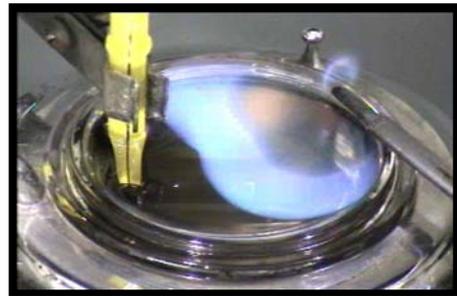
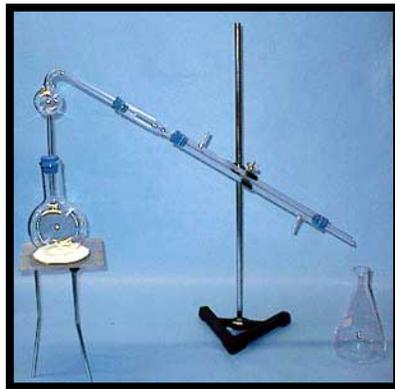


Fractional Vaporization of Ignitable Liquids -Flash Point and Ignitability Issues-



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FRACTION VAPORIZATION OF IGNITABLE LIQUIDS - FLASH POINT AND IGNITABILITY ISSUES -

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ABSTRACT

Explosions or flash fires have occurred under circumstances in which suspected liquid fuel does not appear to explain the fuel source because of its high reported flash point. These instances have posed a conundrum to the fire investigation profession. In some cases, science can explain the fuel source by the application of the principal of fractional distillation.

Commercial ignitable liquid products that are mixtures of various ignitable liquid components or ignitable and non-ignitable liquid components, with varying vapor pressures, can undergo fractional vaporization. In this process normal evaporation can separate the various ignitable or non-ignitable components, with the lighter end fraction (high vapor pressure) compounds evaporating first.

When applied to flammable and combustible liquids, this process is sometimes referred to in the fire and explosion investigation profession as “weathering.” In these situations, the flash point of the remaining (not yet vaporized) liquid will be higher than the measured flash point of the “non-weathered” original liquid. It is possible for such mixtures to evolve concentrated vapors and be ignited even when the parent liquid is at a temperature below its reported flash point.

When applied to mixtures of ignitable and non-ignitable components in which the non-flammable component(s) evolve first, the process is referred to as “outgassing.” When the earlier evolving volatile compounds are generally considered “non-combustible,” such as halogenated hydrocarbons like methylene chloride, the flash point of the original liquid can actually initially increase and then decrease as vaporization continues.

In both situations, fractional vaporization can be extremely dangerous in that the perceived ignitability of the original liquid is masked or underreported in material safety data sheets, labels, warnings, and product use instructions.

In general, the process is observed more frequently in products that are designed to be used in coatings where the distribution or spreading over large surface areas is expected. Evaporation is an intended part of their application. These dangerous situations have been observed in products such as paints, stains, other surface coating materials, cleaning products, and strippers/removers.

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Fractional Vaporization of Ignitable Liquids

INTRODUCTION

Explosions or flash fires have occurred under circumstances in which a suspected liquid fuel does not appear to explain the fuel source because of its high reported flash point. These instances have posed a conundrum to the fire investigation profession. In some cases, science can explain the fuel source by the application of the principal of fractional distillation.

Commercial ignitable liquid products that are mixtures of various ignitable liquid components or ignitable and non-ignitable liquid components, with varying vapor pressures, can undergo fractional vaporization. In this process normal evaporation can separate the various ignitable or non-ignitable components, with the lighter end (high vapor pressure) fraction compounds evaporating first.

When applied to flammable or combustible liquids such as gasoline, this process is commonly referred to in the fire and explosion investigation profession as “weathering.” “Weathering” is most often associated with liquids. In which case, the flash point of the remaining (not yet vaporized) liquid will be higher than the reported flash point of the “non-weathered” original liquid. When this type of fractional vaporization occurs it is possible for such an original liquid mixture’s evolved vapors to be ignited even when the parent liquid is at a temperature below its reported flash point.

When applied to mixtures of ignitable and non-ignitable components in which the non-flammable component(s) evolve first, the process is referred to in the literature as “Outgassing.”^{1, 2} When the earlier evolving volatile compounds are considered “non-combustible,” as with halogenated hydrocarbons - like methylene chloride, the flash point of the original liquid can actually initially increase and then decrease as fractional vaporization continues.³

Both such situations of fractional vaporization can be extremely dangerous in that the perceived ignitability of the original liquid is masked or underreported in material safety data sheets, labels, warnings, and product use instructions. Thusly the true fire danger of the liquid may be unknown to the user.

In general, the process is observed more frequently in products which are designed to be used by coating or spreading over large surface areas and have evaporation as an intended part of their use. These dangerous situations have been observed in products such as paints, stains, other surface coating products, cleaning products and paint strippers/removers.

VAPORIZATION (EVAPORATION) AND VAPOR PRESSURE

Liquids change to vapors (gases) at temperatures below their boiling points. This occurs at any temperature higher than absolute zero, -273° C (-459° F.) (0° on the Kelvin and Rankin scales). Vaporization of a liquid at a temperature below its boiling point is called evaporation, which occurs at any temperature when the surface of a liquid is exposed in an unconfined space. When, however, the surface is exposed in a confined space and the vaporization of the liquid is in excess of that needed to saturate the space with vapor, equilibrium is quickly reached between the number of molecules of the substance escaping from the surface and those returning to it. A change in temperature upsets this equilibrium. A rise in temperature, for example, increases the activity of the molecules at the surface of the liquid and increases the rate at which they fly off. When the new temperature is maintained for a short time, a new equilibrium concentration in the vapor is established.

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The pressure exerted by the vapor evolving from the surface of the liquid is called its vapor pressure. Vapor pressures differ for different substances at any given temperature, but each substance has a specific vapor pressure for each given temperature. At its boiling point, the vapor pressure of a liquid is equal to atmospheric pressure. For example, the vapor pressure of water, measured in terms of the height of mercury in a barometer, is 4.58 mm at 0°C (32° F.) and 760 mm at 100°C (212° F.), its boiling point at sea level.

The Vapor Pressure – Temperature Relationship

The vapor pressure - temperature relationships for each pure material is an exponential function of the heat needed to cause evaporation or ΔH_{evap} and the absolute temperature. The integrated form of the equation is:

$$P^0 = Ae^{-\Delta H/RT}$$

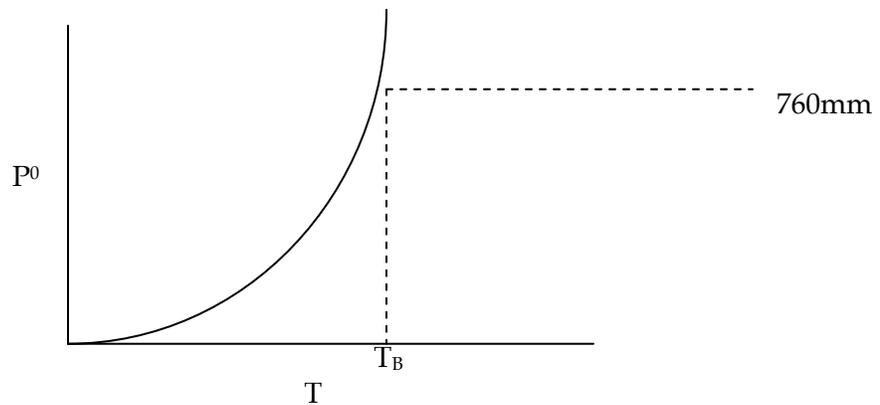


Figure 1 - Vapor Pressure - Temperature Relationships

or

$$\ln P^0 = -\frac{\Delta H}{R} \left(\frac{1}{T} \right) + \ln A$$

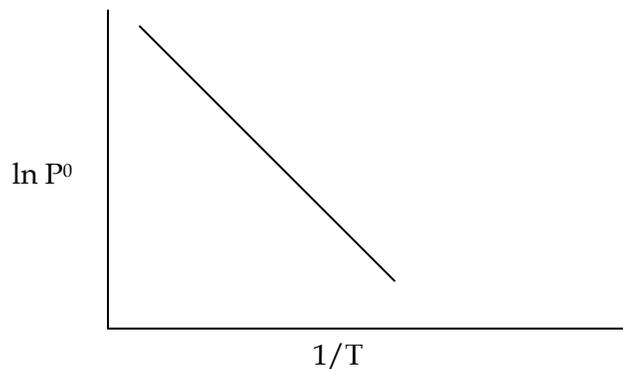


Figure 2 – Vapor Pressure – Reciprocal Temperature Relationships

Fractional Vaporization of Ignitable Liquids

Raoult's Law

At any given temperature, the total vapor pressure of a mixture is the sum of the individual vapor pressures.

$$P_T = P_A + P_B + P_C = \sum P_i$$

If there is no interaction between the molecules of the mixture (Raoult's Law) the vapor pressure of each component is the ratio of the fraction of molecules times the vapor pressure of the pure component.

$$P_A = X_A P_A^0$$

For a two component system $P_T = X_A P_A^0 + X_B P_B^0$ at a given temperature and is graphically represented in Figure 3.

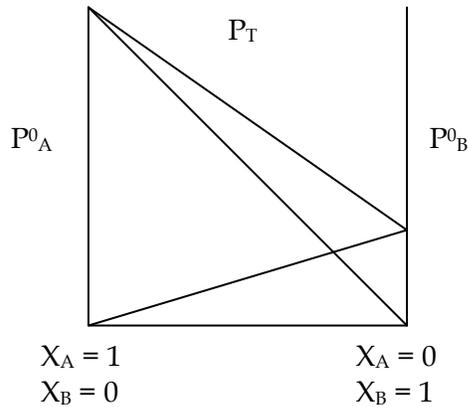


Figure 3 - A Two-Component System at a Given Temperature

The evaporation (distillation) of the more volatile compounds increases the flash point of the residual liquid when the volatile components are dissipated through adequate ventilation. However, should the more volatile fraction be concentrated due to gravity or temperatures or both (a low temperature in a small basement) to a concentration in excess of the LEL, a fire may occur.

Some compounds when mixed have an increase in vapor pressure. A positive derivation of Raoult's Law, which results in higher volatility, lower boiling point and lower flash point as shown in Figure 4.

Fractional Vaporization of Ignitable Liquids

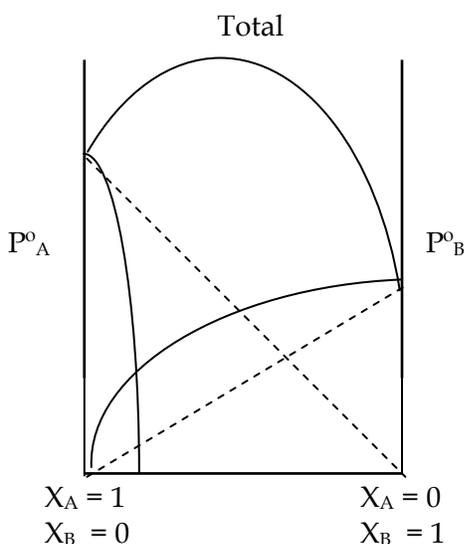


Figure 4 - A Positive Derivation of Raoult's Law

Binary Systems

Examples of binary systems, which have an increase in vapor pressure, are provided in Table 1. The boiling point change from the lowest boiling components is included. The mixing of 2-butanone (methyl-ethyl-ketone) and cyclohexane compounds commonly found in lacquer thinners have a 14°F lower boiling point than the 2-butanone. Mixtures may be more hazardous than the pure materials.

It is this simple physical principle of evaporation and its relationship with the vapor pressure of the liquids which make up the components of a liquid mixture that is at the heart of the fractional vaporization issue of fire safety.

Table 1 - Examples of Binary Systems Which Have an Increase in Vapor Pressure									
Component 1				Component 2					
Compound	Formula	BP°F	Mol. Frac.	Compound	Formula	BP°F	Mol. Frac.	Azeo. Temp °F	CHANGE B.P.°F
Acetone	C ₃ H ₆ O	69	0.68	Hexane	C ₆ H ₁₄	92	0.32	58	-12
Benzene	C ₆ H ₆	112	0.55	Ethanol	C ₂ H ₆ O	109	0.45	90	-19
Benzene	C ₆ H ₆	112	0.61	Isopropanol	C ₃ H ₈ O	116	0.39	97	-16
2-Butanone	C ₄ H ₈ O	111	0.44	Cyclohexane	C ₆ H ₁₂	115	0.56	97	-14
Cyclohexane	C ₆ H ₁₂	115	0.47	Ethyl-acetate	C ₄ H ₈ O ₂	107	0.53	99	-8
1,1-Dichloroethane	C ₂ H ₄ Cl ₂	71	0.71	Methanol	CH ₄ O	84	0.29	56	-15
Hexane	C ₆ H ₁₄	92	0.71	Isopropanol	C ₃ H ₈ O	116	0.29	78	-14
Methylethyl-ketone	C ₄ H ₈ O	111	0.65	Water	H ₂ O	148	0.35	100	-11
o-Xylene	C ₈ H ₁₀	227	0.41	2-Ethoxy-ethanol	C ₄ H ₁₀ O ₂	212	0.59	203	-9
p-Xylene	C ₈ H ₁₀	217	0.55	Propionic-acid	C ₃ H ₆ O ₂	222	0.45	205	-12

Fractional Vaporization of Ignitable Liquids

A Real World Example

A common paint stripper composed of methylene chloride (dichloromethane) (“non-flammable”) and toluene (flammable) as delivered to the consumer is “non-flammable” due to the high concentration of methylene chloride. Due to the high vapor pressure of methylene chloride, the boiling point is low, 40.1°C (104°F.), and this compound evaporates quickly. Toluene has a lower vapor pressure and therefore a higher boiling point, 110°C (231°F.), and evaporates at a slower rate than methylene chloride.

The change in concentration as a result of evaporation causes a “non-flammable” system to become flammable. The flash point of toluene is 4°C (40°F.). This type of mixture is typical of mixed “safety” solvents and poses a serious hazard to the user.

Another problem arises when a product fractionally vaporizes. The more volatile components are at a low concentration and by Raoult’s Law have a small contribution to the volatiles in the vapor of the original product.

IGNITABILITY

For ignitable liquids, their relative safety is largely an issue of fuel availability and potential ignition sources. In turn, ease of ignition of the vapors of an ignitable liquid is a function of the specific compounds in the vapor from the liquid which are available as a fuel and the minimum ignition energy.

A liquid’s availability as a fuel is a function of its composition which controls the vapor pressure as measured by the flash point, lower and upper explosive (flammability) limits, and its flammable range. Flash point itself is, in essence, a consequence of these properties.

The minimum ignition source characteristics of most common ignitable liquids are usually quite similar. These include minimum ignition temperatures in the 300° C (572° F.) to 600° C (1112° F.) range, minimum ignition energies in the range of 0.2 – 1.0 mJ, LEL to UEL and flammable ranges from 1% to 10%. Since these ignition source characteristics are well within the expected normal ranges for fire hazard environments, they are of relatively less importance to the considerations of ignitability for any one particular liquid.

This being the case the primary source of variability in relative ease of ignition of a liquid is its flash point.

FLASH POINT DETERMINATIONS

The flash point of a liquid is generally defined as in National Fire Code© NFPA 921-2004 Section 3.3.71 as “the lowest temperature of a liquid, as determined by specific laboratory tests, at which the liquid gives off vapors at a sufficient rate to support a momentary flame across its surface.”⁴

The flash point of an ignitable liquid forms an important component of the overall evaluation of the liquid’s ignitability along with such properties as minimum ignition temperature, minimum ignition energy, flammable range, upper and lower flammable limits, heat transfer mechanism, and heat flux. The actual scientific concept of flash point in relation to “real world” fire investigations is much misunderstood by many in the fire investigation and even the fire science communities.⁵ Largely controlled by ASTM and ISO standards for the conduct of flash point testing, flash point determination is primarily intended for comparing the relative fire safety of ignitable liquids to each other.

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In the most general terms, flash point testing is conducted by applying prescribed standardized pilot flames or electrical ignition sources to vapor spaces immediately above the surfaces of the tested liquids which are being slowly heated. The temperature of the tested liquid at which the evolved vapors can be ignited, producing a momentary flash of flame across the surface of the liquid, is that liquid's flash point. Figure 5 illustrates the typical manner in which flash point tests are conducted. Figures 6 and 7 display the flashes from the two most common types of flash point tests, closed cup and open cup respectively.

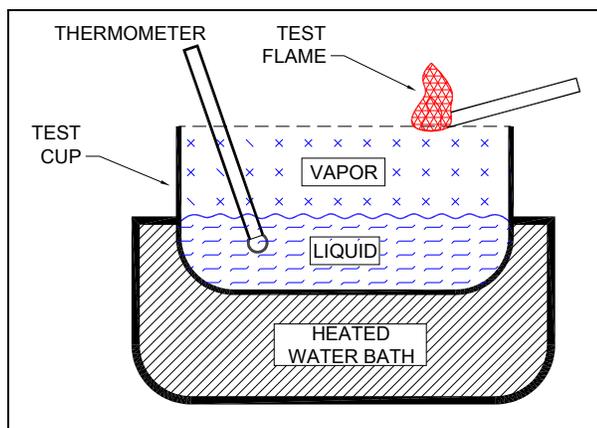


Figure 5 - Schematic of Typical Flash Point Test

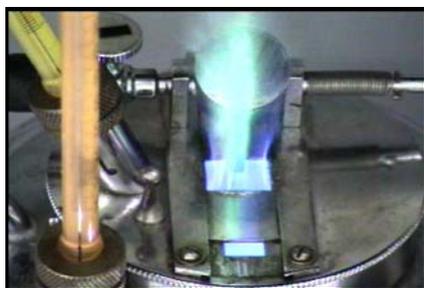


Figure 6 - Closed Cup Flash (Paraxylene)

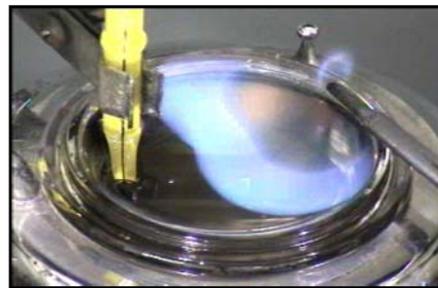


Figure 7 - Open Cup Flash (Paraxylene)

The temperature of the tested liquid at which flame ignites and continues to burn is the liquid's fire point. Fire points of particular liquids are not widely reported in the literature. This, as well as the fact that the flash point describes a certain minimum level of ignitability, has resulted in flash point being the widely preferred method of assessing ignitability in industry and statutory standards.

There are several flash point test apparatus designs and test protocols prescribed by such organizations as the American Society for Testing and Materials (ASTM). Reported flash points for a particular liquid can vary slightly depending upon the actual test apparatus and protocol employed.

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Reported Flash Points vs. “The Real World”

There are some issues about translating published flash point temperatures to real life situations which must be understood. One must remember that reported flash point temperatures are from small-scale bench-top tests. These temperatures are determined with small samples, typically of 2 ml – 70 ml (0.068 – 2.37 fl. ozs.) volume and 38 – 64 mm (1.5 – 2.5”) liquid surface diameters, depending on the actual type of flashpoint tests run.

The tests are done under very strictly controlled conditions with no airflow, and completely still liquids without surface bubbles or liquid films on the inside walls of the test cups, standard flame (or electrical) ignition sources administered into the vapor space immediately above the liquids, and generally (frequently) in small closed cups. “Real world” conditions almost never replicate these test conditions. The test protocols are specifically designed to minimize the uncontrolled evaporation of the test sample.

There are a myriad of variables which exist in the “real world” that are not present in the laboratory. A brief listing of these variables includes: the actual surface area of the liquids from which ignitable vapors are being evolved, the actual temperatures of the “real world” liquids, differences in the ambient atmosphere temperatures and pressures within the vessels in the field, the temperature and heat transfer characteristics of the ignition sources, the actual chemical and physical make-up of the liquids in question, and many more.

Flash point tests are not, and never were, designed to replicate “real world” conditions. They are designed to compare one ignitable liquid to another, largely for regulatory and MSDS purposes under strict laboratory conditions. One must be extremely conservative and careful when using these reported numbers for “real world” analyses of the ignitability of liquids in the field. However, the comparisons of the tested flash points of the various evolved vapor fractions are an excellent method for evaluating the various fractions’ ignitability to that of the parent liquid.

The very ASTM Standards for flash point testing admonish the reader that the tests are “...to be used to measure and describe the properties of materials...in response to heat and flame under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or risk...under actual fire conditions.”⁶

However the determination of the flash points of the original liquid, its evolved fractions, and the remaining “weathered” or “outgassed” parent liquid are essential components in the analysis of whether fractional vaporization took place and the impact of this vaporization on the fire incident under investigation.

ANALYZING THE IMPACT OF FRACTIONAL VAPORIZATION

For this type of laboratory analysis either the controlled evaporation of the subject liquid, as put forward in ASTM Standards E502 – Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods,⁷ E1232 – Standard Test Method for Temperature Limit of Flammability of Chemicals,⁸ and UL Standard 340 - Test for Comparative Flammability of Liquids,⁹ or fractional distillation are used to produce the testable liquid fraction samples. In all cases the relative ignitability and fire hazard of the resultant liquids are compared by the results of flash point testing.

Other standards that deal with fractional vaporization issues include NFPA 30 – *The Flammable and Combustible Liquids Code*,¹⁰ NFPA 35 – *Standard for the Manufacture of Organic Coatings*,¹¹ NFPA 53 – *Recommended Practices on Materials, Equipment, and Systems Used in Oxygen-Enriched Atmospheres*,¹² and NFPA 77 – *Recommended Practice on Static Electricity*.¹³

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ASTM Standard E1232 and UL Standard 340 prescribe methods of processing the parent liquid to produce the fractionally evaporated remaining liquid. The percentage of evaporation is measured by the weight, volume, and thereby the density of the remaining liquid. Fractional distillation produces both the fractionally evaporated remaining liquid and recovered liquid samples of the evolved fractional vapor's distillate.

Fractional Distillation

Fractional distillation is a process by which components in a chemical mixture are separated according to their different boiling points and vapor pressures. Vapors from a boiling mixture are passed along a column. The temperature of the column gradually decreases along its length. Components with a higher boiling point condense on the column and return to the solution; components with a lower boiling point pass through the column and are condensed and collected.

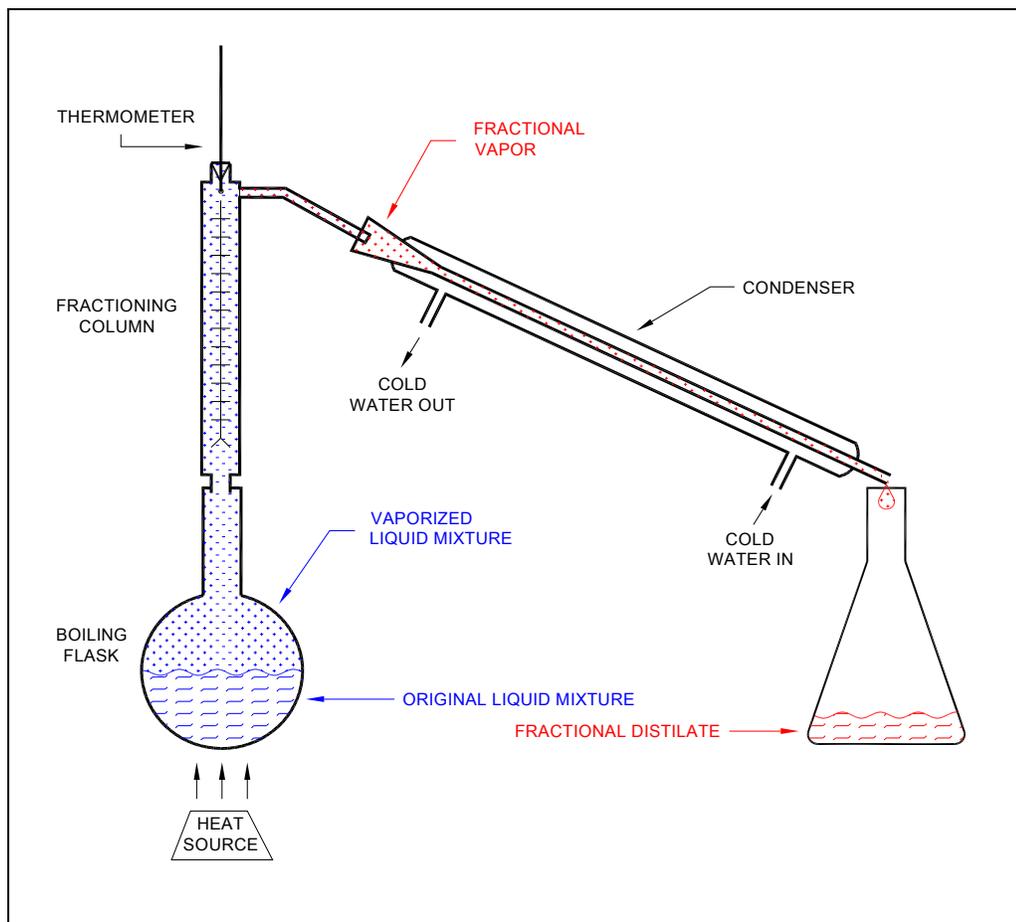


Figure 8 - Typical Fractional Distillation Apparatus

When fractional distillation is used as the medium for creating testable samples, the percentage of evaporation of the parent liquid is determined by volume.

Flash point testing of the resultant fractional distillate and the fractionally evaporated remaining liquid will disclose their relative ignitability. If the distillate has a higher relative ignitability, the

Fractional Vaporization of Ignitable Liquids

basis may have been established for a hypothesis that the vapors from the fractional vaporization had been the first fuel ignited.

Subsequent production of the fractional distillate provides a test medium for incident recreation demonstrations. The resultant fractions are flash point tested and then comparisons are made of the flash points of the recovered distillate fractions, resultant parent liquid, and original parent liquid. Results can then be analyzed to hypothesize the probability of fractional vaporization as a factor in fuel competency.

CONCLUSION

The principle of fractional vaporization of ignitable liquids can serve as a real world explanation of seemingly problematic situations in the analysis of the fuel considerations in fire incidents involving ignitable liquids. This is particularly true where conundrums about the reported flashpoints of the liquids are difficult to resolve.

ABOUT THE AUTHORS

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Dr. Andrew Armstrong is the founder and senior vice president of Armstrong Forensic Laboratory, an internationally recognized laboratory, headquartered in Arlington, Texas. Among its many services, Armstrong Forensic Laboratory provides specialized testing on the detection and identification of ignitable liquids in suspect fire debris. Dr. Armstrong holds a doctorate in chemistry from Louisiana State University. He is an AIC Certified Professional Chemist and a Fellow of both the American Academy of Forensic Science and the American Board of Criminalistics. A member of the IAAI Forensic Science Committee, he is a much sought after expert, consultant, author, and lecturer on forensic chemistry and fire scene chemistry issues.

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Patrick Kennedy is the Principal Expert Fire and Explosion Analyst of John A. Kennedy and Associates, the oldest established fire investigation firm. He is also the senior-most active fire analyst with more than forty-five years of professional fire and explosion investigation experience. Holding a summa cum laude Bachelor of Science degree in fire and safety engineering technology from the University of Cincinnati, he serves as the Chairman of the NFPA Fire Science and Technology Educators Section; a principal member of the NFPA Technical Committees on Fire Investigations and Fire Investigator Professional Qualifications; Chairman of NAFI; and the Director of ISFI.

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ENDNOTES

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