

1 INTRODUCTION

1.1 OBJECTIVES

The goal of this book is to provide information and methods that can be used to estimate the probability of ignition for flammable gas and liquid releases to the external environment. This book and the accompanying software tools discuss technical material that the user should be familiar with prior to use. This book is intended for an audience of engineers and/or scientists who have experience with process safety and risk management systems.

The algorithms that are developed in this book are presented at different levels of sophistication to accommodate a wide range of users, including people in a process hazard analysis team who want an objective but crude prediction for risk ranking purposes or people performing quantitative risk assessments and developing relatively complex risk mitigation plans. Users can adopt the level of complexity and accuracy needed for their particular application with a commensurate level of effort in data input.

The scope of this book is limited to flammable gases, mists, and liquids. The designed application is for onshore facilities, although it may be possible to extend it to offshore applications if the user is able to properly account for the inherent differences between the two settings. This book specifically excludes the treatment of ignitable dusts for various reasons, not the least of which are: (a) the magnitude and physicochemical characteristics of dust clouds are very difficult to quantify for a given situation, particularly for dust “disturbance” events (in which accumulated dust dislodges from the tops of equipment and support structures) and (b) ignition probability data for dust ignitions are very limited at this time.

1.2 MOTIVATION FOR THIS BOOK

Up until the 1990s, many companies maintained groups of process safety specialists whose experience and expertise in different areas allowed in-house problem solving. Often, companies not only maintained safety test laboratories but performed safety research as well. Unfortunately, as safety technology has advanced it has become more complicated and difficult for most companies to apply. This book is intended to assist in-house risk analysts in one of the most difficult areas—estimating the probability of ignition of a given vapor cloud.

The motivation for this book is to achieve the following three primary outcomes:

- A standardized methodology for estimating probability of ignition that is open-source and can be applied consistently across the process industry

- Methods and tools that allow a user to estimate ignition probability quickly
- Ability to account for mitigation measures that reduce ignition probability

On the last bullet above, it is desired that a tool be able to address as many of the elements of the “fire triangle” as possible. In fact, the methods can address all sides of the triangle to varying degrees, but none completely, and all resulting in reductions in ignition probability rather than elimination of ignition altogether.

1.2.1 A Brief History of Fire Protection

Many catastrophic accidents in the process industries have resulted from the ignition of a flammable mass that was released into the environment. For this reason, safety professionals and regulators have continually sought methods to reduce the frequency of such events, and various approaches have been undertaken to accomplish this. Before the implementation of industry standards and codes, professionals used their individual and/or collective knowledge of past events and fire fundamentals to mitigate such events. Even in ancient Rome, the Emperor Nero developed regulations for fire protection after the city burned in A.D. 64. The Roman regulations included requirements for fire-resistant building materials and the use of separation distances, concepts that are still in use today.

The evolution from this knowledge-based approach into a series of industry-driven standards and codes occurred in order to share knowledge of flammable hazard management and to introduce standardized methods for dealing with flammable hazards. Not surprisingly, the nascent insurance industry of the nineteenth century promoted this initial effort, and various professional organizations were created in the twentieth century such as the National Fire Protection Association (NFPA), Society of Fire Protection Engineers (SFPE), and others in the U.S. and overseas. These organizations were instrumental in developing the field of flammables management.

The science of ignitions in the petroleum, chemical, and other industries developed in parallel. Klinkenberg and van der Minne (1958) provide references on static electricity in the industry that date back to the 1910s. The U.S. Bureau of Mines had a leading role in progressing knowledge in this area in the same time frame. Through these efforts and contributions by others in industry, advancements in both the theory and experimental support for these phenomena were made through the middle of the twentieth century.

As the chemical and petrochemical industries matured and grew, the potential for fires and explosions of ever-greater magnitudes also grew, and some tragic events such as those in Flixborough, Piper Alpha, Mexico City, and Pasadena drove regulators to become more intimately involved in the management of flammable hazards. In the U.S., the promulgation of the Occupational Safety and Health Administration’s “Process Safety Management of Highly Hazardous Chemicals” standard in 1992 set the stage for the regulation of such hazards,

although the standard is largely built on and refers to the industry efforts that preceded it.

1.2.2 The Development of Risk-Based Approaches to Flammables Management

The most recent evolution of flammables management is the use of risk-based approaches. In a risk-based approach, the expected frequency of a fire or explosion is quantified and combined with the predicted outcome of the fire/explosion to determine the risk of a potential hazard. To some extent, this evolution has been driven by the increasing availability of the computing power required to perform detailed analyses for thousands of scenario combinations that can be present in a modern process industry facility. This was also coincident with a rise of risk-based “culture” and risk-based regulations in Europe in particular.

The development of the quantified risk-based methodologies in recent years has been accompanied by tremendous advancements in the theory, tools, and software available to predict the consequences of fires and explosions. Although the methods for consequence analysis continue to improve, one can argue that the methods for consequence analysis are fairly mature and thus address half of the “risk equation”:

$$\text{Risk} = f(\text{Consequence, Frequency})$$

or, in terms familiar to practitioners of layers of protection analysis:

$$\text{Risk} = \text{Consequence} \times \text{Frequency/Risk Reduction Factors}$$

The frequency side of the risk equation seems simpler conceptually and does not need to invoke Gaussian plume or computational fluid dynamics or other relatively higher mathematical solutions. In spite of this, or possibly because of this, the frequency of events has been a relatively neglected science. Now that is changing; because some regulators (mainly outside North America) require companies to perform quantified risk assessments, the regulators themselves have started to undertake standardization of frequency inputs to such studies. For example, some risk analysts are required to use specific values for the frequency of a leak of size X from a pressure vessel. While there is broad consensus on the values of many of these numbers in a “generic” situation, some inputs such as ignition probabilities are very situation-specific and so should be handled with greater rigor in many situations than is generally practiced.

Improvements to previous frequency/risk calculation methods are also timely given that the American Petroleum Institute (API) Recommended Practice 752 on building siting (API, 2009) permits use of risk as a basis for making building and personnel location decisions. Since the risk calculation for flammable events invariably incorporates a probability of ignition, greater precision and consistency in estimating this value are needed to ensure that risk assessments are both technically accurate and performed consistently across industry. Among other

purposes, this book is therefore intended to provide new tools for users to comply with this API recommended practice and can be considered as a companion document to the CCPS book *Guidelines for Evaluating Process Plant Buildings for External Explosions, Fires, and Toxic Releases* (CCPS, 2012) as well as a supplemental resource for the CCPS book *Guidelines for Enabling Conditions and Conditional Modifiers in Layer of Protection Analysis* (CCPS, 2013).

1.2.3 Difficulties in Developing Ignition Probability Prediction Methods

From a mathematical point of view, determining ignition probabilities would seem to be a straightforward problem to solve—simply collect information or perform tests on events where flammables have been released and document the instances in which an ignition took place. However, the execution of this strategy is problematic from multiple perspectives, discussed next.

1.2.3.1 Data Bias

The simplest form of data analysis to develop ignition probability predictions is the following:

$$\text{Probability of Ignition} = \text{Observed Ignitions} / \text{Observed Flammable Releases}$$

There are numerous cases in which an event that resulted in a major fire or explosion has been documented in some form or another, especially in modern times. Thus there is some room for optimism in believing that the numerator for the equation above can be quantified with some level of confidence.

The denominator is another story. Ideally, releases that did *not* result in a fire or explosion should be documented with the same rigor as those that did. However, there is a much greater chance that a release that did not ignite will not be documented in an ignition database. It may be documented in other contexts, for example, for environmental reporting requirements. But it is much less likely that this data point will be delivered to someone developing an ignition probability database. Therefore, there could well be a bias toward concluding that ignition probabilities are greater than they actually are.

1.2.3.2 Experimental Problems

In the case of consequence model development, the industry has (at some considerable expense) conducted field test releases, fires, and explosions and measured the outcomes. Thus there are documented experiments that define the basis and calibration for the better consequence models that are available today.

In contrast, it is difficult to conduct experiments in ignition probability under controlled, real-life conditions. For example, no plant management could very well allow experimenters to perform dozens or hundreds of releases of a flammable mass into their unit to collect information on how many times an explosion resulted. A laboratory environment may be suitable for determining

ignition probabilities for releases as they encounter a specific ignition source but can hardly be expected to replicate the hundreds of potential ignition sources available in an operating process plant.

1.2.3.3 Expert Opinion

There is a balance between what can be developed deterministically and the cost of doing so. The difficulty in obtaining objective ignition probability data has led many experts to propose values based on their personal experience. Such information can be valuable. However, it tends to suffer from two opposite problems: (a) widely different experiential outcomes dependent on context that is local to the individual observer and (b) replication of opinions in the literature, so that what appears to be a number of sources of the same probability value may in fact originate from some single source that may be lost in the sands of time.

For these reasons, the science of ignition probability estimation is not as developed as other risk input methodologies. As a result, risk analysts are often compelled to use ignition probability values that are very broad in nature (e.g., “immediate ignition probability of a light hydrocarbon” ~ 10%), whereas it is possible to envision one scenario fitting this description where the ignition probability is virtually nil (weeping flange leak from a remotely located butane bullet) and another scenario fitting this description where the ignition is almost certain to happen (release of a heavy hydrocarbon from a hydrotreater that is operating at a temperature well above the autoignition temperature).

1.2.3.4 “Conservatism”

Risk analysts generally try to use inputs that err on the side of conservatism to compensate for potential unknowns and uncertainties. However, “conservatism” is a difficult concept to apply to ignition probabilities, since choosing a “conservatively” high value for immediate ignition may lower the probability of a delayed ignition whose consequences could be much worse. Similarly, high ignition probabilities may preclude toxic outcomes that are more severe. This important concept is discussed in further detail in Section 4.1.2.

1.2.4 Missing Variables

An additional shortcoming of currently available ignition probability data is that there are variables that are known or suspected to be important but which are not easily quantified. Examples include the impact of the rate of ventilation in indoor releases or the effect of different electrical classification types in the area into which the material is released.

1.2.5 Summary of Industry Needs and Path Forward

The net effect of these and other shortcomings is not only a lack of information but also somewhat inaccurate risk analyses. It also means that risk managers have a greatly reduced set of risk mitigation options in their toolkit. For example, a risk

manager may feel strongly that prohibiting vehicular traffic near a unit will reduce the risk. However, in the absence of quantitative justification of this conjecture, the risk manager will be unable to justify spending the money to implement the change. Thus it can be imagined that prudent risk reduction measures would not be undertaken without a recognized basis for doing so.

For this reason, the effort documented in this book has sought to expand upon both the accuracy and range of variables that can be considered in making an ignition probability estimate. The presumed accuracy of the methods in this book is discussed in Section 4.1.1.

There have been some notable efforts in recent years in developing ignition probability prediction methods. This book provides the reader with additional information on variables that have not been treated adequately up to this point and additional insights to many that have. As noted in the previous paragraph, this is not simply an issue of developing a more accurate tool to quantify risks in absolute terms; it is also critical to provide as many tools to the risk manager as possible to facilitate *reducing* the risks associated with flammable releases.

1.2.6 Applications for This Book

Estimates of ignition probability are useful in situations ranging from semiquantitative methods to conducting fully quantified risk analyses. The former typically require only crude levels of accuracy but are undertaken in situations where minimal effort can be justified to obtain the number. The latter requires a higher degree of accuracy, and the analyst should be willing to expend a little more effort to achieve that accuracy. This book is designed to satisfy a wide spectrum of users, allowing each user to expend the amount of effort necessary to achieve the level of accuracy desired.

While the potential applications of the tools in this book are considerable, the expected uses include the following (in increasing order of sophistication):

Process Hazards Analysis (PHA)—In PHA studies, teams frequently are asked to develop low-resolution measures of the risk associated with a particular scenario. For flammable releases, implicit in the estimate of event frequency is the probability that a release will result in a fire or explosion. The risk matrices commonly used for risk ranking in PHAs are usually delineated by order-of-magnitude levels of risk, and so the accuracy needed is minimal. The “Level 1” analysis as described in this book addresses this kind of application.

Layers of Protection Analysis (LOPA)—In LOPA studies, the probability of ignition is frequently used as a “conditional modifier” in assessing the frequency of a particular event outcome. The level of accuracy desired is greater than that needed for a PHA but only needs to be commensurate with the level of accuracy of the other inputs to the analysis. A “Level 1” or “Level 2” analysis as described in this book is appropriate for this application.

“Screening-Level” Quantitative Risk Assessment (QRA)—In QRAs, a yet higher degree of accuracy is desired, in order to be consistent with the level of effort and accuracy associated with the consequence side of the risk calculation. Other applications that are highly quantitative (e.g., determining optimal gas detector layout) will also benefit from a higher level of ignition probability accuracy. A “Level 2” or “Level 3” analysis as described in this book is justified for these applications.

“Detailed” Quantitative Risk Assessment—Some QRAs offer features that raise issues beyond those normally encountered in such studies. These include cases such as indoor flammable releases, where the ventilation rate or other factors not often described in existing literature are encountered. In these cases, a “Level 3” review as described in this book may be necessary.

1.2.7 Limitations in Applying the Approaches in This Book

This book provides useful algorithms for the purposes of predicting ignition probabilities in “typical” situations. However, in some atypical cases, the knowledge of the local plant staff in predicting ignition probability will be superior to that of any algorithms that could be developed. These include situations where the chemicals being released are pyrophoric or otherwise will react in the environment. Britton (1990a) describes the many nuances associated with the potential ignition of silanes and chlorosilanes, for example. Other situations include cases where the process operates under ultrasevere conditions, the chemicals decompose upon release, or the situation involves unusual chemicals or intermediates whose behavior is known only to company staff.

The methods described in this book should generally be applicable to normal plant layouts and operating conditions, for common chemicals such as hydrogen, hydrocarbons, and others that are not self-reactive or air-reactive. However, this book is not capable of anticipating all the possible physical and chemical influences that could be relevant to ignition of released masses.

Software users should have detailed knowledge of the areas where the software is being used for modeling. This will enable the user to account for the actual ignition sources and electrical classifications in these areas. This may require users to visit the areas where the releases are being modeled and to check out electrical classifications and ignition sources. The correct inputs are required to obtain the useful results from the software.

The algorithms may also be limited in accuracy in situations where the layout or operation of equipment is different than the typical range of operations in an onshore process plant. Thus users might find shortcomings in these tools as they are applied to offshore facilities or to releases during transport by ship, truck, or rail, for example.

It should also be noted that this tool is intended to predict the probability of ignition *given the precondition that a flammable cloud can reach an ignition*

source. There are several reasons a flammable vapor cloud may not contact an ignition source, for example:

- The release rate is very small.
- The release is of a low-volatility liquid.
- The release is in a remote location.
- Drainage is present that directs a liquid spill away from ignition sources.

In cases such as these, the results of the models in this book are expected to have a higher degree of uncertainty, and the results should be used in conjunction with an event tree, augmented by a dispersion model and/or field walkdown, which describes the potential for ignition source contact.

Therefore, the tools described here should be used thoughtfully and need not be used for all possible circumstances. It is presumed that the user of the book is experienced enough in process plant operations to recognize situations in which the tool may, or does, give results that clearly do not reflect common experience for their chemicals, processes, and specific circumstances.

The product of this book is a set of algorithms that have been checked against the available literature and the experiences of people representing hundreds of years of plant operating experience in the aggregate. It is recognized that other models exist and in some cases coded into QRA and other software packages, and the developers of those models may consider their methods to be superior for the intended applications (which may be different than the scope of this book). Where this book provides enhancements to existing models, it may be possible to incorporate elements of this book into other, existing, models without using the entirety of the book. This should be done with appropriate care and testing of the result, since the methods in this book have been tested as a complete package and for a presumed experienced user.

1.3 IGNITION PROBABILITY OVERVIEW

1.3.1 Theoretical Basis for Ignition

1.3.1.1 What Is “Ignition”?

A logical first step in developing the basis for ignition probability is to define “ignition.” The International Organization for Standardization (ISO, 2008) defines ignition as “initiation of combustion.” Babrauskas (2003) notes that “combustion” is often not defined at all in texts dealing with it; he proposes a very simple description of combustion as “a self-sustained, high-temperature oxidation reaction.” The NFPA (2012) defines it as “a chemical process of oxidation that occurs at a rate fast enough to produce heat and usually light in the form of either a glow or a flame.” For the expected applications of the users of this book,

“ignition” is defined as “the sudden transition to a self-sustained, high-temperature oxidation reaction.”

This simple definition is suitable for the purposes of this book and eliminates events such as low temperature/rate oxidation reactions (e.g., rusting) or transient oxidation reactions [e.g., oxidation above the upper flammable limit (UFL), oxidation of “dry” CO] that are not of interest to us because they are not likely to be associated with severe-consequence scenarios.

1.3.1.2 How Does Ignition Occur?

Ignition can occur as the result of “autoignition” or “forced” ignition (Babrauskas, 2003), and in some cases, materials can self-ignite. As mentioned in another CCPS book (1993; page 318):

Apart from obvious ignition sources such as flames, several disparate groups of sources can be considered. These are:

- *Moderate temperature sources that may give rise to spontaneous ignition.*
- *Electrical sources such as powered equipment, electrostatic accumulation, stray currents, radiofrequency pick-up, and lightning.*
- *Physical sources such as compression energy, heat of adsorption, friction, and impact.*
- *Chemical sources such as catalytic materials, pyrophoric materials, and unstable species formed in the system.*

Ignition sources are often considered only in the context of the “fire triangle,” whose sides comprise a fuel, an oxidant, and an ignition source (the three essential ingredients for most fires). However it is important to recognize that some materials can be “ignited” in the absence of an oxidant. Examples include acetylene and ethylene oxide (decomposition flames), and some metal dusts (reaction with nitrogen). Also, under process conditions, some materials may be “ignited” in the absence of oxidant even though at ambient conditions they may have a significant limiting oxidant concentration (LOC). An example is ethylene at elevated temperature and pressure (Britton et al. 1986).

Figure 1.1 illustrates an autoignition temperature-pressure diagram. For the purposes of this book, only the portion at atmospheric pressure is relevant, and only parts of this since the users of this book are assumed not to be interested in “cool” flames. Autoignition aside, ‘point’ ignition via a spark or other energetic source results in a reaction in which the local rate of energy release exceeds the rate of heat losses, with the result that the flame can propagate. The time scale for spark heating is on the order of 1 microsecond, with temperatures on the order of 55,000 °F (30,000 °C). This should be considered separately from “bulk” ignition such as autoignition, where ignitable mixtures are heated slowly.

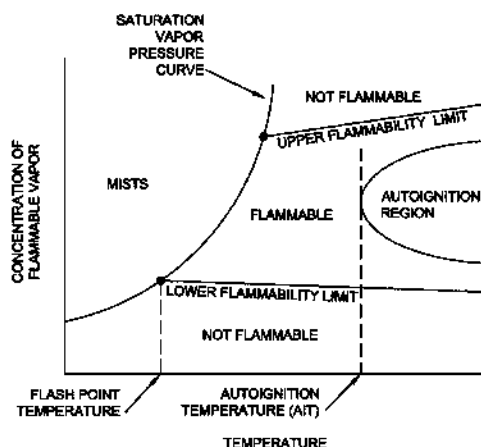


Figure 1.1. Relationships between various flammability properties (Crowl, 2003; adapted from Kuchta, 1985).

It must be recognized that many of the “ignition” examples are beyond the scope of this book to address quantitatively, and the user should not use this book to justify, for example, the use of a low ignition probability for the release of a pyrophoric material. Of primary interest in the scope of work of this book are autoignition and forced ignition, described in further detail next. In autoignition, the flammable mixture is present at a temperature hot enough to initiate and sustain the oxidation reaction. Forced ignition, on the other hand, requires a separate “agent” that supplies heat or energy.

Autoignition—Autoignition “is the result of self-ignition from any initial condition (temperature, pressure, volume) at which the rate of heat gain exceeds the rate of heat loss from the reacting system” (CCPS, 1993). It is difficult to define in real-life terms, since a flammable mixture simply does not transition from “no reaction” to “complete reaction” by increasing its temperature by some trivial amount. It is also a property that is difficult to predict using other readily available physical property measures such as boiling point, as illustrated in Figure 1.2.

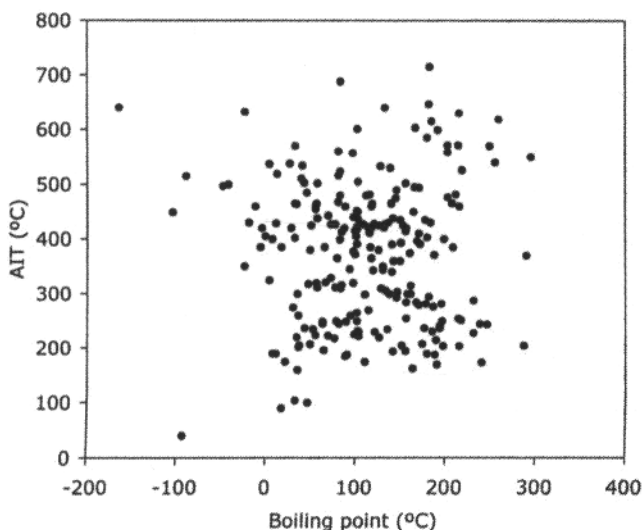


Figure 1.2. Nonrelationship between AIT and boiling point (Babrauskas, 2003).

Autoignition temperature (AIT) is a function of the oxidation reaction kinetics and can be related to some extent to the molecular structure of the chemical (such as the degree to which there is branching in the molecule). Babrauskas (2003) notes an example of the branching of two octane isomers—normal octane and isooctane. The former has a relatively low AIT of 220 °C and the latter has an AIT of 415 °C. This dependence of the AIT on the degree of molecular branching has been described by Zabetakis (1965) for some classes of compounds and is illustrated in Figure 1.3. Although dated, this seminal reference is still readily available and covers a broad range of flammability issues.

The effect of chain length on AIT has been ascribed to the influence of chain length on the frequency of chain breaking into radicals. This can also be related to the “cetane” and “octane” numbers used to describe the performance of diesel and gasoline engine fuels, respectively. Kinetic theory says that increased temperature increases the probability that a molecule will be provided with sufficient energy to break apart and subsequently take part in radical reactions with oxygen.

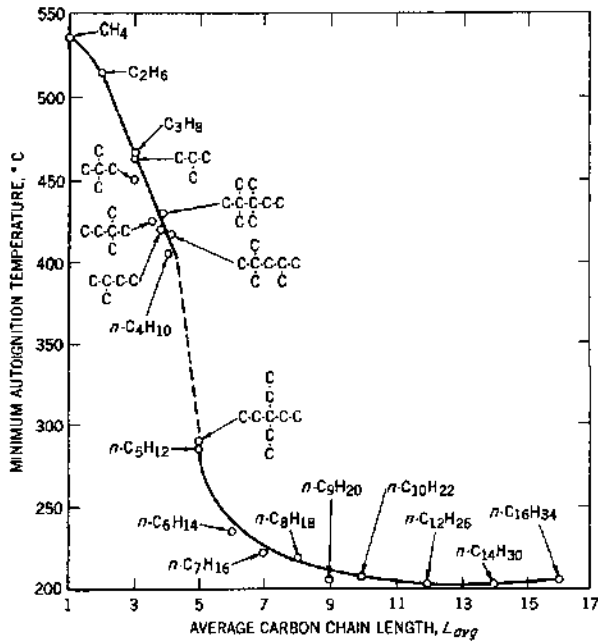


Figure 1.3. AIT as a function of chain length (Zabetakis, 1965).

Other Self-Induced Ignition—A likely source of immediate ignition for released flammables is static discharge. In this case, the movement of the process fluid through a pipe or other equipment prior to discharge may be greater than the normal flow, thus generating electrical charges that are greater than were anticipated by the designers. Upon release, this charge may be imparted to the released material.

Britton and Smith (2012) provide a detailed methodology for assessing charging currents caused by flow of low-conductivity liquids. Appendix A is helpful for identifying “static accumulating” liquids. Methods are presented for assessing the probability of ignition. Flash point safety factors are given and it is shown how the decreased ambient pressures associated with high elevations (such as in mining operations) can be accounted for, both for single-component liquids and complex mixtures such as diesel oil.

Forced Ignition—Ignition of a flammable mixture can obviously occur if there is a preexisting flame present. Note that all flames are not sufficient to the task. For ignition to occur, the flame must:

- have a sufficient temperature
- be of sufficient size and shape
- be applied for a sufficient time

The required flame application time may be on the order of milliseconds but may also be substantially longer.

If a sufficient flame is not present, the ignition must be “forced” in some other manner. The simplest forced ignition is supplied by a hot surface. An electrical discharge, while hot, also provides excited chemical species that can aid in propagating the combustion reaction. A spark can be provided by supplying a sufficient voltage or by opening or closing an electrical contact—for example, if an electrical supply wire is broken through mechanical damage.

The most effective spark ignition sources are when the sparks are delivered quickly (microseconds) and over a limited space (“point source”). Little energy may be needed; the energy required for ignition is often under 1 millijoule (mJ). However, applications of larger energies may not be sufficient if the energy input is too spread out over time. In process plant releases, the time issue is generally not of concern with respect to the energy source, since the energy sources tend to be sustained for some period during an emergency event. Time may still be a relative variable, however, but more with respect to the duration of a release and its ability to find an ignition source in the time available.

1.3.2 Key Ignition Factors Related to the Properties of the Fuel and Available Surrogates That Can Be Used for Developing Probability of Ignition Predictions

A number of chemical properties are significant in determining the propensity of a release to ignite. These properties have been determined experimentally for many chemicals, but not all. For the purposes of developing a predictive tool, the following text discusses those factors that are relevant as well as the availability of data for a broad spectrum of chemicals. It should be noted that while the factors that follow are relevant, some are not included in the subsequent model development, generally because the variable is closely related to one or more other variables that are being used and so does not need to be repeated.

Where data is not readily available for some chemical properties, more widely available chemical properties are proposed as surrogates. The CHETAH program of ASTM International (ASTM, 2011) calculates various flammability parameters for hydrocarbons (C+H) and molecules containing C+H+O atoms (alcohols, ethers, ketones, etc.). The same methodology is applied to organic C+H compounds that contain nitrogen atoms (amines, etc.) but with less accuracy.

Estimates are allowed for lower flammable limits of some chlorinated organic species.

Mixtures of chemicals introduce another level of complexity. The treatment of mixtures is discussed in Section 2.10.2.

1.3.2.1 Flammability Limits

Most fuels will burn only within a given range of concentrations in air. If the fuel mixture is too “rich,” there is not enough oxygen available to initiate combustion. If the fuel mixture is too “lean,” not enough fuel is available. The importance of the flammability limits to the ignition probability question lies in the size of the cloud that is in the flammable range. If the flammability range is very broad, the resulting dimensions of the flammable cloud are also very large (given all other things being equal).

Note that the flammability limit varies with the temperature of the chemical, becoming broader at higher temperatures. However, for most chemicals the effect of flammability limits is not as great as for some other chemical properties, and hence the impact of temperature on this flammability limit is small enough that it can be neglected, inasmuch as temperature is incorporated directly as an input for other reasons. It is also true that, in contrast to a laboratory flammability test, a release into the open environment will present a range of concentrations such that if the process stream is flammable at all, it will pass through the flammability range during its dispersion.

Lastly, many of the applications for this tool such as QRA will also involve use of dispersion models. It must be remembered that such models may have something like a factor of two accuracy, and any given dispersion may be nonuniform—with pockets of flammability beyond the predicted lower flammable limit (LFL), or places of nonflammability within the predicted LFL distance. For this reason, many models have outputs that report $\frac{1}{2}$ LFL distances as well as LFL. It is not within the scope of this book to discuss whether the ignition probability models here should be applied to LFL or $\frac{1}{2}$ LFL or some other endpoint. This is a decision left to the user, knowing the larger context and conservatism built into the other methods used in the combined analysis.

1.3.2.2 Flash Point and Flame/Fire Point

The more widely used of these two terms, the “flash point,” is defined as the lowest temperature at which a liquid produces a flammable vapor (has a vapor pressure that produces a vapor concentration equal to its LFL concentration). The flame (fire) point may be a better measure of the propensity to ignite, however, as it is defined as the lowest temperature at which a liquid creates a *continuous* flame. In any case, it must be noted that neither flash point (“open cup” or “closed cup”) nor flame/fire point measurements are perfect reflections of behavior in an open-air release; for our purposes they are merely surrogates that are intended to describe a relative tendency to ignite.

The Society of Fire Protection Engineers provides some overview and background data, although not probability data, in their “Handbook of Fire Protection Engineering” (SFPE, 2008). Specifically, physical property data such as flammability ranges, autoignition temperatures, flash points, and more are included. In addition, there is a discussion of the basis for ignition of liquids, and the relationship between flash point and fire point, illustrated in Table 1.1.

The physical basis for differences in these values relates to the manner in which the tests are conducted. The closed-cup flash point apparatus allows vapor to accumulate above the liquid until it reaches equilibrium, whereas the open-cup apparatus allows the vapor to diffuse away. Thus the latter produces higher ignition temperatures. Higher temperatures still are required to reach the “fire point,” which consists of a self-sustaining diffusion flame. The fuel-rich fire point flame can be contrasted with the lean flames developed for the flash point tests; in the flash point tests the flammable vapors are completely consumed and not sustained.

The flame/fire point is not available for many chemicals, however. Fortunately, although there are significant exceptions, the flame/fire point is typically 5–15 °F higher than the flash point (closed cup). Therefore the flash point is chosen as a reasonable surrogate to the flame/fire point. In turn, several investigators over the years have explored the relationship between flash point and boiling point. A good synopsis of this work is described in Catoire and Naudet (2004), which points toward an example of a correlation that is accurate enough for the purposes of this book that boiling point might be used as a surrogate variable in place of flash/fire point. Alternatively, the flash point might be predicted using methods such as those described in Rowley et al. (2010).

That said, there are difficulties in using boiling point—for example, when mixtures are involved. In these cases it is typical practice to pick the temperature at which the most volatile 10% of material has flashed, although this is imperfect.

Table 1.1. Some values of closed-cup flash point, open-cup flash point, and fire point temperatures (SFPE, 2008)

| | Closed-Cup FP | Open-Cup FP | Fire Point |
|-------------------------|--------------------------|---|---|
| <i>n</i> -Hexane | -22 °C [-8 °F] | N/A | N/A |
| <i>n</i> -Heptane | -4 °C [25 °F] | -1 °C [30 °F] | 2 °C [36 °F] |
| Methanol ^(b) | 12 °C [54 °F] | 1.0, 13.5 ^(a) (°C) [34, 56 ^(a) °F] | 1.0, 13.5 ^(a) (°C) [34, 56 ^(a) °F] |
| <i>p</i> -Xylene | 25 °C [77 °F] | 31 °C [88 °F] | 44 °C [111 °F] |
| <i>n</i> -Butanol | 29 °C [84 °F] | 36 °C [97 °F] | 36, 38, 50 (°C) [97, 100, 122 °F] |
| <i>n</i> -Nonane | 31 °C [88 °F] | 37 °C [99 °F] | 42 °C [108 °F] |
| JP-6 | N/A | 38 °C [100 °F] | 43 °C [109 °F] |
| <i>n</i> -Dodecane | 74 °C [165 °F] | N/A | 103 °C [217 °F] |
| Fuel oil no. 2 | 124 °C [255 °F] | N/A | 129 °C [264 °F] |
| Glycerol | 160 °C [320 °F] | 176 °C [349 °F] | 207 °C [405 °F] |

N/A = Not available

^(a)The lower value was obtained from ignition by a pilot flame; the higher number is from ignition by a spark.

1.3.2.3 Vapor Pressure

The vapor pressure of a material is a function of the chemical itself and the temperature at which it is released. This material property describes its propensity to vaporize if it is released in liquid form and thus is a key factor on how large a vapor cloud could become—which in turn relates to the odds that it will encounter an ignition source.

Since the vapor pressure is dependent on the chemical's temperature, using vapor pressure as an explicit input to an ignition model would require building vapor pressure/temperature curves into the model for the large number of chemicals potentially of interest. For this reason, the chemical's boiling point (a readily available property) relative to its release temperature (known by the

analyst) is used as a surrogate for vapor pressure. The treatment of mixtures in this regard is discussed Chapter 2.

1.3.2.4 Autoignition Temperature (AIT)

Also known as the “ignition temperature” or the “spontaneous ignition temperature,” the AIT is the temperature at which a material will ignite in the absence of an external ignition source. It presumably is the point at which a fire is guaranteed to happen and an explosion is guaranteed not to happen (since there is no time for an unignited cloud to accumulate).

However, the reality of AIT is not as clear as that. The measured AIT has a number of shortcomings related to predicting the actual spontaneous ignition of a chemical, including:

Test Apparatus Variability—The test apparatuses used for measuring AIT vary considerably, with container surface effects greatly affecting the results. Therefore the AIT values reported for individual chemicals can vary by 200 °F or more. Usually the effect is that a chemical has to be at a temperature that is considerably higher than the reported AIT in order to actually autoignite, since the medium into/onto which a material is released will cool the release. The API Risk-Based Inspection protocol (API, 2008) takes this into account by assuming that AIT has no effect on ignition probability until the release temperature is 80 °F higher than the reported AIT. However, it should be noted that, in principle, if a released cloud is *confined* in a hot space larger than the test apparatus used to measure AIT, the actual AIT could be lower than measured.

Surface Encountered—There are cases where autoignition has been reported at temperatures below the AIT. This is generally attributed to a hot liquid release encountering a high surface area space, such as might be present as insulation on a high-temperature vessel. This can also happen if the release reacts with the surrounding surface (e.g., rusty steel). These situations are quite dissimilar to an AIT test apparatus, which is typically a clean, smooth surface.

The AIT is clearly an important factor in the ignitability of a flammable release. However, since it is an imperfect measure in the real world of a release, it is not treated as a discrete value above which ignition is 100% certain and below which autoignition is impossible. Rather, it is assumed that there is a range of temperatures above and below the reported AIT at which autoignition can actually occur. Appendix A provides AIT values for some common industrial chemicals.

1.3.2.5 Minimum Ignition Energy (MIE)

The MIE is the most significant chemical property in the forced ignition of a flammable mixture. As with AIT, the MIE is not readily relatable to commonly available physical properties. In fact, about the only other parameter to which it is reliably related is the “quenching distance,” which is itself a comparatively arcane measure of the “minimum dimension that a flame kernel must acquire in order to

establish a freely propagating flame” (Babrauskas, 2003) in order to avoid self-extinguishment due to having greater heat losses than heat gain.

Probably the most useful relationship between MIE and another chemical property is that by Britton (2002), who correlated MIE to the heat of combustion per mole of oxygen consumed. This correlation is explored further in Chapter 2. MIE may also be related to more fundamental chemical properties such as the Lewis number (ratio of thermal diffusivity to mass diffusivity) and activation energy (Tromans and Furzeland, 1986).

There is a broad range of MIE values among commonly used chemicals (having typical MIEs > 0.2 mJ), with hydrogen (MIE ~ 0.017 mJ) being on the extreme low end. However, such disparities in MIE may not be as significant as they appear at first glance. Dryer et al. (2007) note that the MIE for hydrogen (like other materials) occurs near the stoichiometric concentration—which is 29 volume % in air. However, at the LFL, the MIE “is more similar to that of methane” (Dryer et al., 2007). Appendix A provides some reported MIE values that range almost six orders of magnitude.

1.3.2.6 Multiple Release Phases

The phase of the material being released is relevant for two primary reasons. Most obvious is the need for the discharge to be a vapor, form a vapor, or be sufficiently atomized to have access to the oxygen necessary for ignition.

However, the phase is also important with respect to electrical charge buildup. The Occupational Safety and Health Service (OSHS, 1999) notes that “pure gases discharged at high velocity through jets under conditions where neither liquid droplets nor solid particles are present, seldom acquire sufficient static charge to result in ignition. However, when the gases contain liquid droplets or solid particles, or when these are formed during the discharge, sufficient charges can accumulate to ignite flammable vapours present.”

Thus streams that form droplets during discharge, such as liquefied petroleum gas (LPG), or releases that are accompanied by particulates discharged from the same equipment are more prone to static ignition than they might otherwise be based on their chemical properties alone. Static development on droplets or particulates can also explain anecdotes such as ignitions caused by application of water sprays and carbon dioxide intended to blanket flammable releases. Static formation on particulates may also help explain the highly disparate anecdotal evidence for either high or low probabilities of ignition of hydrogen.

1.3.2.7 Summary of Chemical Property Factors

In order to minimize the effort for the user, it is useful to reduce the number of variables that are input as much as practical without greatly affecting the accuracy of the results. For this reason the flash/fire point and vapor pressure factors discussed above will be “bundled” into a single variable that is dependent on the

normal boiling point or flash point of the material. The flammable range of a material is also assumed to be indirectly bundled into the boiling/flash point factor according to arguments made in Chapter 2. However, AIT and MIE are not reducible to more common physical measures and so will be utilized as is.

1.3.3 Key Ignition Factors Related to the Release Source

Many of the variables that follow depend to some extent on how the release event unfolds and the physical layout near the point of release. The major relevant factors are discussed next.

1.3.3.1 Release Rate

Previous incident data indicate that the larger the release rate, the greater the probability of both ignition overall and explosive ignition. Presumably this is related at least in part to the simple fact that the greater the release rate, the greater the size of the flammable cloud that results, and hence greater opportunity to reach ignition sources. A greater release rate may also be associated with greater static formation, discussed later.

1.3.3.2 Release Pressure

The release pressure is obviously related to the release velocity, finer aerosolization of liquids, and the potential for static discharge near the source. These features are presumed to represent the key influences of pressure on ignition probability, at least for liquid or two-phase releases, with higher pressures leading to higher chances of ignition.

The situation for vapor releases may be more complex. There are anecdotal indications that higher pressures lead to higher chances of ignition; the ignition mechanism in this case may result from electrical buildup on particles (e.g., scale) that are discharged with the vapor. However, there is a potential countereffect of high pressure, namely, the potential for an incipient flame to be “blown off” the end of the flammable cloud. In principle, this could occur when the flame speed of the flammable gas is less than the velocity of the flammable gas jet leaving the release source. In practice this phenomenon has been observed by Swain et al. (2007) and others and is discussed further in Chapter 3.

Another possible mechanism for ignition at low pressures is suggested by Britton (1990a). This mechanism presumes that pyrophoric solids are present at the point of discharge but are not exposed to air unless the release velocity is very low, typically, at the end of a release event. At the low pressures, air entrainment (dilution) is reduced, and the pyrophorics may be exposed to air that migrates into the equipment that is the source of the release.

1.3.3.3 Release Temperature

Aside from the obvious importance of release temperature relative to the AIT, the temperature has other influences on ignition potential; among them:

- Increased temperature often broadens the range in which a cloud is flammable or otherwise lowers the threshold for ignition to take place.
- The temperature influences the degree to which a liquid or two-phase release will vaporize and to a lesser degree affects the buoyancy of a gas cloud.

1.3.3.4 Event Duration

For a given release rate, a longer duration event may be more likely to ignite than a short duration event because: (a) there will be greater opportunity for the ignition sources to act upon the vapor cloud and (b) the vapor cloud itself may be larger and thus cover more ignition sources until it reaches its maximum profile. There is probably a time limit beyond which an ignitable cloud will not ever ignite—that is, given the conditions for ignition that last for 10 minutes or so without ignition, the event most likely will never ignite for reasons that are outside the ability of this book to quantify.

1.3.3.5 Static Discharge At/Near the Point of Release

The environment at or near the point of release is critical, primarily in determining whether immediate ignition occurs or not. The configuration of the equipment feeding the release and the geometry of the release hole are important (along with the fuel ignition properties) in determining whether a static discharge occurs that ignites the release at the source. Perhaps indistinguishable in impact, but also important, is whether any static or other ignition sources are present in the immediate vicinity of the release. The issue of static discharge is an important one that is discussed in further detail below.

Static Ignition—Two excellent books on the subject of static ignition hazards have been published by CCPS (Britton, 1999; Pratt, 2000). A synopsis of these, as they apply to the ignition of released flammable masses, follows.

Britton provides a summary of typical ignition sources and energies, and their applicability to a variety of flammable masses (Figure 1.4).

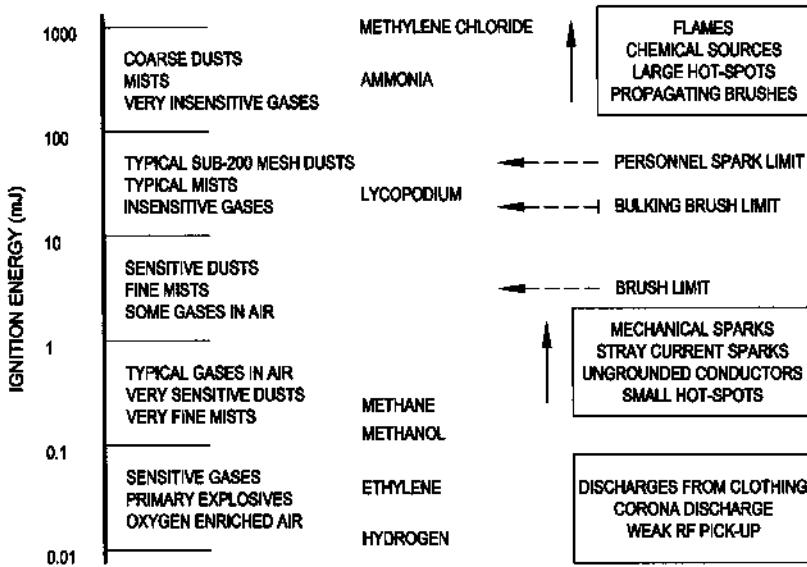


Figure 1.4. Ignition energies of various materials and types of ignition source that may ignite them (updated from Britton, 1999).

Most of the materials of interest to the readers of this book have ignition energies under 1 mJ, and the focus of this book is therefore on those situations. Although other ignition sources exist (e.g., lightning), they are generally not relevant to this work because they are transient events that have a very small probability of occurring coincident with a flammable material release.

The differences between the various types of static discharge are very briefly discussed next, largely based on illustrations in Pratt and Britton. The reader is invited to review these books for a much more thorough understanding of this subject.

Corona Discharge—Figure 1.5 and Figure 1.6 depict a corona discharge. Corona discharge occurs when a sharp point is present in the air near a charged surface, inducing ionization in the air. By definition, the charges are diffuse, and so this ignition source is capable of igniting only the most sensitive chemicals.

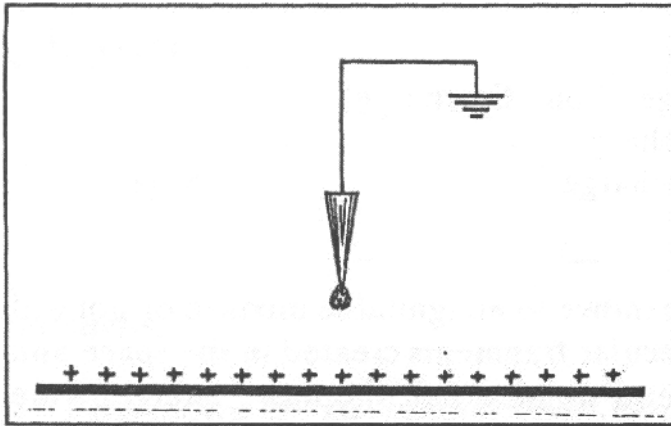


Figure 1.5. Corona discharge (Pratt, 2000).

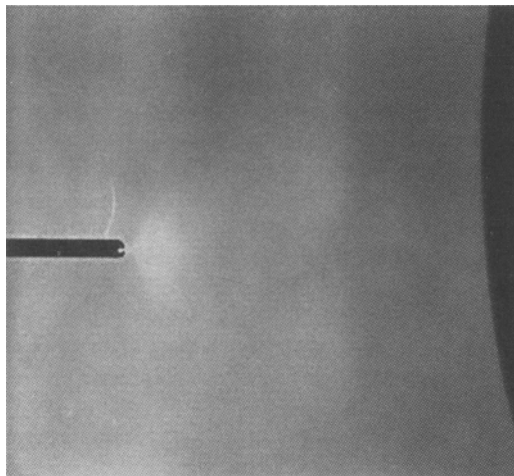


Figure 1.6. Corona discharge in point-sphere gap (Britton, 1999).

Brush Discharge—Brush discharge is illustrated in Figure 1.7 and Figure 1.8.

In contrast to corona discharge, the electrode in a brush discharge has a shape that is curved in some way (that is, not sharp). Tools, extensions from vessels, and fingers are examples. As before, the ignition potential is created with a charged surface (e.g., pipes, mists), but this is much more energetic than a corona discharge.

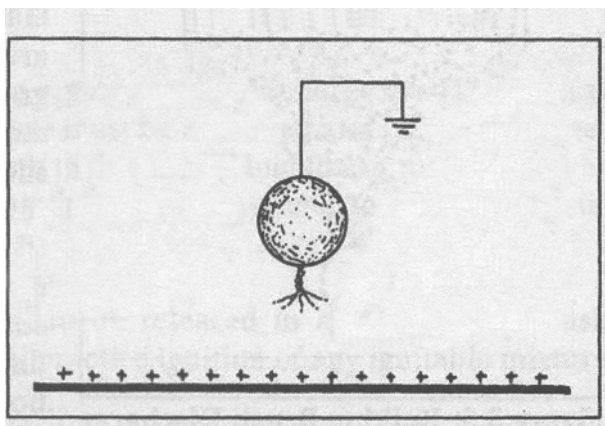


Figure 1.7. Brush discharge (Pratt, 2000).



Figure 1.8. Positive brush discharge from negatively charged plastic to grounded sphere (Britton, 1999).

Bulking Brush Discharge—This type of discharge is associated with an accumulation of powder and so will usually not be relevant to the intended audience of this work. However, it could be quite relevant to those who handle solids that off-gas flammable vapors while in storage (noting that storage applications are outside the scope of this book). Britton and Smith (2012) also show that similar discharges can be produced in liquid systems.

Propagating Brush Discharge—This extremely energetic form of brush discharge is depicted in Figure 1.9 and Figure 1.10. The surface must have an extremely high charge density that is supported by a grounded conductor for this type of discharge to occur, since this condition allows most of the electrical field to exist between the surface and the backing rather than in the air where it would dissipate.

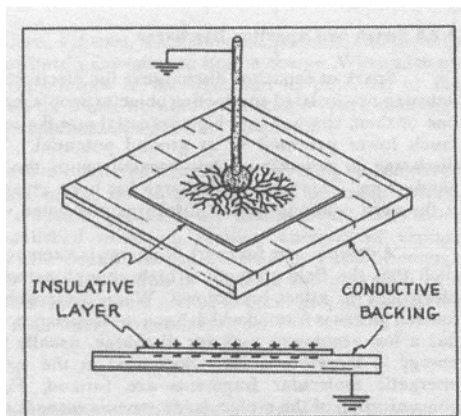


Figure 1.9. Propagating brush discharge (Pratt, 2000).

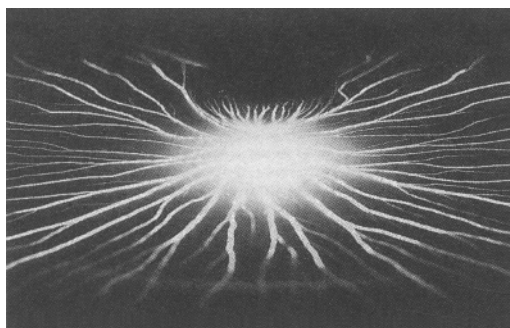


Figure 1.10. Propagating brush discharge on charged layer initiated by grounded electrode (Britton, 1999).

Spark or Capacitor Discharge—This type of discharge is of primary interest in the ignition of flammables in a process environment. The spark discharge occurs between capacitors. The discharge is shown in Figure 1.11 and Figure 1.12.

Common objects in a process plant can store a static charge and thus be a sufficient capacitor for the purposes of providing an ignition source: buckets, tanks, vehicles, machinery components, and humans are just a few of the possibilities. Some chemicals (e.g., low-sulfur diesel fuel) have recently been discovered to harbor charges.

Release Equipment Type—There is some evidence that the type of equipment may influence its propensity to build a static charge, all else being equal. For example, it is noted in Glor (1999) and others that static buildup in piping systems is a function of the velocity of the fluid through the pipe. This may be relevant for pipe rupture cases discussed in this book in which the velocity through the pipe may be much larger than is the case in typical process situations (and for which static dissipation measures have presumably been designed).

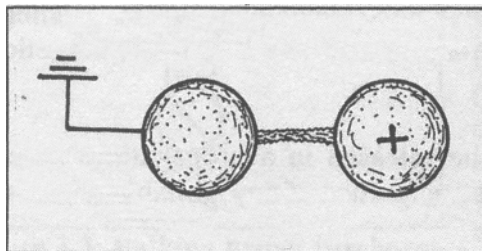


Figure 1.11. Spark discharge (Pratt, 2000).

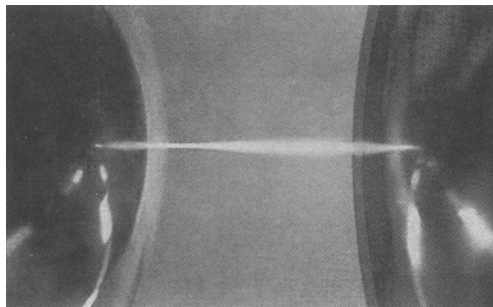


Figure 1.12. Spark discharge between spherical electrodes (Britton, 1999).

Summary—There are potentially several types of static discharge that could ignite a flammable release near the source (or farther away). For the purposes of predicting ignition probabilities, the distinction between the different types of static ignition is probably not important. Even if it was important, there is likely no practical way to account mathematically for the numbers and strengths of the sources in normal operation, let alone in the possible chaos of damaged equipment coincident with the release of material. For this reason, generalized approaches to predicting ignitions near the source (e.g., based on size of release, average equipment density) are probably as good as more complex schemes that might be devised.

1.3.3.6 Restrictions at Point of Release

Dryer et al. (2007) performed a series of experiments with hydrogen (and to a much lesser extent natural gas) in which the presence of obstructions or confinement at the point of release (in this case, tubing/fittings downstream of a hydrogen cylinder rupture disk) can influence the odds of ignition. He concluded that “similar phenomena apparently do not necessarily occur for sudden boundary failures of storage vessel or transmission piping into open air that have no downstream obstruction.” The same is considered credible for methane and natural gas, but not for heavier hydrocarbons.

The presumed principle is illustrated in Figure 1.13.

As seen in Figure 1.13, after the pressure is released from the rupture disk, the high pressure of the hydrogen shock heats the air in the confined space of the discharge piping. The effect is enhanced when there are obstructions in the line such as fittings that promote mixing. There are ranges of pressure and configuration over which this phenomenon appeared to occur, discussed further in Chapter 3.

The ignition phenomenon was only observed for release pressures greater than about 200 psig. The requisite confinement was effective down to a discharge piping length of about 1.5 inches. However, ignition did not occur at lengths greater than about 10 feet, which was attributed to combustion heat removal by the piping.

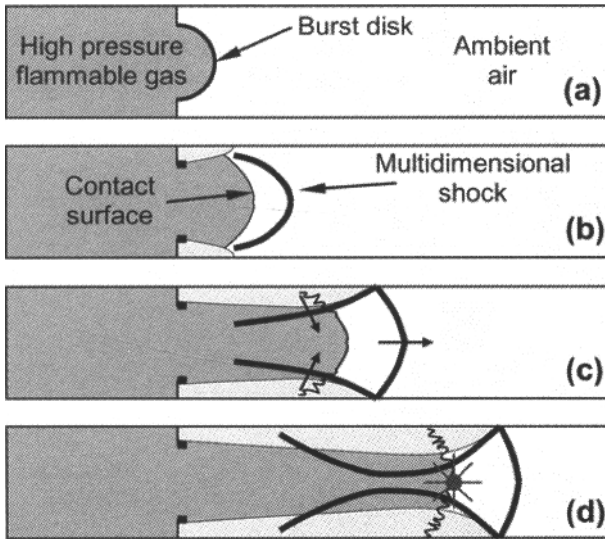


Figure 1.13. Schematic of shock wave formation downstream of a release of high-pressure gas into a confined space (Dryer et al., 2007).

1.3.4 Key Ignition Factors Related to the External Environment After the Release

1.3.4.1 Existing Flames

Flammable mixtures can be ignited by preexisting flames such as those from fired heaters. These may be logically treated as point sources of ignition, and accounted for individually. Alternatively, it may be simpler to assume a certain density of such sources in a normal process plant.

1.3.4.2 Burning Particles and Sparks

Flammable mixtures may be easily ignited by the energies available in sparks generated by rotating cutting equipment, from friction in machinery, or through impact of sparking tools or falling objects. There is no ready measure for this, and so it is treated as an “area” source of ignition—that is, in a given area of a process plant it is assumed that there may be some concentration of such ignition sources, but it is not practical to try to quantify them except perhaps through the electrical classification of the area.

In principle, sparks could be caused by someone dropping a tool while escaping from a flammable gas cloud. However, this does not appear to be a significant cause of fires or explosions, and the use of nonsparking tools instead of

ferrous tools should not be considered a preventive measure with quantifiable benefit (API, 2004).

1.3.4.3 Electrical Equipment

Equipment including electronic circuits and power lines are capable of providing the energies required to ignite a flammable mixture. Objects close to ground level with overhead ultrahigh voltage (i.e., >800 kV) transmission lines are situated in an electric field which may be on the order of 5 kV/m (CCPS, 1993).

Whether or not ignition actually takes place is a function of the available voltage, current, and other factors. Because of the wide range of electrical sources that are available in a typical process plant, either they may be assigned an ignition “strength” based on the type of exposure that is present (for point sources) or an assumption can be made based on the “intensity” of the process equipment.

1.3.4.4 Hot Surfaces

Hot surfaces will be present in a typical process unit in some form (e.g., hot piping, motors). However, hot surfaces do not offer the same ignition properties as sparked ignition—that is, the temperature at which a surface will ignite a material is not the same as the laboratory autoignition temperature.

The reason is attributed to convection of heated gases away from the hot surface, which, if rapid enough, does not allow enough eduction time for the ignition to take place. In contrast, an autoignition apparatus uniformly heats and contains a mixture that cannot escape. Duarte et al. (1998) illustrated this phenomenon (Figure 1.14), described it in some detail, and conducted bench-scale experiments that supported this explanation.

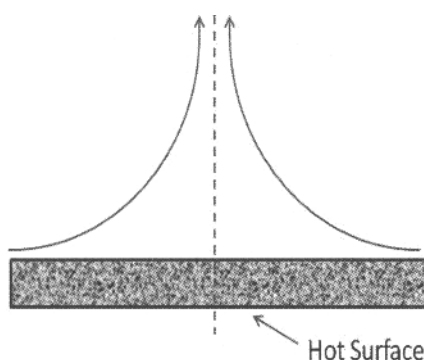


Figure 1.14. Flow patterns of a horizontal upward-facing heated surface (Duarte et al., 1998).

A hot surface cannot be treated as a point source in the same sense as a spark would be, but it is assumed that hot surfaces are limited in dimension. Figure 1.15 illustrates the effect of the area of the hot surface on the ignition temperature of various fuels; note that the largest area considered in the figure is still small enough to be considered as a “point source” for the purposes of these methods.

Figure 1.15 also illustrates that the ignition temperatures for hot surfaces can be substantially higher than those from an autoignition apparatus (e.g., AIT of hexane = 223 °C; of hydrogen = 528 °C; of diethyl ether = 195 °C). API has also compared experimental AIT values with ignition temperatures observed over hot surfaces (API, 2003).

On this basis, hot surfaces can be considered on either a point-source or area-source basis, but with assumed lesser “strength” than the preceding ignition sources. However, certain administrative practices may be considered to modify hot-surface ignition sources; for example, if vehicular traffic is prohibited from the vicinity of the release location. Note that later in this book vehicles are not treated specifically as hot-surface ignition sources, since the cause of ignition may be either a hot surface or the vehicle’s ignition system.

Further discussion of this topic can be found in Sections 3.3.4 and 3.3.5.

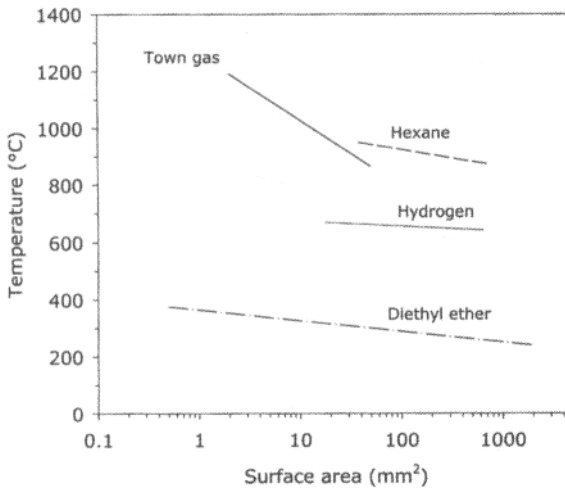


Figure 1.15. Effect of hot-surface area on ignition temperature (Babrauskas, 2003).

1.3.4.5 Discharge into Open or Closed Space?

The vast majority of ignition data has been collected for releases into open (outdoor) spaces. However, if an indoor release occurs, it may be more likely to ignite because the vapor cloud will be contained and will not disperse as readily without wind or turbulence to promote the dispersion—in fact, the dispersion will probably be dominated by the release of jet-induced turbulence. This might be considered the general rule; in some cases the confinement may result in the space being *unignited* due to being above the upper flammability limit.

Dilution of the vapor cloud will occur as the result of natural or forced ventilation in the room. Whether or not the ventilation rate is sufficient to reduce the size of the cloud that is in the flammable range is a function of the size of the release, size of the room, ventilation rate, and release/ventilation/room geometries.

In terms of impact, a release inside a building also increases the probability that the ignition will result in an explosion, since the building interior provides a degree of confinement that, as explained in Section 1.4, can promote damaging blast wave overpressures.

1.3.4.6 Electrostatic Sources, Including Human Sources

The basis for electrostatic discharge was discussed earlier and doubtless has a role to play in far-field ignitions as well as “immediate” ignitions. The focus of this discussion is therefore on human sources of electrostatic discharges. This topic has been discussed by Johnson (1980) and others.

Johnson relates these requirements for human electrostatic ignition of flammables:

- Presence of a vapor/air mixture within a fairly narrow concentration range
- Sufficient electrostatic charge generated on the person
- Storage of the charge on the person for a significant length of time (which requires low absolute humidity)
- Large or grounded object available to discharge the spark

Johnson goes on to cite conflicting reports on the viability of humans as electrostatic ignition sources but through experimental studies concluded that the energy required for human electrostatic ignition of flammables was only 2–3 times that of a capacitive spark for ignition of acetone/air mixtures. Furthermore, it was anticipated that any vapor/air mixture with an MIE of 5 mJ or less could be ignited by a person. A value of 25 mJ being discharged from people due to static charges has been suggested (OSHS, 1999), although other values ranging from 10 to 30 mJ are also assumed.

1.4 CONTROL OF IGNITION SOURCES

1.4.1 Ignition Source Management

By far the most common method for managing ignition sources is through instituting proper hazardous area classifications as per various currently available fire protection standards. However, there are limits to the effectiveness of this and other ignition control measures. This is discussed next.

1.4.1.1 Hazardous Area Classification

All modern petrochemical facilities are designed to one or more industry standards that regulate the type of ignition sources that are allowed in a given area based on the expected flammable environments to which the ignition source will be exposed. Some commonly used English language standards are from the National Fire Protection Association (NFPA, 2012, and others), British Standards (BS, 2009, and others), and the American Petroleum Institute (API, 2002); examples of various standards as applied to a storage tank are shown in Figure 1.16.

Attributes of ignition control measures are also described by CCPS (2012).

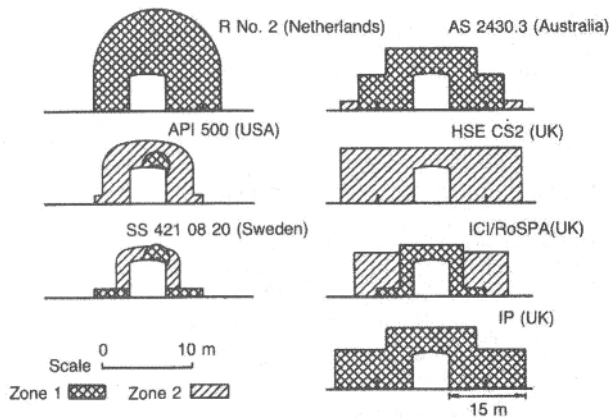


Figure 1.16. Depictions of hazardous area classification (Mannan, 2005).

In these standards, the environment at a particular location is characterized in broad terms of the frequency and persistence of flammable atmospheres. These standards have enjoyed great success over the years, although for the purposes of this book, they have two significant shortcomings:

- They are designed to address continuous or incidental (e.g., maintenance activity) releases but not major losses of containment.
- The integrity of the devices may be compromised by the same event that ultimately becomes ignited if the initiating event is energetic (e.g., dropped object).

Therefore, while area classification is an important component of an ignition prevention program, it is not fool-proof.

1.4.1.2 Work Permit Systems

It is assumed that any facility utilizing this book will have an active and effective work permit system that is designed to minimize ignition hazards from hot work such as welding, grinding, and the like. However, even a “best of class” work permit system does not provide perfect control—even if hot work is discontinued at the first signs of a flammable release, residual hot surfaces may still provide an ignition source. Job safety analyses provide a supplemental level of safeguard in cases where there is a hazard introduced by simultaneous but unrelated activities, such as hot work in the area where a pump is being opened for maintenance.

Daycock and Rew (2004) cite statistics regarding how the failure of work permit systems have led to ignitions that might otherwise have been avoided. Notably, around one-fourth of the fire/explosion events they reviewed were associated with permit-to-work failures: *“A common theme, which was apparent across all of the incidents reviewed, was that the hazards associated with the task were not adequately assessed pre-job.”*

The effectiveness of a work permit system in preventing ignition is important but difficult to quantify. The statistics mentioned above are likely not specifically attributable to the magnitude of release events of interest to the readers of this book. Therefore no attempt is made here to quantify the effect of work permit systems—good, bad, or otherwise, although this may be worthy of consideration by safety managers. However, the algorithms developed in this book do consider the broader issue of ignition source control, including and beyond that related to work permits.

1.4.1.3 Vehicle Limits

Some fraction of historical fire and explosion events were found to have ignited due to the presence of vehicles in the area of the release. There are at least two mechanisms by which this can happen: (1) the gas cloud is ingested into the combustion system of the vehicle or (2) the gas cloud is ignited by a hot surface on the vehicle such as the engine or the exhaust system.

For these reasons, it is appropriate to give credit for site programs that prevent vehicular traffic from being near to an operating unit—or to penalize locations that do allow such traffic except under controlled situations (e.g., hot-work permit).

1.4.1.4 Control of Electrical Ignition Sources

The algorithms in this book assume that typical electrical classification and work permit programs are in place for the facilities being evaluated. However, it should be possible, in principle, to provide credit for instituting controls that are more aggressive than those required under the usual standards, and this can be considered in developing ignition prediction algorithms.

Also important is control of frequent/continuous static sources such as accumulation of static in the handling of hydrocarbons, presence of electrical lines, or accumulation of static charge (particularly indoors) from clothing, footwear, or floors.

Proper grounding is the solution to each of these issues, although it is also appropriate to consider that even properly designed electrical equipment (e.g., those with proper location and protection of instrument/power cables, location of high voltage lines) have the potential to ignite a release.

In the case of indoor releases, Johnson (1980) and others have suggested the use of conductive (e.g., lead) floors, conductive footwear, and maintaining the relative humidity above 60% for rooms operating at typical temperatures.

Lightning is also an obvious ignition source and to some extent can be mitigated through lightning protection systems. For the purposes of this book it is assumed that the probability of lightning coincident with a major flammable release is remote, although there are certainly instances where lightning can lead to a flammable release.

1.4.2 Minimization of Release

There are several methods commonly employed to minimize the amount of material release or to contain it or otherwise reduce its potential for spreading or ignition. These include:

- Suppressing the release with water or foam
- Using fluid curtains or fogs to contain the spread of a release
- Secondary containment to minimize vaporization from a pool (e.g., dike)
- Leak detection/isolation systems

These are described in CCPS (1997), Fthenakis (1993), Murphy (2009), and others.

Note that there have been occasional reports of fire/explosion suppression systems actually *causing* an ignition due to static generation or other factors (Britton, 1999). For the purposes of this book it is assumed that such systems are

properly designed and maintained for the application and at worst provide no benefit.

1.5 VAPOR CLOUD EXPLOSION PROBABILITY OVERVIEW

Flammable releases can have various outcomes (illustrated later in event tree form in Figure 2.1). Explosions are one of these possible outcomes. Vapor cloud explosions (VCEs) are caused by combustion of a dispersed cloud of vapor in a congested and/or confined volume, which is defined as a space containing turbulence-inducing obstacles. The VCE produces an overpressure wave that propagates into the surroundings. For the purposes of this book, explosions are assumed to occur only if ignition is delayed, such that a sufficiently large, unignited vapor cloud can form.

The variables that determine whether an explosion takes place or not include the following:

- The fundamental burning velocity of the fuel
- The degree of congestion in the space in which the flame front develops
- The degree of confinement in the space in which the flame front develops

The greater that each of these variables is, the greater is the propensity for an explosion. Note that the last two variables may well depend on the magnitude of the release—that is, the larger the release, the greater the chance that the resulting vapor cloud can reach an area or areas of sufficient congestion/confinement to generate an explosion.

The fundamental burning velocity is an intrinsic property of the fuel. The congestion and confinement are properties of the environment into which the fuel is released but can be described in general terms for the purposes of developing an ignition probability model. Alternatively, the analyst can use standard blast overpressure models described in CCPS (2010) to determine whether an explosion is likely.

1.5.1 Explosion Venting

An incipient flame front may not develop damaging overpressures if there is sufficient venting present. In the case of an outdoor release, when the ignited mass expands into the surrounding environment (assuming that it is not unduly restricted in some way), effective mitigation can be provided by sufficient spacing between equipment such that dangerous flame front velocities never develop.

Inside a building, mechanical venting may be needed to prevent or minimize an explosion/detonation. Since this discussion is limited to preventing explosions outside of process equipment, this can primarily be accomplished through use of blowoff panels. As noted in the SFPE Handbook (2008):

“The most effective explosion venting systems are those that deploy early in the deflagration, have as large a vent area as possible, and allow unrestricted venting of combustion gases. Early vent deployment requires that the vent release at the lowest possible pressure ... usually slightly larger than the highest expected differential pressure associated with wind loads—typically 0.96 to 1.44 kPa (0.14 to 0.21 psig).”

If a building’s explosion vents conform to industry standards (e.g., NFPA 68), it may be possible to lower the probability of explosion/detonation to account for the vents. However, the issue should be evaluated carefully before giving credit for such measures. It has been shown that the NFPA methods are not always sufficient (Thomas et al., 2006), for example, when a high-speed flame is generated in a space with significant obstacle arrays.

1.5.2 Explosion Suppression

An incipient explosion may be prevented by rapidly introducing a suppression agent into the (generally enclosed) space. Again, credit may be given for such measures in explosion probability calculations if the suppression can be demonstrated as being effective.

1.6 DETONATION OVERVIEW

Detonation of a flammable mixture may occur either directly, through a very strong ignition source, or indirectly, via a deflagration-to-detonation transition (DDT). These are very different and are discussed briefly below. However, the prediction of a detonation probability is beyond the scope of this book due to the many physical and other complexities associated with the issue.

Note that the *detonation* limit of a chemical may be different than the flammable or explosive limits. However, detonation ranges reported in the literature should not be relied upon because more recent testing has shown that the ranges vary significantly depending on the equipment used to perform the test.

1.6.1 Detonation Using a Strong Ignition Source

In this type of event, detonation is initiated by the presence of a very strong ignition source—one that provides many thousands of joules of energy or more, in contrast to simple ignition, which often occurs at less than 1 mJ. In a typical process plant environment, this type of ignition source should only be present as a result of gross failure of significant electrical equipment.

1.6.2 Deflagration-to-Detonation Transition

This phenomenon is an extreme form of the flame acceleration process that leads from a deflagration to a detonation but is qualitatively different, as described in

detail in Babrauskas (2003) and more concisely in CCPS (2010). Although the precise mechanism of DDT is described differently by different observers, it basically involves a combustion process that is non-uniform and in the process develops unstable folds and waves at the flame front that build on each other until a shock wave forms. Two versions of this process, and the resulting instability, are described by CCPS (2010).

1.6.3 Buncefield

The Buncefield explosion [Health and Safety Executive (HSE), 2012] is a case study of an event that for some period of time defied explanation since there is some debate whether a detonation actually occurred or not. The proposed explanations are instructive; however, this type of event is enough of an anomaly that an ignition probability tool of the type described in this book may not be capable of identifying it as a possibility.

1.7 OTHER IGNITION TOPICS—HYDROGEN

Hydrogen is a subject of special interest because of its widespread use, extremely low ignition energy (see also the earlier discussion of MIE), and high fundamental burning velocity (which can promote damaging explosion overpressures). Hydrogen is also unique in that anecdotally people have widely different experiences (or opinions) on the ignitability of hydrogen in a given situation.

1.7.1 Ignition Mechanisms

Remarkably, the mode by which hydrogen ignites is still under debate, and several possible mechanisms have been suggested that are potentially applicable to releases into an open environment:

Electrostatic Ignition—Ignition due to sparks, brush discharges, and corona discharges have each been attributed to hydrogen ignition events. Interestingly, a comment is made in Gummer and Hawksworth (2008): “*Studies undertaken many years ago on hydrogen vents ... showed that ignition was rare during fine weather, but was more frequent during thunderstorms, sleet, falling snow, and on cold frosty nights.*”

Reverse Joule-Thompson Effect—Hydrogen is an unusual chemical in that, when depressured, its temperature will rise rather than fall. However, this temperature rise is generally modest and so would normally be insufficient to cause the hydrogen to reach its AIT.

Hot-Surface Ignition—As noted earlier, the ignition of a material by a hot surface typically requires temperatures substantially higher than the AIT. From experimental work with hydrogen, it appears to follow this rule.

Diffusion Ignition—Ignition of a 3:1 mixture of hydrogen and nitrogen at 575 K (well below the experimental AIT for hydrogen) has been reported experimentally in a shock tube environment in which the material reached Mach 2.8. This might be analogous to the conditions during a high-pressure hydrogen leak, although under such circumstances it is not clear whether any ignition would be due to this ignition mechanism or by one of the previous mechanisms. Refer to Wolanski and Wojcicki (1972) for more details.

Adiabatic Compression/Turbulence—In this case, the equipment geometry at or near the point of release drives compression that results in a shock wave, as described in Section 1.3.3.6 by Dryer et al. (2007) and recounted by Hooker et al. (2011). The importance of back-mixing in this mechanism was discussed for ethylene/oxygen systems by Britton et al. (1986).

Gummer and Hawksworth (2008) summarized the work through 2007 by saying that the proposed mechanisms do not account for the reported ignitions (or nonignitions) of hydrogen. They cite some specific incidents (see Section 3.7.3) in which ignitions occurred in an obstructed discharge but not in unobstructed discharges. This is similar to what was observed by Dryer et al. (2007) and Hooker et al. (2011) and was attributed to the relative presence or absence of the formation of turbulence near the point of release and may be symptomatic of the adiabatic compression mechanism above.

Swain et al. (2007) conducted experiments which noted some combinations of hydrogen concentration and discharge velocity in which the mixture was “flammable” but ignition did not occur or was not sustained. This was attributed to insufficient local flame speed to burn back to the source, leading the flame to burn outward until there was insufficient hydrogen available.

Bragin and Molkov (2011) reviewed much of the research above and provide a computational fluid dynamics approach to analyzing the ignition mechanism as it relates to the “shock wave” ignition mechanism.

1.7.2 Other Hydrogen Ignition Topics

An older review of actual industrial hydrogen incidents by Zalosh et al. (1978) is discussed in some detail in Chapter 3. The data could be interpreted as suggesting that the vast majority of hydrogen releases ignite and that about two-thirds of those ignitions are explosive. However, aside from not knowing the environment surrounding the releases that might tend to explosiveness (or not), there is nothing suggested in the report that eliminates the potential for data bias—that is, the propensity for ignition events to be reported more often than nonignitions or for explosions to be reported more often than fires. For this reason, one might consider the Zalosh results to be upper bounds on the ignition/explosion probabilities.

A comprehensive view of hydrogen ignition/safety phenomena is provided by Molkov (2007). In addition to many of the references discussed above, Molkov notes the following observations:

Although the experimental value of hydrogen MIE is a comparatively very low, 0.017 mJ, “at the lower flammability limit the ignition energy requirement of hydrogen is similar to that for methane.” Thus hydrogen may not be as easy to ignite as might be assumed based solely on the reported MIE. One might even make an argument that the effective MIE for immediate ignitions (where the hydrogen concentration is highest) should be treated as being lower than the effective MIE for delayed ignitions (after the hydrogen concentration has dropped nearer to LFL).

“Gaseous hydrogen storage cylinders and vehicle storage tanks with pressures up to 1,000 atm can be characterized by a high probability of the spontaneous ignition ... *if special measures are not undertaken*” (italics added).

There appear to be many mechanisms for hydrogen ignition; ignition itself appears to be highly dependent on environmental factors near the point of release that can be expected to vary widely from one release to the next. This aspect of hydrogen ignition likely explains the wide variety of experiences people have had, but as a result introduces a greater level of uncertainty in the analysis. It does not seem practical to accommodate all the possible variables in a hydrogen analysis, if for no other reason than the circumstances of the release may alter these conditions from the normal physical environment. One might make an argument that a release from equipment that is immutable into an open environment (e.g. release through a clean orifice) is less likely to ignite than similar releases resulting from equipment damage or otherwise have flow paths that result in turbulence-induced shock waves.

