

Using Physical and Chemical Properties

To

Manage Flammable Liquid Hazards

[R Roberts, Roberts & Roberts, February 5, 2011]

INTRODUCTION

This is a general guidance for using physical, chemical, thermal, and electrical properties to identify and control hazards of flammable liquids and their vapors. Five motor fuels (hydrogen, compressed natural gas (CNG), propane, methanol, ethanol, no. 2 diesel, and biodiesel) are used as examples. Properties of these materials are listed in Table 1.¹

Data in Table 1 are available within various web pages on the internet and in published sources. Some of the data is difficult to locate and even more difficult to interpret and verify. Flame speed is an example of this difficulty. Some sources indicate the flame speed of methanol is greater than that for unleaded gasoline; others sources state the reverse. Still others report that small additions of methanol increase the flame speed of gasoline. It is likely that all are correct, depending on circumstances.

The purpose of collecting and comparing data for different fuels is to determine and compare the severity of potential consequences: fires, explosions, and toxic plumes. Consequence analysis is an emerging science and does not provide exact results. Flame speeds of both methanol and gasoline are sufficiently close to one another that the difference does not affect first order explosion overpressure and fire ball heat flux calculations.

Both gasoline and methanol are known to BLEVE in non-bulk containers, and tank trucks, tanker rail cars, and above and below ground tank storage. Vapors of both gasoline and methanol are explosive in confined spaces, and form vapor plumes when unconfined. If consequence severity must be determined at a second order level, then the user should verify that data in Table 1 is adequate for the desired level or precision and accuracy when calculating overpressure and radiant heat flux hazard zones. Proprietary consequence analysis software contains what the software providers have judged to be appropriate parameter values. It is good practice to confirm software modeling results with hand calculations to verify that results provided by the software are reasonable.

¹ Information and data are collected from a variety of sources including various web pages. Data in some sources conflicts with data in other sources. Effort has been made to use reliable sources; however, no responsibility is taken for correctness, accuracy, or errors in Table 1 information.

A word of caution, values presented in Table 1 are determined in a controlled laboratory environment, and therefore characterize a narrow range of conditions. Test results for pure materials are not representative of fuel blends, contaminated materials, complications associated with switch loading, and properties at elevated temperature and pressure which are typical of a process environment.

FLAMMABLE LIQUIDS

OSHA and NFPA classify liquids as flammable and combustible. Each of these designations is divided into sub-classes based on selected physical and chemical properties. These properties are indicators of conditions at which ignition and combustion occur. Liquids are assigned to classes based on the values of identifiable and measurable properties; each class contains materials whose properties are within specified ranges. For example, class IA flammable liquids have flash point temperatures below 73 °F and boiling point temperatures below 100 °F (e.g., *n*-pentane); class IB flammable liquids are defined as having flash point temperatures less than 73 °F and boiling point temperatures at or above 100 °F (e.g., methanol, ethanol, unleaded gasoline); class IC flammable liquids have flash point temperatures at or above 73 °F, and boiling point temperatures below 100 °F (e.g., turpentine). This guidance focuses on IB flammable liquids, because this class contains three widely-used motor fuels which are transported, handled and stored in large bulk quantities.

To an extent, fire hazards that characterize a particular flammability class are common to all of the materials within that class. Class IB flammable liquids include motor fuels, solvents, reactants and feed stocks. Benzene, toluene, acetone and alcohols are examples of IB class solvents and reactants.

Knowing that a liquid is assigned to a particular flammability class is useful; however in order to adequately control material hazards and implement an effective safety program, it is important to understand the differences in the hazards posed by specific hydrocarbons² and chemical compounds within each group. Hazard severity is assessed within the context of the properties of the liquid, the circumstances in which the liquid is being used, and the manner in which the chemical is handled (transported, stored, blended, and processed).

Generalized statements such as “handle and store methanol in a manner similar to the way in which gasoline is handled and stored” are useful as far as they go. They set the stage for what must be done. However guidance based solely on flammability class seldom goes far enough, or is specific enough to allow selection of a suite of measures which provide multiple independent

² Hydrocarbons are understood to be liquids which boil over a range of temperatures; chemical compounds are understood to boil at a single characteristic boiling temperature.

layers of protection. In general, between 3 and 8 levels of protection should be established for each chemical. Some levels of protection will safeguard multiple hazards. Other safeguards are necessarily specific to a particular hazard.

No two hydrocarbons, fuels, or chemicals have identical properties. It is therefore essential that users implement safeguards based on properties specific to their materials, to their specific circumstances, and to their particular use. Guidance provided by NFPA, ASME, API, NEC, NACE, ISA, IEEE, and other groups can be construed as 'generally-accepted good practices.' The intent is to provide a minimum standard of care. Depending on users' circumstances and a company's aversion to the risk of accidental release, additional measures beyond those indicated in codes and regulations may be appropriate. Some regulations, such as those for occasional vehicular transport of non-bulk quantities of methanol and gasoline must be obtained from local fire authorities. There is little or no specific guidance for personal use of methanol for backyard manufacture of biodiesel in national standards such as NFPA. The necessity of using material-specific parameters to assess and control hazards is illustrated by three examples. The examples are selected to characterize the range of methanol users from private individuals making biodiesel 25-50 gallons in a batch, to oil refineries, international chemical manufacturers, shipping companies, and terminal operators.

1. Boutique-Users: Handling and Transfer of gasoline/methanol in non-bulk containers:

Gasoline is not classified as a toxic material. There are minimal consequences associated with inhaling gasoline vapor when mouth-siphoning gasoline. However, liquid methanol is toxic in tea-spoon-sized amounts and toxic effects of methanol vapor are cumulative within the body. Methanol must not be ingested or inhaled. If siphoning transfer of methanol is warranted, then use a siphon pump, wear PPE, and provide spill containment. Methanol siphoning must never be mouth-initiated.

Static accumulation is another consideration associated with siphoning, pouring, and other forms of package transfer. The electrical conductivity of gasoline is 25 pS/m, and that of low sulfur diesel fuel is 5 pS/m. Conductivity of gasoline and diesel is so low that these fuels accumulate static charge during pumping, filtering, and splash transfer operations. Grounding and bonding during liquid transfer is a necessary protection against static discharge when handling all flammable liquids. This is especially true for liquids which have conductivities less than 50 pS/M. Liquids with conductivity > 50 pS/m accumulate static charge.

By comparison, the electrical conductivity of methanol is in the range of 300,000 pS/m. Methanol, like water is a polar material, and has relatively high conductivity compared to non-polar materials such as gasoline and diesel fuel. Conductivity above 50 pS/M does not alleviate the necessity of bonding and grounding. Rather, the high conductivity of methanol indicates that accumulation of static charge within the liquid is less likely and ignition by static discharge is not

expected to occur except in abnormal circumstances. Two examples of consequences of failing to bond and ground in abnormal circumstances during methanol transfer are as follows:

- March 2006, Green Star Products, Inc., of Bakersfield, California reported a serious "fire incident" late last month at the site of ABF's biodiesel plant. According to GSPI, the accident occurred outside of the plant building when, during a transfer of methanol, a small spill ignited. While the ignition source remains unknown, GSPI expects it was likely caused by static electricity. ... ABF suffered a total loss of the building and equipment No plant personnel were injured during the blaze.
- 2008, Canada, during abnormal transfer of methanol from one tank truck to a second tank truck, the methanol ignited, causing one fatality destroying the trucks, and damaging a load out facility. Investigators suggested the source of ignition was static discharge resulting from a damaged transfer hose which interfered with grounding and bonding.

2. Refineries and Biodiesel Manufacturers: Hot Work and Liquid Vapor Control

Gasoline floats on water; methanol is fully miscible with water. Methanol floats on water as mixing takes place. Methanol-water mixtures burn at high concentrations of water in methanol (79 v% or 75 wt% water; 21 v% or 25 wt% methanol). If floating methanol is ignited, it continues to burn as it mixes with water. In this situation, addition of water may increase the volume of flammable liquid.

Gasoline vapor pressure is 190 mmHg; the vapor pressure of methanol is 90 mm Hg. Gasoline releases twice as much vapor as methanol. The amount of heat required to vaporize a pound of gasoline is about a third of that necessary to generate a pound of methanol vapor. The flammability range for gasoline is 1.4 to 7.6 v%, compared to 6.0 to 36.5 v% for methanol. Gasoline vapor is within its flammable range at 30% of the concentration of methanol under identical circumstances. Ignition energies of gasoline and methanol are similar (0.2 mJ and 0.14 mJ respectively). Gasoline vapor is heavier-than-air and tends to accumulate in low lying areas; methanol vapor is near neutral buoyancy and responds more readily to natural and forced ventilation. Non-bulk storage of both gasoline and methanol must be grounded, bonded, and well ventilated. Storage areas should be equipped with detectors. Detectors for gasoline must be positioned to detect gasoline as a dense vapor. Positioning of methanol detectors may be different from that of gasoline vapor detectors because of the difference in relative density of gasoline versus methanol vapors. Vapor density of methanol is 1.1 relative to that of air; the vapor density of gasoline is 3 to 4. Vapors of both gasoline and methanol may be explosive in confined spaces.

A shipping terminal may decide to use an inert gas to pad storage tanks for both gasoline and methanol, but for somewhat different reasons. The purpose in padding gasoline storage may be

fire protection because of the relatively low concentration of the lower flammability limit. The purpose of padding methanol may serve multiple purposes: 1. fire protection due to the wide flammability range, and to maintain purity in an area that has characteristically high humidity.

At normal liquid storage temperatures, vapor space for gasoline storage quickly exceeds the upper flammability limit; that of methanol at 36% does not. Methanol storage tanks may remain in the flammable range even at relatively high liquid temperatures.

Never transport methanol or gasoline in the trunk of a car, even if the trunk lid is open. Vehicular transport must be placarded, and transport must comply with other DOT requirements such as transport manifest papers, driver emergency response training, and emergency response equipment. Always store these materials outside, under cover, and in a well ventilated location. It is not normal practice to store and use 55-gallon quantities of methanol in a suburban environment. Contact your local fire marshal before bringing this amount of material to your residence.

3. All Users: Non-Bulk and Bulk Storage Fire Protection and Response:

Fire response for a methanol fire is different than that for a gasoline fire.

- Gasoline fires produce luminous combustion byproducts which make gasoline flames readily visible during day time. Methanol flames are non-luminous, and are difficult to detect visually in day time, particularly in bright sunlight. In order to effectively fight a liquid fire, it is necessary to identify the location of the fire. Hand held infra-red sensors are available to assist fire fighters responding to methanol fires. As good practice, methanol users should have at least one sensor onsite and available to first responders. Sensors should be calibrated and functional. Local fire response should also have infra-red sensors.
- Gasoline floats on water and application of water spray, particularly as a cohesive stream from a fire monitor may cause the fire to spread. By comparison, methanol floats on and rapidly mixes with water. Methanol water mixtures will burn at very high water concentrations. Water is most effective as a suppressant when applied as a spray mist or as a fog. Both gasoline and methanol may form running fires if fire water is not contained. The difficulty in the case of methanol is that the fire propagation may not be immediately noticed by responders.
- Gasoline is non-toxic; methanol is toxic, even to skin contact. Responders to a methanol fire must wear PPE that protects against chemical exposure as well as exposure to radiant heat. Turnouts provide heat protection, but not chemical protection.
- Given identical circumstances, vapor cloud explosions are more likely to result from spilled gasoline than from a methanol spill. The specific gravity of gasoline vapor is 3-4 times heavier than that of methanol vapor. Gasoline vapor has higher tendency to

accumulate in low lying and poorly ventilated areas than methanol vapor. Gasoline has a lower flammability range, lower flash point temperature, and lower autoignition temperature. Ignition energies are similar. Ignition of vapor within a confined space may cause an explosion.

- Non-bulk and bulk shipping containers holding gasoline are marginally more likely to BLEVE in a fire than those containing methanol. Gasoline has higher vapor pressure, lower specific heat, and lower latent heat of vaporization than methanol. Pressures within methanol containers will increase more slowly than for gasoline containers exposed to the same heat flux. The heat of combustion of methanol is 9,900 Btu/lb compared to that of 20,000 Btu/lb for gasoline. Radiant heat released by a gasoline BLEVE will be twice that of methanol. The experimental laminar flame speed of methanol is 50% higher at stoichiometric fuel/air ratio and approaches that of gasoline at less than stoichiometric ratios. Flame temperatures are similar. The greater flame speed of methanol may cause a marginally greater overpressure. This is likely offset by the much higher heat release of gasoline.
- Fire suppression foam used to fight gasoline fires is not suitable for use on methanol fires. Methanol requires alcohol resistant foam. Good practice consists of inventorying alcohol resistant foam both on a user's property and at the location of first responders. It is also good practice to periodically perform response exercises for various scenarios. Table-top exercises may also be useful.

In summary, gasoline may be more or less hazardous than methanol depending on circumstances. Without context and material specific properties, users are less apt to identify and apply appropriate safeguards.

Principles of Ignition, and Combustion

1. 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 and a fourth condition is necessary for combustion and fire propagation:
 - A fuel must be present (methanol)
 - An oxidizer must be present (21 v% oxygen as air)
 - A source of ignition must be present with sufficient energy to initiate formation of chemical radicals
 - An exponentially increasing chain reaction must occur which generates an increasing number of chemical radicals which sustain the combustion process and cause the fire to release increasing amounts of heat which result in fire propagation.

2. Vapors burn; 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.
 - a. flammable liquids must have sufficient energy (measured as temperature) to enable a sufficient amount of vaporized fuel to support combustion. This temperature is termed the flame point temperature of the liquid. The vapor point temperature does not have sufficient vapor to support combustion.
 - b. volumetric concentration of flammable vapor in air must be within the flammable range of that specific liquid
 - c. fuel molecules must be mixed and have intimate contact with oxygen molecules in the surrounding air
 - d. an ignition source must be active and transfer sufficient energy to the vapor/air mixture to initiate a chain reaction
 - e. the chain reaction must release sufficient heat to sustain combustion.
3. The source of energy which causes ignition can be *autoignition* (e.g., a hot surface or hot air), or *induced* 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 into combustion products (e.g., C, CO, CO₂ and H₂O) thereby releasing heat.
4. 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 has started. If the chain reaction continues unchecked, then combustion occurs and the fire begins getting 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.
5. The exothermic combustion reactions of fuel in air release heat, characterized by four parameters, two for the liquid phase and two for the vapor phase:
 - Gross or High Heating Value (HHV) of a unit volume of liquid
 - Net or Low Heating Value (LHV) of a unit weight of liquid

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

Gross or high heating value 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 the amount of energy which is released by an exothermic combustion reaction, when all combustion products are cooled to the temperature which existed before combustion, INCLUDING the energy released as heat by cooling and condensing water vapor combustion product. The HHV is essentially the heat of combustion. This is the heat released by the fire per lb or gallon of fuel.

Net or low heating value 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 radiant heat flux. 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 affected zone for a fire. The radius of the affected zone for overpressure must be determined separately.

6. *Ignition* is a time dependent process of starting with reactants and evolving over time to combustion: i.e., a steadily burning flame,³ 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 and propagate flames rapidly. Fuels with high heat capacity, and high thermal conductivity are more difficult to ignite than fuels with low heat capacity and low thermal conductivity.
7. Fires can be prevented using several strategies:
 - 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
 - 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
 - Isolate the fuel from contact with air using natural gas or inert gas padding and internal floating roof tanks.
8. Fires can be extinguished using several strategies:
 - Allow the fire to consume all available fuel and burn itself out
 - Remove the heat of combustion by spraying the fire with water fog and fine water droplets. The heat of vaporization of the fire water droplets removes heat from the

³ Ignition processes are always time dependent.

fire and slows the rate of the combustion reaction thereby reducing the amount of heat available for fire propagation.

- Exclude air from contact with the fuel (CO₂ deluge at loading racks and solid fire extinguishers for small isolated fires)
- 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 (liquid temperature, vapor pressure at liquid temperature, vapor release rate, flash point temperature, and flame point temperature, boiling temperature)
- availability of air (air is 21 v% oxygen)
- an ignition source with sufficient energy or temperature to start an oxidation reaction (ignition energy, ignition temperature, and autoignition temperature)
- a fuel/air mixture that is capable of burning (flammability limits, stoichiometric air to fuel ratio)
- sufficient exothermic heat of reaction to sustain combustion (heat of combustion or HHV).

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 increases as temperature of the liquid increases. Typically, if flammable liquid evaporation rate $\geq 0.047 \text{ lb/ft}^2$ (2 g/m^2), then sufficient vapor is available to support combustion..

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 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.

If ignition energy is relatively small, then ignition occurs more readily, and fire propagation is rapid. If a large amount of energy is required for ignition, then the vapor is less likely to contact an ignition source and ignition is less likely to occur. Fire propagation is slower. Flame speed and heat release rate should also be considered when assessing flame front propagation.

Liquid Properties, Source Terms, and Worst Case Consequences

First order worst case consequences⁴ of spills and accidental releases can be estimated using considerations and parameters listed in Table 2.

Explosions present two hazards: overpressure and radiant heat flux. Severity of fire/explosion damage is greater for fuels with higher flame speed, higher flame temperature, and higher specific energy than for materials with lower flame speed, lower flame temperature, and lower specific energy. Over-pressure and fire hazard severity both increase as the above parameters increase. As flame front velocity increases, over-pressure increases. People within the perimeter of the blast zone 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 and large 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 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.

Once formed, vapor clouds may float upward, remain more or less stationary, or flow down slope or 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

⁴ 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

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 range.

“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 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.”⁵

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
 - the plant
 - process units that comprise the facility
 - equipment items that comprise the process units
2. preserve the engineering design basis (documentation and equipment configuration)
3. identify and control hazards
4. seek out and apply best practices, and generally accepted good engineering practices
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.

Ever-occurring incidents involving flammable and combustible liquids at facilities worldwide is testimony to the difficulty of transforming the above objectives into an effective and disciplined

⁵ Reza Pourdarvish, Shahrya Khajennajafi, and Chris Cowles: *OH&S Magazine*, Dec 01, 2010

management system. The following lists a few of the many reported flammable and combustible liquids accidents during 2010.

- 3 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. Friday's 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.

CONCLUSION

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 devise strategies for 'safeguarding in depth'. Consider using at least 3, and in high hazard situations, as many as 8 independent protective control measures. Prevent abnormal operating conditions.

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

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

TABLE 1.

Chemical & Physical Properties of Selected Flammable Fuels								
Property/Information	Hydrogen H ₂ (gas)	CNG CH ₄ 83-99%; C ₂ H ₆ 1-13% (gas)	Propane C ₃ (liquid)	Methanol CH ₃ OH (liquid)	Ethanol C ₂ H ₅ OH (liquid)	Gasoline C ₄ -C ₁₂ (liquid)	No. 2 Diesel C ₈ -C ₂₅ (liquid)	B100 Biodiesel C ₁₂ -C ₂₂ (liquid)
DOT Number	UN 1049 UN 1966	UN 1971	UN 1075 UN 1978	UN 1230	UN 1170	UN 1203	UN 1202 NA 1993	-
DOT Hazard Class or Division	2.1 flammable gas	2.1 flammable gas	2.1 flammable gas	3.6.1 flammable liquid	3 flammable liquid	3 flammable liquid	3 flammable liquid	3 flammable liquid
DOT Guide Number	22	17	22	28	26	27	128	
CAS Number	1333-74-0	74-82-8	74-98-6	65-56-1	64-17-5	8006-61-9	68476-34-6	67784-80-9
STCC Number	4905746	4905755	4905781	4909230		4908178		
OSHA/NFPA Flammability Class				IB	IB	IB	2 combustible liquid	2 combustible liquid
Mfg Name	Chem Tree; Airco Industrial Gases	E.I. Du Pont	Shell Oil Company	Allied Corp	Fisher Scientific	Shell Oil Company	Hess Corporation	NREL/TP-540- 43672
DOT Packing Group	-	-	-	PG II	PG II	PG II	PG III	PG III
DOT Packaging (non-bulk/bulk)	302/302	302/302	304/314	202/242	202/242	202/242	203/242	203/242
Type of Shipping Container	cylinders & tank cars	cylinders only	pressurized cylinders, tank cars, tank trucks	bulk in tank cars; 1-119 gal DOT PG-II performance- oriented containers	bulk in tank cars; 1-119 gal DOT PG-II performance- oriented containers	tanker trailers, rail cars, pipelines	tank trailers, rail cars, pipelines	tank trailers, rail cars, pipelines
Container Hazards	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	Rupture, BLEVE & fire	Rupture, BLEVE & fire
Special Fire Hazards	blue flame invisible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	yellow luminous flame visible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	yellow luminous flame visible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	blue flame invisible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	blue flame invisible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	yellow luminous flame visible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	yellow luminous flame visible in daylight; dense black smoke	yellow luminous flame visible in daylight; dense black smoke
Other Information	liquid floats & boils on water; visible heavier-than- air vapor cloud	LNG liquid floats & boils on water; LNG produces visible heavier-than-air vapor cloud; vapor cloud from CNG gas release is buoyant and invisible	liquid floats & boils on water; heavier- than-air visible vapor cloud	liquid floats & mixes with water; near neutral vapor buoyancy	liquid floats & mixes with water; near neutral vapor buoyancy	liquid floats on water; negative buoyancy vapor cloud	liquid floats on water; low vapor pressure, formation of vapor cloud not expected	liquid floats on water; low vapor pressure, formation of vapor cloud not expected

Chemical & Physical Properties of Selected Flammable Fuels - continued

Property	Hydrogen H ₂ (gas)	CNG CH ₄ 83-99%; C ₂ H ₆ 1-13% (gas)	Propane C ₃ (liquid)	Methanol CH ₃ OH (liquid)	Ethanol C ₂ H ₅ OH (liquid)	Gasoline C ₄ -C ₁₂ (liquid)	No. 2 Diesel C ₈ -C ₂₅ (liquid)	Biodiesel C ₁₂ -C ₂₂ (liquid)
Molecular Weight (gm/mole)	2.02	16.04	44.1	32.04	46.07	100-105	~200	~292 (q)
Chemical Composition (wt%)								
Carbon	0	75	82	37.5	52.2	85-88 (b)	87 (g)	77 (g)
Hydrogen	100	25	18	12.6	13.1	12-15 (b)	13 (g)	12 (g)
Oxygen	0	-	-	49.9	34.7	0	0 (g)	11 (g)
Solid Melting Pt Temperature (°F)	-435 (p)	-296	-305.8 (m)	-143.5	-173.2	-140 to -131	-30 to -40(4)	26-66 (g) (7)
Liquid Specific Gravity (60 °F/60 °F)	0.071 (o)	0.42	0.59	0.796 (h)	0.794 (h)	0.72-0.78 (b)	0.85 (g)	0.88 (g)
Liquid Density (lb/gal @ 60 °F)	-	1.07 (n)	4.22	6.63 (b)	6.61 (b)	6.0 – 6.5 (b)	7.079 (g)	7.328 (g)
Liquid Viscosity (mm²/s)								
@ -4 °F	-	-	-	1.345 (f)	3.435 (f)	0.8 - 1.0 (f)	9.0 - 24.0 (f)	-
@ 68 °F	-	-	-	0.74 (f)	1.50 (f)	0.5 – 0.6 (f)	2.8 – 5.0 (f)	-
@ 104 °F	-	-	-	-	-	-	1.3 – 4.1 (g)	4.0 – 6.0 (g)
Thermal Conductivity (Btu/h-ft-°F)	0.097	0.17		0.12	0.099	0.086		
Coefficient of Thermal Expansion (???/??? @ 60 °F & 1 atm)				0.00067	0.00062			
Electrical Conductivity (pico Siemens per meter)	-	-	-	0.3 E 6 pS/m	< 500 E 6 pS/m	25 pS/m	5 pS/m	-
Liquid Boiling Pt. Temperature (°F)	-423 ^(m)	-259	-44 ^(m)	149 ^(h)	172 ^(h)	140 to 390	356 – 644 ^(g)	599 – 662 ^(g)
Latent Heat of Vaporization								
(Btu/gal @ 60 °F)	-	-	775	3,340 (b)	2,378 (b)	≈900 (b)	≈710	-
(Btu/lb @ 60 °F)	192.1 (p)	219	193.1	506 (b)	396 (b)	≈150	≈100	-
Vapor Pressure (psi @ 100 °F)								
Reid (psi @ 100 °F)	-	2,400	208	4.6 ⁽ⁱ⁾	2.3 ⁽ⁱ⁾	8 – 15 ^(c)	<0.2	<0.04 ^(r)
Vapor Pressure (mm Hg @ 68 °F)	n/a	n/a	>760	92		190		
Relative Evaporation Rate (n-Butyl acetate=1)				4.1				
Vapor Specific Gravity (?? °F)								
Vapor Density (lb/ft³ @ ?? °F)	0.067	0.55-1.0	1.5	1.1		3 to 4		
Flash Point Temperature								
Closed Cup (°F)	-	-300	-156 ^(m)	52 ⁽ⁱ⁾	55 ⁽ⁱ⁾	-36 ^(b)	140 - 176 ^(g)	212 – 338 ^(g)
Open Cup (°F)								
Ignition Temperature (°F)	752/1,065	999	842					
Autoignition Temperature (°F)	932 (m)	900 – 1170 (m)	842 (m)	867 (b)	793 (b)	495 (b)	≈600	-
Specific Heat								
Liquid (Btu/lb/°F)	-	-	-	0.60 (j)	0.57 (j)	0.48 (e)	0.43	-
Vapor (Btu/lb/°F)								

Chemical & Physical Properties of Selected Flammable Fuels - continued

Property	Hydrogen H ₂ (gas)	CNG CH ₄ 83-99%; C ₂ H ₆ 1-13% (gas)	Propane C ₃ (liquid)	Methanol CH ₃ OH (liquid)	Ethanol C ₂ H ₅ OH (liquid)	Gasoline C ₄ -C ₁₂ (liquid)	No. 2 Diesel C ₈ -C ₂₅ (liquid)	Biodiesel C ₁₂ -C ₂₂ (liquid)
Flammability Limits								
Lower (vol %)	4.1 (o)	5.3	2.2	6.0	4.3 (i)	1.4 (b)	1.0	-
Upper (vol%)	74 (o)	15.0	9.5	36.5 (i)	19.0 (i)	7.6 (b)	6.0	-
Flammability Range (vol %)	3.3	9.7	7.3	30	14.7	6.2	5	-
Stoichiometric air/fuel ratio (weight)	34.3 (o)	17.2	15.7	6.45	9.00	14.7	14.7	13.8
Vol % Fuel in Vaporized Stoichiometric Mixture	-	-	-	12.3 (b)	6.5 (b)	2.0 (b)	-	-
Minimum Ignition Energy (mJ)	0.017	0.03	0.26	0.14		0.2		
Ignition Temperature (°F)	752 °F	540 °C		867		536		
Adiabatic Flame Temperature: (°F)	4,010	3,562	3,596	3,470	3,281	3,525		
Flame Temperature: (°F)				3,398	3,488	3,686		
Laminar Flame Speed (ft/s)	10.6-14.4		1.3	6.6-14.4	5.2-13.8	5.2-9.8		
Energy Density or Specific Energy								
By weight (mJ/kg)	120	50				44		
By Volume (mJ/L)	8.5	40				21		
Energy Release @ Stoichiometric volume (Btu/ft³)				94.5	94.7	95.2		
Heat of Combustion (Btu/lb)	60,000	23,000	21,500	9,900	12,900	20,000	20,700	≈18,145
Heating Value								
Lower (Btu/gal) (d)	-	-	84,250	57,250	76,330	116,090	128,450	119,550
Lower (Btu/lb) (d)	52,217	20,263	19,900	8,637	11,585	18,676	18,394	16,131
Higher (Btu/gal) (d)	-	-	91,420	65,200	84,530	124,340	137,380	127,960
Higher (Btu/lb) (d)	59,806	22,449	21,594	9,837	12,830	20,004	19,673	17,266
Water Solubility @ 70 °F								
Fuel in Water (vol %)	no	Negligible	Negligible	100 (h)	100 (h)	Negligible	Negligible	-
Water in Fuel (vol %)	-	-	Negligible	100 (h)	100 (h)	Negligible	Negligible	-

Table 2.

**PARAMETERS and FACTORS WHICH DETERMINE
WORST-CASE CONSEQUENCES**

1. physical and chemical properties that determine flammability hazard severity
 - latent heat of vaporization
 - equilibrium vapor pressure
 - vaporization rate
 - flash point temperature
 - flame point temperature
 - boiling point temperature
 - liquid thermal conductivity
 - liquid heat capacity
 - vapor heat capacity
 - heat of combustion
 - flame temperature
 - flame velocity
 - liquid electrical conductivity

2. conditions associated with a spill or accidental release (i.e., source term)
 - liquid flow rate
 - liquid temperature
 - confining pressure
 - equilibrium vapor pressure
 - letdown pressure (ΔP between containment & atmospheric pressure)
 - liquid viscosity
 - vapor viscosity
 - release rate (gal/h, lbs/h)
 - release velocity
 - release direction

3. type of consequence
 - pool fire
 - jet fire
 - container BLEVE
 - unconfined vapor cloud explosion (UVCE)
 - confined vapor cloud explosion (VCE)

4. vapor buoyancy relative to air
 - lighter-than air (hydrogen and CNG): vapor rises and migrates downwind
 - near neutral to air (i.e., methanol and ethanol): vapor migrates downwind
 - heavier-than air (i.e., propane, gasoline, diesel, and biodiesel) vapor migrates down slope and downwind

5. ease of ignition (thermal properties)
 - flash point temperature
 - fire point temperature
 - boiling point temperature
 - lower and upper flammability limits
 - flammability range
 - autoignition temperature

6. probability of encountering an induced or temperature ignition source

Theoretical/Ideal/Approximate Temperatures of Potential Ignition Sources

Potential Ignition Source Item	Environmental Conditions	Approximate Temperature (°F)
Fluorescent Light	ambient air @ room temperature	140 to 176
Incandescent Light	ambient air @ room temperature	212 to 572
Lighted Cigarette	unventilated ambient air @ room temperature	550
Lighted Cigarette	ventilated ambient air @ room temperature	752 to 1,436
Lighted Cigarette	insulated & smoldering in ambient air @ room temperature	950 to 1,150
Hot Electric Stove Element	ambient air @ room temperature	>1,026
Burning Match Flame	ambient air @ room temperature	1,112 to 1,472
Tungsten Halogen Light	ambient air @ room temperature	1,112 to 1,652
Burning Candle Flame	ambient air @ room temperature	1,112 to 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 to 3,540
Plasma Torch	ambient air @ room temperature	≈ 8,492
Lightning Strike	ambient air @ room temperature	54,032