

APPENDIX A FLAMMABILITY CONCEPTS

A flammability hazards analysis associated with a given site requires that one first identify the numerous ignition sources and then to assess the probability or likelihood of their involvement as an ignition source. This is done within the context of the information on the general properties of hydrocarbon liquids being off loaded from the Kittitas storage tanks to trucks on the site and the potential ignition sources associated with the tank truck, immediate surroundings and other factors dependant on environmental conditions (e.g., static electricity and lightning). In addition, a similar assessment is conducted to include the Chicago, Milwaukee-St. Paul railroad tunnel at Snoqualmie pass and the North Bend Community area. In order to provide a rational basis for such an assessment, it is necessary to discuss a number of important flammability and combustion concepts. This is done in the sections to follow.

1. Ignition Concepts

Ignition may be defined as the process of initiating self-sustained combustion. This requires a hydrocarbon fuel and an oxidizing agent (air - around 21 mole% oxygen and 79 mole % nitrogen). There are two general types of ignition to consider:

a. Piloted ignition - requires an external means to effect ignition, such as, a flame, spark, glowing object, etc.

b. Autoignition - occurs without assistance from a pilot source. Because there is often confusion associated with this mode it will be considered in greater detail in this Section under the heading of "Autoignition Temperature".

It is also convenient to define ignition temperature as the minimum temperature that a substance must be heated for it to ignite. Usually piloted ignition of a substance is considerably lower than its autoignition temperature. It is also important to emphasize that ignition of a fuel/air mixture can occur only if the composition is flammable, i.e. within the flammability limits, and some critical volume is heated sufficiently to produce an exothermic reaction that propagates flame beyond the point of ignition. This is discussed in Section 2 to follow.

The various ignition sources of present interest are highlighted in general terms in Table I. For small hot surfaces both the temperature and heating rate are important such as for heated wires, metal fragments and frictional sparks. As a rule of thumb the ignition temperature generally decreases with an increase in the size or surface area of the heated surface. Self heating, pyrophoric, and catalytic combustion modes are not relevant to the present study and are included only for the sake of completeness. Based on the known temporal and spatial characterizations of electrical and hot surface ignition sources and given similar situations, hot electrical sparks would generally produce ignition easier than frictional sparks as would frictional sparks be easier than heated wires etc.

2. Flammability Limits

Flammability limits represent the extreme concentration limits of a combustible (gaseous or liquid vapors) in an oxidant through which a flame, once ignited, will continue to propagate at the specified temperature and pressure. The lower concentration value or the lean limit is often denoted by the symbol LFL while the upper or fuel rich limit is given the symbol UFL. Fuel/air mixtures within these limits are said to be within their flammable or explosive range. Ignitions are much more intense within this range than if they were close to either the LFL or UFL. It should be emphasized that outside of the flammability limits i.e., either below the fuel lean or above the fuel rich limit one cannot effect ignition of a fuel/air mixture regardless of the intensity of the ignition source.

The effect of temperature on changing the flammability limits is well known (3-6). When the mixture temperature is increased the flammability range widens; however when the temperature is lowered the flammability range narrows or decreases. In addition, a decrease in temperature can cause a previously flammable mixture to become non-flammable by placing it above or below the limits of flammability.

Flash point may be defined as the minimum temperature at which a liquid vaporizes sufficiently to form an ignitable mixture with air. At temperatures below the flash point there isn't sufficient vapor in the gas phase to sustain homogeneous combustion. In the fire field combustible liquids are broadly classified according to their flash points and boiling points into classes I to III as follows:

Class I - liquids having flash points below 100 °F (37.8 °C).

Class IA - those having flash points below 73 °F (22.8 °C) and boiling point (BP) below 100 °F.

Class IB - those having flash points below 73 °F and BP at or above 100 °F.

Class IC - those having flash points at or above 73 °F and BP below 100 °F.

Class II - liquids having flash points at or above 100 °F and below 140 °F (60 C).

Class III - liquids having flash points at or above 140 °F.

Flash points are tabulated in various references such as (3-5) and denoted by a tag closed cup (TCC) or tag open cup (TOC) values.¹ TCC's since they are usually a few degrees lower than TOC's appear more meaningful from a conservative safety viewpoint. It should be emphasized that flash point should never be used as the sole criterion of an engineering flammability hazard analysis. This is perhaps best stated in the ASTM standard D 93-77 for flash point by the Pensky-Martins closed cup tester:

¹ Tag closed cup and tag open cup are standard testing devices used for determining flash point.

This standard should be used solely to measure and describe the properties of materials, products, or systems in response to heat and flame under controlled laboratory conditions and should not be considered or used for the description, appraisal, or regulation of the fire hazard of materials, products, or systems under actual fire conditions.

With regard to the hydrocarbons involved the following brief descriptive information is provided below:

Gasoline - a refined petroleum naphta which by its composition is suitable for use as a fuel in internal combustion engines. NFPA classification is that of a IB liquid on a flash point basis.

Reformulated Gasoline - gasoline containing methyltertiarybutylether (or met-tert-butyl-ether for short, MTBE) as an octane booster and for smog and ozone abatement as mandated by the US Environmental Protection Agency (EPA). Some winter grades of reformulated gasolines have a 10 percent distillation point that is below 100 °F making them a Class IA liquid.

Diesel - a distillate fuel generally classified as types 1-D (flash points range from around 106 °F - 169 °F and from 137 °F and as high as 240 °F for types 2-D. Used in a variety of different types of engines such as trucks, tractors, buses, railroad diesel engines and in heavy-distillate and residual fuels for large stationary and marine-diesel engines.

Kerosine - falls under the ASTM fuel classification of No. 1 grade heating oil (Class II).

Naphtha - a generic term applied to refined, partly refined, or unrefined petroleum products and liquid products of natural gas, not less than 10% of which distill below 347 °F (175 °C) and not less than 95% of which distill below 464 °F (240 °C) when subject to distillation in accordance with ASTM D 86. It has a NFPA classification of IB.

3. Autoignition Temperature

The autoignition temperature (AIT) of a combustible may be defined as the minimum temperature at which the material ignites spontaneously. Values are higher for air than in oxygen enriched atmospheres. AIT's are complex functions of composition, pressure, shape and size of container, location of ignition source, heating rate and time of heating, initial temperature of combustible (e.g. preheating) and other parameters (Table 2). The time scale can extend over a wide range but is about 5 minutes or less at the minimum AIT for most fuels in air at atmospheric pressure. However, it should be emphasized for heated surface temperatures that are way above tabulated AIT's, ignition can in essence be instantaneous. Selected AIT highlights are presented in Table 3 for gasoline, kerosine, diesel fuel and other pure liquids that are in the typical C₅ to C₁₀ compound blends in gasoline. AIT values in Table 3 range from 371 °C for automotive gasolines to kerosine - 229 to 293 °C. Thus, it should be noted that as far as ease of ignition from a heated surface is concerned it is easier to ignite diesel (i.e., it requires a lower surface temperature) than gasoline.

4. Explosions

Considerable information in the literature and books is available on explosions (see e.g. Refs. 1,2,6-8,11). The interested reader is referred to these sources since only a brief accounting of selected highlights will be given herein.

The practical definition of an explosion is any pressure rise in a system which ruptures a container or enclosure causing pressure wave damage. An explosion due to steam overpressure in a boiler is an example of common usage. Here we are concerned with flame propagation. For subsonic propagation rates the process is termed "deflagration" while for supersonic propagation it is termed a "detonation". In the latter, the pressure wave develops without confinement and has the characteristics of an explosion because of the overpressure across a propagating shock wave. A deflagration, since it is a subsonic propagating wave, cannot produce a shock wave. With most combustible/air mixtures, at normal temperature, the ratio of peak to initial pressure will seldom exceed 8 to 1 in a deflagration, but may be more than 40:1 in a detonation. The ignition energy required to initiate a detonation is usually many orders of magnitude greater than that required for deflagration.

The possibility of a specific type of explosion known as a "BLEVE" i.e. boiling liquid expanding vapor explosion, is ruled out for the storage tanks since they will fail before the pressure necessary for superheating of the contents can be achieved. However, the tank trucks that are proposed for loading of fuels at the terminal can undergo a BLEVE if the truck contents are impinged upon by a flame in the vapor state above the liquid contents.

5. Minimum Ignition Energy

The concept of minimum ignition energy is based on determining the minimum spark energy in a capacitance type experimental test setup (11-13) to ignite a combustible vapor/oxidant mixture. For known system capacitance and applied voltage to a set of metal electrodes one can calculate the energy from

$$E = CV^2 \times 10^{-9} \quad (\text{millijoules})$$

where C = capacitance in picofarads, pF
V = applied potential in volts, V

As a rough rule of thumb, the following minimum values apply to vapors, mists and dusts in air (14):

vapors - 0.1 mj
mists - 1.0 mj
dusts - 10.0 mj

These minimum values apply only to the most readily ignitable materials under the most ideal conditions. Reference 11 presents a minimum ignition energy plot for diethyl ether/air as a function of concentration and for helium in place of nitrogen in the air. Here the minimum ignition energy - 0.25 mj, lies close to the stoichiometric concentration and that around 10 mj are required for ignition at the fuel lean and fuel rich limits. Substituting helium for nitrogen in air increases the minimum ignition energy by almost a factor of ten. The literature reveals considerable differences in experimentally determined values of minimum ignition energy (9). Selected values from Calcote, et. al. (10) and other references are given below:

Fuel	Minimum Ignition Energy ^(9-11,15) (Millijoules - mj)
Hydrogen	0.02
Ethylene	0.096
n-pentane	0.49
Benzene	0.55
n-heptane	0.70
Acetone	1.15
Kerosine*	20

* Flash Point Typical of a Diesel Fuel

Since gasoline consists predominantly of C₅ to C₁₀ paraffins (and n-heptane and n-pentane fall in this range too) it is reasonable to assume that the minimum ignition energy of gasoline will be approximately 0.7 mj. Minimum ignition energies for kerosine with a flash point typical of diesel fuel were about 20 mj at 15 °C (15). At lower temperatures the minimum energy increased.

6. Electrostatic Induced Ignition

Ignition of hydrocarbon fuels from static sparks is a well known phenomena in the petroleum industry (14-16). Many of the examples in the literature deal with static charging during tank truck, storage tank, or aircraft fueling operations. They are, thus, applicable to the present fire situation. A brief review of the basic fundamentals of static charge generation, accumulation and discharge are presented below. For example, static can readily be generated by a truck driver sliding across his seat and spark discharge can easily occur by touching a point of lower potential such as a door handle for egress out of the truck. The important concepts needed to carry out a static hazard assessment are, therefore, outlined below.

The tendency of static sparking may be assessed either on a voltage or a charge density basis i.e. coulombs/sq.cm. basis using the following experimentally determined values:

- X 14,000 volts are needed to produce a spark between needle points 1/2 inch apart; over 20,000 volts are needed between spheres.
- X 76,000 volts/in. (30,000 volts/cm.) are needed for sparking.
- X A minimum of 350 volts is needed for a spark to jump plates 0.01 in. apart.
- X Charge densities of 1.1×10^{-9} to 2.2×10^{-9} coul/ sq.cm. are sufficient to ignite a number of flammable vapor/air mixtures, including gasoline.
- X The breakdown strength (the point at which air ionizes (produces a spark)) in air is 2.65×10^{-9} coul/cm²

The importance of relative humidity (RH) on static is illustrated in Refs. (4, 12). Gibson and Lloyd's data show that below 40% RH the charge density is independent of RH and at its maximum value for charging of plastics. In going from an RH of around 40% to around 50% the charge density decreases by a factor of 1.7. Increasing the RH still higher leads to further decreases in charge density, while at 85% RH no charging was obtained.

The Factory Mutual Research Corporation (4) states that a RH of 60 to 70% will generally produce enough moisture on materials to prevent accumulation of static. Even though static electricity is generated, the charge usually leaks away and no accumulation results. Most static electricity fires occur in winter when the indoor relative humidity is 30% or less.

The usefulness of the minimum ignition energy concept discussed earlier as applied to static hazard assessment follows from a simple example. If we assume a human is charged to 5,000 V by sliding across the seat of a motor vehicle or removing, for example, a nylon or polyester jacket, and take his capacitance as 200 pF (human capacitances range from 100 - 400 pF) and assume the equation for minimum ignition energy E is roughly applicable then $E = 2.5$ mj. This energy is sufficient to ignite various hydrocarbon mixtures especially gasoline with E estimated to be around 0.7 mj over a range of concentrations. This example shows that static from a human has the potential to ignite gasoline especially when sufficient fuel is vaporized such as during a large accidental spill.

Methods for control of static (4,12-14) which include grounding and bonding, use of antistatic additives, relaxation techniques are sometimes not considered during loading of tanker trucks from fuel depots. However, while static charge generation from pumping a low dielectric constant liquid such as gasoline into a storage tank could self ignite as demonstrated by the Shell Oil Company over 40 years ago (16), the presence of a fuel rich environment in the tanks except when near or entirely empty and generally accepted safety methods to avoid sloshing or splashing, plus the occurrence of more intense or "hot" ignition sources (e.g., a turbo-charger on a diesel engine or a heated exhaust manifold or even an on board liquified petroleum heater on certain large trucks) makes this type of ignition scenario lower in terms of ignition probability. However, it cannot be entirely ruled out.

7. Energetics of Some Common Ignition Sources

In an accidental ignition involving a heavy truck with a running diesel engine, one must consider a number of potential ignition sources, such as, heated surfaces (turbo-charger, heated exhaust, heating tapes or filaments to maintain free flowing diesel in fuel lines during cold days, etc.), electrical sparking (from faulty wiring, or use of truck radios and communication equipment not suitable for an environment containing combustible vapors, i.e. not approved for a Class I Group D environment). The use of smoking materials (striking a match, using a butane lighter, smoking a cigarette etc.), switching on and off of a flashlight and electrostatic sparks are some other operator generated types of ignition sources. Not all of these sources have known energies or surface temperatures. Table 4 therefore presents the energetics of similar common ignition sources, such as, e.g. a pilot light for comparison purposes. The usefulness of this comparison is seen that because of the strong variation of ignition energy with composition, humidity, inert gases and other variables, the most energetic ignition sources are capable of effecting ignition of the widest composition limits. Implicit here is that we are within the lower and upper flammability limits. Alternatively, electrostatic sparks because of their low energies are generally only capable of igniting materials close to their stoichiometric composition.

Lightning which is reported to produce voltages up to billions of volts and exceedingly high temperatures (e.g. around 30,000 °C) was not included in Table 4 because voltage and millijoules are non-comparable units.

8. Tabulated Flammability Data

Selected flammability highlights are presented in Table 3 for various components in gasoline, different grades of gasoline, kerosine and diesel fuel. Here LFL₂₅ and UFL₂₅ are the lower and upper flammability limits at 25 °C, respectively. AIT is the autoignition temperature. All flash points are closed cup values. The vapor densities are included to show that relative to air, which is arbitrarily set at one, they will layer on the ground and can thus travel to a distant ignition source without appreciable dilution especially during quiescent (i.e., no wind) conditions. Noteworthy here are that kerosine and diesel fuels have much lower AIT's than gasoline. Low values range from 176 °C for light diesel, 229 °C for kerosine, 254 °C for no 2-D dieselfuel in contrast to 371 °C for automotive gasoline and 427 °C for aviation gasoline. This means that, if both are caused to strike or impinge upon a heated surface, kerosine and the diesel fuels will ignite at a much lower temperatures than gasoline. The flash points are considerably lower for the gasolines (less than - 40 °C) in contrast to values greater than around 38 °C. The low values of flash point are an indicator of extreme volatility, and because of its low ignition energy requirement, gasoline presents a flammability hazard at practically all ambient temperatures normally encountered in the U.S. Since the literature data in Table 3 for the AIT's did not state that the various hydrocarbon fuels were preheated, it is assumed that these studies were carried out at ambient temperatures i.e., around 20 °C.

9. Brief Overview of Liquid Hydrocarbon Fire Extinguishment using Foams: Current State-of-the-Art

Industrial Fire World (17) presents an overview of various fire extinguishing monitors capable of delivery of up to as high as 16,000 gallons per minute of combined water and foam concentrate (foam concentrate is typically at the 3% level for common hydrocarbons and at the 6% level for alcohols). Based on personal communication with Williams Fire & Hazard Control (18) who have put out the largest tank fires to date, namely 152 and 150 ft. diameter tank fires in Shalmet, LA and Los Angeles, CA the following important information was noted:

- X Both 152 and 150 ft. diameter tanks required a foam delivery system of 3,200 gpm (water flow equals total flow of 3,200 gpm - foam concentrate flow $3,200[0.03] = 3,104$). Both tank fires were extinguished in around 45 minutes from the start of the foam delivery.
- X Enough water must be available for up to 2 hours of delivery with the remaining time (i.e., after fire extinguishment) required for tank cool down.
- X Larger tank fires such as 300 ft. diameter tank fires require two 10,000 gpm foam delivery systems.

X Operating pressure for the foam nozzles is around 100 psi.

Using the above information and assuming one is planning on extinguishing a 150 ft. diameter tank fire, it is interesting to note that total water requirements for the recommended two hour treatment amount to a water need or storage reservoir of 372,480 gallons.

10. Estimation of Vapor Concentration

For illustrative purposes we will assume that gasoline that contains mostly $C_5 - C_{10}$ straight chain hydrocarbons is adequately approximated by n-heptane with a formula of C_7H_{16} (Molecular weight of 90). It is informative to calculate the vapor concentration for the condition of no wind velocity and the simplifying assumption of layering of the heavier-than-air vapor close to the ground. Earlier calculations by the author (for a proprietary client) based on a model of diffusion of hydrocarbons from a point source, taking into account the effect of wind velocity and axial and radial diffusion, have shown that a flammable concentration was limited to a region 6-8 inches off the ground. Although this model is not directly applicable to the present situation because of the possibility of a large spill of gasoline which does not represent a point source emitter it, nevertheless, provides important information about the maximum zone of flammability.

Calculations in § 3.8 are carried out for a 100 gal spill (note it was assumed that the ambient temperature was 20 °C). Thus, for a 100 gallon spill under the assumptions given in § 3.8 for a theoretical spill having square dimensions for length and width and a thickness of 12 inches, the spatial dimensions for vapor concentration at the lower limit of flammability works out to be 432 ft. in length or width. This simplified "worst case" situation demonstrates that a flammable region can extend to very large distances provided quiescent ambient conditions are experienced. The recommendation by NFPA Code 30 that deals with "Flammable and Combustible Liquids" suggests that the minimum distance that a floating roof tank can be from the property line is only ½ times the diameter of the tank. For the Kittitas terminal assuming 150 ft. is the diameter of the largest tank this distance is only 75 ft. The potential for ignition occurring outside of the property line for a 100 gallon spill is thus readily evident.

11. Effect of Relative Humidity on Static Charge Generation

The equation given in this appendix, § 5 may be used to estimate the voltage required for a human to be charged to ignite n-pentane. Let us take the capacitance of a human as 200 pF (literature values quoted range from 100-400 pF) and use the literature value from Calcote et. al.(10) of 0.5 mj for the minimum ignition energy of n-pentane. Substituting in the above equation gives $V = 2235$ volts for ignition to occur. This is certainly a reasonable voltage for a human to become charged via electrostatics. However, to be more precise in the hazard assessment, one must consider the relative humidity (RH) of the environment in dealing with static generation and accumulation on the human body. For example, materials having specific conductivities equal to or greater than $1 \times 10^{-11} \text{ohm}^{-1} \text{cm}^{-1}$ rapidly lose charge to ground and, thus, rarely if ever accumulate sufficient charge

to produce an energetic spark. The importance of RH is demonstrated in the hospital operating theater during administration of flammable anesthesia as per NFPA Code 56 A where relative humidities (RHs) at 50% and above and other control methods have successfully eliminated static induced ignition. Because the RH in the Kittitas and Snoqualmie pass regions and elsewhere along the pipeline route at times are less than 50% RH, electrostatic induced ignition is considered very probable.

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