

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards Part Three of a Three Part Series¹

INTRODUCTION

This is the last section of the three-part Technical Bulletin, which provides guidance for using physical, chemical, thermal, and electrical properties to identify and control hazards of flammable liquids. Eight fuels [hydrogen, compressed natural gas, propane (a compressed gas), methanol, ethanol, gasoline, No. 2 diesel, and biodiesel] are used as examples. The table in Part 1-B lists the physical and chemical properties of these materials.²

PRINCIPLES OF IGNITION AND COMBUSTION

Combustion is a chemical oxidation process that requires formation of chemical radicals by transfer of electrons between an oxidizing agent (21 v% oxygen in air) and reducing agents (flammable liquids). Three conditions are necessary for ignition to occur. A fourth condition is necessary for combustion to occur, and a fifth condition is necessary for fire propagation.

- 1) A fuel must be present (e.g., methanol)
- 2) An oxidizer must be present (21 v% oxygen as air)
- 3) A source of ignition must be present with sufficient energy to initiate formation of chemical radicals
- 4) A chemical chain reaction must occur which generates an exponentially increasing number of chemical radicals which sustain the combustion process and cause the fire to release increasing amounts of heat.
- 5) Heat released by the exothermic combustion reaction must be sufficient to pre-heat and ignite surrounding material.

Vapors burn, while liquids do not. Flammable and combustible liquids must be heated to a temperature at which sufficient vapor is generated at the liquid surface to enable ignition and then support combustion. The temperature at which ignition occurs is the *flash point temperature*. Flash point temperature is determined in the laboratory by standardized experimental testing. Fuels ignite but do not combust at their flash point temperature.

- 1) Flammable liquids must have sufficient energy (measured as temperature) to release a sufficient amount of vaporized fuel (vapor in equilibrium with the liquid) to support combustion. This temperature is termed the flame point temperature of the liquid. In practical terms, flash point temperature is used instead of flame point temperature to assess likelihood of ignition. Flame point temperature is typically 10–15 °F higher than the flash temperature for most flammable liquids. The flash point temperature is the minimum temperature at which ignition can occur, but does not generate sufficient vapor to support combustion

¹ This three-part Technical Bulletin was written by Mr. Robert R. Roberts of Roberts & Roberts Risk & Reliability Engineering and edited by Alliance Consulting International, San Diego, California under contract to the Methanol Institute.

² Information and data are collected from a variety of published and internet sources, though different sources may contain conflicting data regarding the same information. Effort has been made to use reliable sources; however, no responsibility is taken for correctness, accuracy, or errors in information.

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- 2) The molar or volumetric concentration of flammable vapor in air must be within the flammable range of that specific liquid
- 3) Fuel molecules must be mixed and have intimate contact with oxygen molecules within the surrounding air
- 4) An ignition source must be active and transfer sufficient energy to the vapor/air mixture to initiate a chain reaction. Alternately, the fuel/air mixture must be in contact with a surface above the autoignition temperature of the fuel
- 5) The exothermic combustion chain reaction must release sufficient heat to propagate ignition, thereby sustaining combustion

The energy source that causes ignition can be *auto-ignition* (e.g., a hot surface or hot air), or *induced* or *piloted* ignition (e.g., a spark, an electric arc, or an open flame). Regardless of whether ignition is auto- or induced, the ignition source must be sufficiently energetic to raise the temperature of an infinitesimally small mixture of fuel and air to the fuel's *ignition temperature*. The *ignition temperature* is the temperature at which covalently-bonded molecules of fuel and oxygen begin to spontaneously transform into positively and negatively charged radicals which then recombine as combustion products (e.g., CO, CO₂ and H₂O), thereby releasing heat.

If an ignition source is sufficiently energetic to drive the rate of formation of free chemical radicals to the point at which the exothermic heat of reaction of combustion products generates a sustainable, exponentially accelerating number of positively and negatively-charged radicals, then combustion has occurred, flames and heat are generated, and a fire begins to burn. If the chain reaction continues unchecked, then combustion occurs and the fire gets larger. Once combustion occurs, flames spread and grow in size as a kinetic process characteristic of exponential chain reactions. Fire propagation will continue as long as there is unburned fuel, or until the fire is extinguished by external intervention. The rate at which fuel is converted (burned) is termed the "mass burning rate." If the mass burning rate, the surface area of the pool, and the lower heating value (LHV) of the fuel are known, then it is possible to estimate the rate of radiant heat flux from the fire.

TYPES OF FIRES AND FIRE HAZARDS

Fires are generally classified as belonging to one of four categories:

- 1) Pool fires- resulting from spills, leaks, and condensation of vapor from pressure flashing liquids
- 2) Jet fires- resulting from a pressurized containment vessel or pipe into free air
- 3) Flash fires- occurs when a cloud of flammable gas is ignited
- 4) Fireball- fireballs occur when a quantity of flammable liquid or gas suddenly releases from pressurized containment and is immediately ignited as in boiling liquid expanding vapor explosions (BLEVEs)

Behavior of pool fire flames is entirely under the influence of their own buoyancy; flames are easily displaced by wind and can change shape rapidly and unexpectedly. Jet fires typically have a long flame which is unaffected by wind. Fire duration is dependent on release rate and pressure of the exiting fluid at the point of release. The shape of flash fires is determined by the shape of the flammable cloud and the position of the cloud relative to the location of the ignition source. Flash fires are usually short in duration and are known to flash back to the source of fuel vapor, be that a pool, or a jet release. When flame speed and fire propagation are slow then deflagration occurs and

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overpressure is small. When flame speed is high, approaching sonic velocity (1,126 ft/s @ NTP) the deflagration transitions to an explosion, and overpressure becomes an additional consideration for life safety and damage. Overpressure estimation should be performed by someone who is trained in that subject matter. The hazard of pool, jet, flash, and fireball fires is primarily exposure to radiant heat flux. Exposure to 37.5 kW/m² will result in instantaneous death. Safe exposure levels are typically around 5 kW/m². Phani K. Raj provides a summary of radiant heat exposure criteria in a 2007 article in *Journal of Hazardous Materials*.³ A brief summary of overpressure effects on humans is summarized by The Institution of Chemical Engineers.⁴

POINT SOURCE MODEL FOR ESTIMATING RADIANT HEAT FLUX

A point source model can be used as a quick and simple method of estimating thermal radiation. The point source model assumes heat of combustion radiates in all directions equally from a single point. The total heat available for transfer by radiation is calculated as the product of the fuel mass burn rate (a characteristic parameter of each particular fuel), the surface area of burning fuel (not the surface area of the flames), and the LHV for the fuel (preferably the heat release rate of vapor reacting to form non-condensable gaseous combustion products and water vapor).

Incident radiant heat flux (I) at any distance from a pool fire is determined as

$$I = \frac{f(\text{LHV as Btu/lb})}{4\pi d^2}$$

where f is the fraction of the heat which is released (use $f = 1$ to determine an upper bound), LHV is the heat released when a pound of fuel vapor is converted to gas and vapor combustion products, and d (in feet) is the radius at which one wishes to estimate incident heat flux. A disadvantage of the point source model is that it underestimates incident radiation levels for distances within two diameters of the fire. More refined point source methods are also available.⁵

Behavior of liquid pool fires can be useful in first order estimation of heat flux from large fireballs since both pool fires and fireballs are buoyancy dominated. Fireballs with maximum diameter of 30 to 35 feet have measured surface emissive power of 185 to 224 kW/m². Larger fireballs can be approximated using values of surface emissive power between 250 and 300 kW/m². Calculating incident radiation levels for fireballs is complicated and depends heavily on the value selected for the emissive power of the fireball. It is recommended that users enlist the assistance of a qualified consultant if second order results are required for radiant heat flux from fireballs.

In small fires, heat is released by conduction, convection, and radiant heat transfer processes. Heat release in large fires (> 1-2 feet diameter) is primarily by radiant heat transfer. Radiant heat flux determines the radius of the hazard zone for a fire. The radius of the hazard zone for overpressure must be determined separately.

³ Article by Pani K. Raj, "A Review of Criteria for People Exposure to Radian Heat Flux from Fires," available on <http://cms.totalsafety.nl/uploads/Criteria%20for%20people%20exposure%20to%20radiant%20heat%20flux.pdf> as of March 2011

⁴ Institution of Chemical Engineers: *The Effects of Explosions in the Process Industries, Overpressure Monograph, First paper of the Major Hazards Assessment Panel – Overpressure working party*, © 1989 by The Institution of Chemical Engineers, p. 8, ISBN 0 85295 235 X.

⁵ Institution of Chemical Engineers: *Calculation of the Intensity of Thermal Radiation from Large Fires, Thermal Radiation Monograph, First Report of the Major Hazards Assessment Panel – Thermal Radiation Working Group*, © 1989, by The Institution of Chemical Engineers, 22pp., ISBN 0 85295 236 8.

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HEAT OF COMBUSTION

The exothermic combustion reactions of fuel in air release heat and are typically characterized by four parameters: two for the liquid to gaseous-plus-liquid phase and two for the liquid to gaseous-plus-vapor phase:

- Gross or High Heating Value (HHV) of a unit volume of liquid
- Net or LHV of a unit volume of liquid
- Gross or HHV of a unit weight of flammable vapor
- Net or LHV of a unit weight of flammable vapor

An additional value, which is more useful for first order consequent modeling, can be determined which takes fuel from the vapor state to combustion products in the gaseous-plus-vapor state. This value is also a LHV, but is more representative of conditions for consequence modeling in that released heat is determined as the heat of combustion of fuel vapor-to-gaseous products plus water vapor. This parameter appears in the table for flammability parameters in Part 1-B of this Technical Bulletin.

Gross or HHV is the amount of heat produced by complete combustion of a unit quantity of fuel (measured either as units of volume or weight) determined as energy released by an exothermic combustion reaction when all combustion products are cooled to the temperature which existed before combustion (e.g., 60 °F), including the energy released as heat by cooling and condensing combustion-derived water vapor. The HHV is essentially the heat of combustion. This is a thermodynamic parameter, which represents theoretically available heat when a pound or gallon of fuel is burned.

Net or LHV is the amount of energy released as heat when all combustion products are cooled to the temperature which existed before combustion, excluding heat associated with cooling and condensing combustion-derived water vapor.

When assessing consequences of fire events, it is appropriate to use the heat of combustion or HHV to determine the theoretical upper limit of radiant heat flux. The LHV should be used if a more realistic value for heat flux is desired. It is preferable to use the LHV of fuel vapor to combustion product vapor when this value is available.

IGNITION

Ignition is a time-dependent process of starting a fire that begins with reactants and evolves over time to combustion: i.e., a steadily burning flame,⁶ combustion products, and heat release. *Induced ignition* is initiated by a spark or flame; *autoignition* is a result of temperature. Generally speaking, fuels which ignite easily also grow quickly with rapid flame propagation. Fuels with high heat capacity (the ability to absorb large amounts of heat without increasing liquid temperature) and high thermal conductivity (the ability to readily transfer heat) may be more difficult to ignite than fuels with low heat capacity and low thermal conductivity. Temperature near the source of heat rises rapidly in the latter.

⁶ Ignition processes are always time dependent.

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A list of commonly encountered ignition sources and their respective energy is shown in the table below.

Theoretical/Ideal/Approximate Temperatures of Potential Ignition Sources⁷

Potential Ignition Source Item	Environmental Conditions	Approximate Temperature (°F)
Fluorescent Light	ambient air @ room temperature	140 - 176
Incandescent Light	ambient air @ room temperature	212 - 572
Lighted Cigarette	unventilated ambient air @ room temperature	550
Lighted Cigarette	ventilated ambient air @ room temperature	752 - 1,436
Lighted Cigarette	insulated & smoldering in ambient air @ room temperature	950 - 1,150
Hot Electric Stove Element	ambient air @ room temperature	> 1,026
Burning Match Flame	ambient air @ room temperature	1,112 - 1,472
Tungsten Halogen Light	ambient air @ room temperature	1,112 - 1,652
Burning Candle Flame	ambient air @ room temperature	1,112 - 2,552
Electrical Spark	ambient air @ room temperature	2,400
Electrical Arcing	ambient air @ room temperature	< 6,782
Lighted Bunsen Burner Flame	ambient air @ room temperature	2,858
Methanol Flame	ambient air @ room temperature	3,470
Methane Flame	ambient air @ room temperature	3,488 - 3,540
Plasma Torch	ambient air @ room temperature	≈ 8,492
Lightning Strike	ambient air @ room temperature	54,032

FIRE PREVENTION

Fires can be prevented using several strategies:

- 1) Declare areas surrounding fuel storage and handling as hazardous locations. Remove potential ignition sources to a safe distance (i.e., a distance beyond the farthest expected concentration of the lower flammability limit) from the area in which fuel vapor may be present
- 2) Suppress formation of fuel vapor below the lower flammability limit (e.g., reduce liquid temperature, or prevent liquid temperature from rising above a predetermined set point
- 3) Isolate the fuel from contact with air using natural gas or inert gas padding and/or internal and external floating roof tanks as appropriate

⁷ "Approximate Temperatures of Potential Ignition Sources"; <http://www.derose.net/steve/resources/engtables/flametemp.html>

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FIRE SUPPRESSION

Fires can be extinguished using several combinations of strategies and tactics:

- 1) Allow the fire to consume all available fuel and burn itself out
- 2) Remove the heat of combustion by spraying the fire with water fog and fine water droplets. The heat of vaporization of the water droplets removes heat from the fire and slows the rate of the combustion reaction, thereby reducing the amount of heat available for fire propagation
- 3) Exclude air from contact with the fuel (CO₂ deluge at loading racks, solid fire extinguishers for small isolated fires, and fire suppressing foam for large fires)
- 4) Interrupt the chain reaction with fire suppressant extinguishing media (i.e., foam)

FUEL PROPERTIES

The severity of a liquid flammability hazard is determined by the following properties:

- Availability of vapor which is determined by the following properties:
 - Liquid temperature determines the partial pressure of a vapor in equilibrium with its liquid
 - Flash point temperature and flame point temperature determine the minimum temperature at which ignition can occur
 - Boiling point temperature is the temperature at which the partial pressure of the vapor equals atmospheric pressure
- Availability of air (air is 21 v% oxygen)
- Ignition source with sufficient energy or temperature to start an oxidation reaction determined by:
 - Minimum ignition energy
 - Autoignition temperature
- A fuel/air mixture that is capable of burning which is determined by:
 - Upper and lower flammability limits
 - Stoichiometric air-to-fuel ratio
- Sufficient exothermic heat of reaction to sustain combustion which is determined by:
 - Exothermic heat of reaction or net heating value
 - Rate at which energy in the form of heat is conducted away from the fuel

Combustion of fuels with higher heats of combustion release more heat, propagate more quickly, and may be more difficult to extinguish than fuels with lower heats of combustion.

Liquid vapor pressure and therefore evaporation rate increase as temperature of the liquid increases. Typically, if flammable liquid evaporation rate ≥ 0.047 lb/ft² (2 g/m²), then sufficient vapor is available to support combustion.

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If the lower flammability limit is comparatively small, such as that for gasoline, then combustion can occur at a relatively low vapor pressure and therefore at relatively low temperature. If the upper flammability limit is close to the lower flammability limit, then the temperature range capable of supporting combustion is relatively small.

Conversely, if the difference between the flammability limits is large, such as the upper and lower limits of methanol, then the temperature range capable of supporting combustion is large, and ignition can occur at high vapor concentrations. The upper flammability limit of gasoline is the same as the lower flammability limit for methanol. This has implications for the flammability limits of gas/methanol blends.

Boiling point is another consideration. Gasoline boils over a range of temperatures, and methanol boils at a single temperature. Depending on the composition of the gasoline, substantial amounts of vapor may be released at relatively low temperature. Typically Reid vapor pressure is used as an indication of initial boiling point and boiling point range. If Reid vapor pressure is high, then true vapor pressure is high at low temperatures. If Reid vapor pressure is low, then true vapor pressure is low at high temperatures.

If a liquid has a low flash point temperature, low minimum ignition energy, and large LHV, then ignition occurs more easily, and fire propagation is rapid. If a large amount of energy is required for ignition, then the vapor is less likely to contact a sufficiently energetic ignition source and ignition is less likely to occur. If LHV is low, then fire propagation is slower. Flame speed and heat release rate should also be considered when assessing flame flash back, and the rate of flame front propagation.

LIQUID PROPERTIES, SOURCE TERMS, AND WORST-CASE CONSEQUENCES

First order worst-case consequences⁸ of spills and accidental releases can be estimated using parameters listed in the table in Part 1-B of this Technical Bulletin.

Confined space explosions, BLEVEs, and unconfined vapor cloud explosions (deflagrations) present two hazards: overpressure and radiant heat flux. Severity of fire/explosion damage is greater for fuels with higher flame speed such as hydrogen, higher flame temperature, and higher specific energy than for materials with lower flame speed, lower flame temperature, and lower specific energy. Over-pressure hazard severity increases as flame speed increases. Pressure and temperature also increase flame speed. Within the perimeter of the blast zone, people are subject to serious injury, and the range and severity of damage to plant equipment is greater.

Worst-case process accidents are those involving large amounts of flammable liquid with high vapor pressure, high flame speed, high flame temperature, high specific energy, high heating value, and large mobile vapor plumes. When liquid flammability hazards are combined with process safety hazards (e.g., operating temperature and pressure), consequences may be catastrophic, involving multiple fatalities, extensive destruction and damage to equipment, and forced outage for extended periods of time.

An elevated process temperature creates high vapor pressure and a high rate of vaporization; large and abrupt pressure letdown promotes vapor flashing and conversion of large amounts of escaping liquid to vapor and aerosol. Initial release rate for letdown pressures ≥ 110 psig occurs at speeds approaching sonic velocity. Vapor flashing causes turbulence at the point of release, which increases air entrainment and mixing within the vapor cloud. Kinetic energy supplied by an escaping jet may launch the vapor cloud, causing the plume to travel further than a plume released from a pool fire.

⁸ injuries, fatalities, physical damage and destruction of equipment, business interruption, and environmental remediation costs attributable to accidental release events: toxics, flammable liquids, and explosive vapors and aerosols

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Once formed, vapor clouds may float upward, remain more or less stationary, flow down slope, or move downwind away from the breach point. Moving vapor clouds are more likely to encounter an ignition source than non-moving clouds. Combustion may flash back to the point of breach and forward to the outside edge of the vapor cloud. Vapor concentrations at the surface of the vapor cloud form a steep concentration gradient with ambient air and are almost certain to form a zone that is within the flammable limits.

According to an article on the causes of industrial fires, “Fire and explosion accidents are of major concern to the owners and operators of refineries and petrochemical plants, gas processing plants, terminals, and offshore facilities. Statistics have shown that the majority of monetary loss in these types of complexes is due to fire and explosion. According to recent statistics, 77 percent of the monetary loss in refinery and petrochemical complexes is due to fire and explosion. The breakout of accidents due to fire and explosion is 65 percent vessel failure and vapor cloud explosion and 35 percent fire. The causes of these accidents are mostly attributed to mechanical issues, process upset, and operator error.”⁹

Unconfined and confined vapor cloud explosions (UVCEs and VCEs) pose the greatest hazard. BLEVEs, UVCE’s, and VCEs, jet fires, and pool fires are credible worst-case scenarios when handling flammable liquids.

PREVENTING FIRES AND EXPLOSIONS

Avoiding worst-case accidents involving flammable liquids requires diligence in establishing and maintaining multiple levels of protection. A facility’s ‘levels of protection’ strategy evolves directly from fundamental operational practices. A list of suggested objectives may be to:

1. Establish a clear understanding of the design intent and performance expectations of
 - o The plant
 - o Process units that comprise the facility
 - o Equipment items that comprise the process units
2. Preserve the engineering design basis (documentation, equipment configuration) through a rigorous management of change program
3. Identify and control hazards
4. Seek out and apply best practices, and generally accepted good engineering practices (be familiar with applicable codes, standards, regulations, and recommended practices and the underlying rationale)
5. Preserve equipment mechanical integrity and fitness for purpose
6. Develop job skills and establish standards and responsibilities for job performance of operations and maintenance functions
7. Recognize and learn from mistakes (your own and those of others)
8. Anticipate, prepare for, and practice recovery from abnormal operations and hazardous material release events

⁹ Reza Pourdarvish, Shahryar Khajehnajafi, and Chris Cowles: “The Many Faces of Fire Hazards in Industrial Settings” *OH&S Magazine*, Dec 01, 2010. <http://ohsonline.com/Articles/2010/12/01/The-Many-Faces-of-Fire-Hazards-in-Industrial-Settings.aspx>

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Ever-occurring incidents involving flammable and combustible liquids at facilities worldwide are testimony to the difficulty of transforming the above objectives into an effective and disciplined management system. The following lists a few of the many reported flammable and combustible liquid accidents during 2010:

- Three hurt in fire and explosion at Sparks, Nevada biodiesel clean fuels plant
- Fire and explosion at Khark, Iran petrochemical complex
- Taiwan's biggest oil refinery complex catches fire for the third time in six months, second time in July
- More trouble for one of Taiwan's largest companies. Formosa Petrochemicals Corp has had another fire in one of its factories
- One person critically injured in an explosion and fire at a refinery in San Antonio, Texas. "Immediate cause of the fire appears to have been an explosion on one of the trucks loading a light hydrocarbon from the AGE loading rack." AGE facility is a refiner of jet fuel and diesel products that refines 13,500 barrels a day and has tank farm storage capacity of 208,000 barrels. The explosion/fire is the second that has occurred since 2008
- TESORO (Anacortes, Washington) Anacortes refinery fire. The blast was the largest fatal refinery accident since a 2005 explosion at a BP American refinery in Texas killed 15 people and injured 170.
- Burning taxi pulled into a gas station in Baltimore, Maryland
- Car Fire explosion in Detroit, Michigan broke firefighter's legs

CONCLUSIONS

Flammable liquids can be handled safely if they are handled properly. Flammable liquids are dangerous when mishandled.

Each of the hundreds of OSHA and NFPA IA, IB, and IC flammable liquids has characteristic physical, chemical, thermal and electrical properties which are useful in identifying and judging the severity of specific hazards. Use these properties to identify hazards and to devise strategies for controlling those hazards.

Consider using at least three, and in high hazard situations, as many as eight independent protective control measures. Learn to anticipate, prevent, recognize, and respond to abnormal operating conditions.

Users do not deliberately cause fires and explosions. On most occasions, users are unaware of the severity of the hazards. Mishandling is typically the result of a lack of knowledge, not willful destructive intent.

It is users' responsibility to continuously strive to be better informed, and more adept at identifying and controlling hazards