Fire Chemistry of Hazardous Materials

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Fire is a chemical reaction. Specifically, fire falls within a large classification of chemical reactions called **oxidation** (or more technically oxidation/reduction). **We define fire as the rapid oxidation of a fuel with the production of heat and light**.

Simply, an oxidation reaction involves the chemical combination of an oxidizer, usually oxygen with a fuel.

- Slow oxidation at room temperature (e.g. rust: with a metal as the fuel)
- Faster oxidation at room temperature (e.g. drying paint, browning of an apple: with organic materials as the fuel)

These slow oxidation reactions are the same process as fire. The only difference is that these oxidation reactions are not proceeding rapidly enough to produce the excess heat and light which we consider to be the hallmarks of fire. Because oxidation is a chemical reaction, if we raise the temperature, the reaction rate should increase.

- Rapid oxidation at elevated temperatures with the evolution of heat and light (e.g. fire)

When oxygen combines with a fuel, we have an oxidation reaction. When we add heat to that reaction it may elevate to the status of a fire. Thus the three essential elements for a fire are:

- Fuel
- Oxygen
- Heat

These are the three legs of the traditional **fire triangle**. We now recognize a fourth essential leg, the **chain reactions** that occur as the oxygen and the fuel molecules combine. The four legs make up the **fire tetrahedron**. All four legs are essential. If any one is removed, the fire cannot continue. Breaking the legs of the fire tetrahedron is the basis of fire extinguishment.

The Fire Tetrahedron

Fuel

At a hazardous materials incident, we usually encounter fuels in two types of situations: fuels that are already on fire, and fuels that are at risk of catching fire. If a fuel is already on fire, we are concerned with breaking a leg of the fire tetrahedron. If it is not yet on fire, we are concerned with preventing the fire tetrahedron from forming. We can evaluate the hazard posed by a fuel that is not yet on fire by answering the question: is it '**ready to burn'**? By ready to burn, we mean that the fuel only needs heat to initiate the chain reaction that completes the fire tetrahedron.

Fuel States

For a fuel to be ready to burn, it must be in the appropriate physical state.

- Fuels can be found in any of the three states of matter: solid, liquid, or gas.
- For a fuel to be ready to burn, however, it usually must be in the gas (or vapor) state.

For a fuel to be ready to burn its vapor concentration must be such that when the chain reaction has been initiated, it will continue.

- The fuel must form a **flammable mixture**.
- Too much fuel vapor can be just as effective as too little in rendering a fuel <u>not</u> ready to burn.

Gaseous Fuels

A fuel in the gaseous state has already satisfied one of the ready to burn conditions. It only needs to be in the right concentration and to be provided with an ignition source.

Liquid Fuels

A fuel in the liquid state may be ready to burn or it may not.

Amount of flammable vapors being generated.

- The rate of vaporization increases with temperature
- The rate of vaporization is maximum at the boiling point (vapor pressure equal to atmospheric pressure)

If we compare liquids on the basis of boiling point, we can predict that the liquid with the lowest boiling point will be vaporizing fastest at any given temperature. Consider 2 flammable liquids, acetone and mineral spirits

- At room temperature (70°F) acetone is closer to its boiling point (134°F) than are mineral spirits (350°F).

Comparing boiling points however, is not really a satisfactory method of evaluating the fire hazard of a liquid. We know that acetone is highly flammable and is ready to burn at temperatures well below its boiling point. What we would like to know is:

- What is the minimum temperature at which a liquid is vaporizing fast enough to produce a flammable mixture?

The temperature at which a liquid is generating enough vapor to produce an ignitable mixture is called the **flash point** of the liquid. Flash point gives us a useful method of evaluating the hazard of a liquid fuel.

- If the temperature of a liquid fuel is above its flash point, it should be considered to be ready to burn.
- If the temperature of a liquid fuel is below its flash point, it will not be ready to burn.
- In comparing the relative hazards of different liquids, the lower the flash point, the more likely the liquid is to be ready to burn.
- Flash point and boiling point are linked. A low boiling point equates to a low flash point and a high hazard. A high boiling point equates to a high flash point and a lower hazard.

Flammable Range

- **Lower Explosive Limit**: The lowest % of vapor in air at which combustion will occur.
- **Upper explosive Limit**: The highest % of vapor in air at which combustion will occur
- Flash point is the temperature at which % vapor reaches the lower explosive limit
- 10% of LEL = consider a potentially combustible situation
- Examples:

Hydrocarbon fuels:	1 - 8%
Natural gas:	5 - 14%
Ketones:	2 - 12%
Alcohols:	1 - 36%
Ethers:	2 - 48%
Aldehydes:	3 - 55%
Hydrogen:	4 - 75%
Acetylene:	2.5 - 81%

Ignition

If a fuel is ready to burn, but is not on fire, we need to be concerned about ignition sources.

- Ignition sources:
  Match, electric arc: over 2000°F
  Lit cigarette: 550-1350°F
  Static electricity: over 1000°F
- Auto ignition will occur (without ignition source) if temp is raised to **ignition temperature**
- The minimum temperature needed to ignite a combustible material.
- Provides the activation energy necessary to initiate the chain reaction.
- Once ignition has taken place the fire will provide its own energy.

Ignition through Heat Transfer

- Conduction (direct contact)
- Convection (air currents)
- Radiation (electromagnetic waves)

Flammable Liquids

Hazard analysis

Consider:

- Flash point

above or below ambient temperature?

- Flammable range

where is 10% of LEL?
does it burn rich?

- Ignition temperature/sources

static electricity will ignite most flammable vapors
heat transfer from fire

- Vapor density

where are vapors going?
> 1 for most flammable liquids
may reach ignition source and flash back

- Specific gravity

consequences for fire suppression
<1 for most flammable liquids

Fuel Family (Paraffin Series)

- Petroleum refining
- Relationships among boiling point, flash point, flammable range, ignition temperature

Hydrocarbon Fuels

Fraction	Formula	Products	Boiling Point	Flash Point	Ignition Temperature	Flammable Range
Lubricating Oils	C_{21}	Lubricating Oils	680	300-450	500-700	
Heating Oils	C_{17}-C_{20}	Fuel Oils #4,5,6	>600	140-270	400-600	
High Test Fuels	C_{13}-C_{16}	Fuel Oil #1 (Kerosene)	300-500	110-160	444	.7 - 5
		Jet Fuel		100-150		
		Diesel Fuel		100-130	500	
		Mineral Spirits		104		
		Stoddard Safety Solvent	357	100-140	300-450	1.1 - 6
Low Test Fuels	C_5-C_{12}	Naptha High Flash	280-350	85	450	1 - 6
		Naptha Regular	212-320	28	450	1 - 6
		Petro Ether	95-140	<0	550	1.1 - 5.9
		Gasoline	100-400	-40	500-800	1.4 -7.6
Natural Gas	C_1-C_4	Propane (LPG)	-44	NA	871	2.2 - 9.5
		Methane (Natural Gas)	-259	NA	1000	5.3 - 14

Spontaneous Combustion

- Slow oxidation
- Heat accumulation
- Associated with animal/vegetable oils
- Large molecules with reactive points: double bonds, esters
- High flash points but low ignition temperatures
- Not associated with hydrocarbon fuels

Gases

Hazard Analysis

Consider:

- No flash point, material is already in vapor state
- Flammable range

where is 10% of LEL?

use 10% of LEL as LOC in ALOHA

- Ignition temperature/sources

static electricity will ignite most flammable vapors

heat transfer from fire

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Vapor density

where are vapors going?

> 1 for most flammable gases (exceptions: hydrogen, acetylene, methane, ethylene, carbon monoxide, ammonia, hydrogen cyanide)

may reach ignition source and flash back

- BLEVE (Boiling Liquid, Expanding Vapor Explosion)
- LPG (propane, butane)/LNG (methane)/Cryogenics (e.g. hydrogen, ammonia)

cold vapors will be less bouyant than normal until warmed to ambient temperature

- LPG fires

try to cut off flow

let it burn (but consider exposures)

Flammable Solids

Ordinary combustibles such as wood, paper (Class A fuels)

- Do not exist in the liquid state, when heated they move directly from solid to vapor state
- As with liquids, they must be in the vapor state to burn
- Produce flammable vapors only at their ignition temperatures, not over a range of temperatures, thus flammable vapors do not build up
- Flash point and ignition temperature are the same

Flammability of solid fuels is closely related to surface area

Large block of solid fuel: heat conduction away from the surface prevents surface temperature from reaching ignition temperature until much of the block is heated.

Combustible metals

- Magnesium
- Ease of ignition related to surface area (e.g. steel block vs steel wool)
- Dusts of many normally noncombustible metals may be explosive (e.g. copper, tungsten)

Spontaneously Combustible Materials/Air Reactive

Solids that react or ignite when exposed to air (e.g. white phosporus: IT 84 °F)

Some metal powders may ignite spontaneously in air (e.g. alkali metals, alkali earth metals)

Dangerous When Wet/Water Reactive

Alkali metals/Alkali earth metals

- react vigorously with water
- produce hydrogen gas and heat
- may produce enough heat to ignite the hydrogen

Oxidizers

Oxygen: 21% in air

- oxygen enriched atmosphere can intensify a fire and widen flammable limits

Halogens: F, Cl, Br, I

Unstable oxidizers: decompose readily releasing oxygen and heat, may ignite nearby combustibles

- Oxysalts: KNO_3, $KMnO_4$, $NaClO_4$
- Peroxides, organic peroxides: O:O bond

Organic peroxides:

- provide all 3 legs of the fire triangle
- highly unstable, shock sensitive, explosive

Consider:

- instability
- proximity of combustibles
- don’t walk in spilled oxidizer

Fire Safety Notes

Smoke detectors

- 1 on each level and outside sleeping areas
- test monthly, replace batteries annually

Fire extinguishers

3 types of fires

Get out fast, don't go back

Pre-plan your escape, meeting place

On the way out:

- Avoid fire gases

highly toxic (CO, combustion products from plastics)
may be invisible, odorless
hot gases will rise and spread out
stay low

- Close doors to prevent fire spread
- Feel a closed door before you open it, don't open a hot door, find another way out
- Stop, drop, and roll

Cooking:

- Put a lid on it
- Keep pot handles turned in
- No metals in microwave ovens

Combustible materials

- Keep away from space heaters, water heaters, gas appliances
- Keep flammable liquids in original containers

Electrical

- replace worn cords
- keep cords out from under rugs
- avoid running cords through doorways
- replace lightweight extension cords with power strips