppm. There will also be various products of incomplete combustion that will be part of the smoke.

Bromoxynil is an herbicide with the chemical formula $C_7H_3Br_2NO$. In a fire, combustion of this material is expected to produce some hydrogen bromide (HBr). The NIOSH and OSHA 8-hour exposure limit for HBr is 3 ppm. There will also be various products of incomplete combustion that will be part of the smoke.

Diazinon is an insecticide with the chemical formula $C_{12}H_{21}N_2O_3PS$. In a fire, combustion of this material is expected to produce some sulfur dioxide, phosphorus oxide, NOx, as well as various products of incomplete combustion. If there is insufficient air, there could be some carbon monoxide (CO), hydrogen sulfide (H_2S), sulfur oxide (SO), and even some phosphine (PH_3). Phosphorous oxide can react with water producing phosphoric acid. Phosphoric acid has a NIOSH and OSHA 8-hour exposure limit of 1 ppm. The NIOSH and OSHA 8-hour exposure limit for phosphine (time weighted average, TWA) is 0.3 ppm.

Conclusions

- It is important as part of Community Right-to-Know Laws that emergency responders know what chemicals are stored or used at a location. As seen by these examples, predictions can be made from the chemical formula of what toxic pollutants might be given off in case of a fire.

- When fighting or responding to fires, especially chemical fires, respiratory protection may be necessary. A lot of toxic chemicals can be in that smoke cloud. Carbon monoxide poisoning is a real possibility especially with fires inside buildings or under air-starved conditions.