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Principles of Combustion

1.1 Introduction

Flaring is defined as the controlled burning of off gases in the course of routine oil and gas or chemical manufacturing operations. This burning or combustion is accomplished at the end of a flare stack or boom.

Combustion is often described as a simple chemical reaction in which oxygen from the atmosphere reacts rapidly with a substance, generating heat. But it is in fact a very complex series of chemical reactions. The most common organic compounds are hydrocarbons, which are composed of carbon and hydrogen. The simplest hydrocarbon is methane, each molecule of which consists of one carbon atom and four hydrogen atoms. It is the first compound in the family known as alkanes. The physical properties of alkanes change with increasing number of carbon atoms in the molecule, those with one to four being gases, those with five to ten being volatile liquids,

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those with 11 to 18 being heavier fuel oils and those with 19 to 40 being lubricating oils. Longer carbon chain hydrocarbons are tars and waxes. The first ten alkanes are:

- CH_4 methane (gas)
- C_6H_{14} hexane (liquid)
- C_2H_6 ethane (gas)
- C_7H_{16} heptane (liquid)
- C_3H_8 propane (gas)
- C_8H_{18} octane (liquid)
- C_4H_{10} butane (gas)
- C_9H_{20} nonane (liquid)
- C_5H_{12} pentane (liquid)
- $\text{C}_{10}\text{H}_{22}$ decane (liquid)

Alkenes are similar but their molecular structure includes double bonds (examples are ethylene and propylene). Alkynes contain triple bonds (example is acetylene). The above compounds are all known as aliphatics. Aromatic hydrocarbons such as benzene have a ring molecular structure and burn with a smoky flame.

When hydrocarbons burn they react with oxygen, producing carbon dioxide and water (although if the combustion is incomplete because there is insufficient oxygen, carbon monoxide will also form).

More complex organic compounds contain elements such as oxygen, nitrogen, sulfur, chlorine, bromine, or fluorine, and if these burn, the products of combustion will include other compounds as well. For example, substances containing sulfur such as oil or coal will result in sulfur dioxide whilst those containing chlorine such as methyl chloride or polyvinyl chloride (PVC) will result in hydrogen chloride.

This chapter focuses on combustion principles which are essential to the selection and safe operation of flares. Without a fundamental understanding of combustion principles, the

proper selection of and safe operation of flares are not possible. Note also that Appendix A contains various physical and thermodynamic properties data for gases. The information has been assembled for the more knowledgeable reader to aid in any preliminary calculations for estimating flare sizes, specifying flow conditions, and determining flammability.

1.2 Combustion Basics

Combustion is a chemical reaction, and specifically it is an oxidation reaction. Oxidation is defined as the chemical combination of oxygen with any substance. In other words, whenever oxygen (and some other materials) combines chemically with a substance, that substance is said to have been oxidized. Rust is an example of oxidized iron. In this case the chemical reaction is very slow. The very rapid oxidation of a substance is called combustion.

There are three basic explanations that are used to describe the reaction known as combustion. They are the fire triangle, the tetrahedron of fire, and the life cycle of fire. Of the three, the first is the oldest and best known, the second is accepted as more fully explaining the chemistry of combustion, while the third is a more detailed version of the fire triangle.

The fire triangle explanation is simplistic, but provides a basic understanding of the three entities that are necessary for a fire to occur. This theory states that there are three things necessary to support combustion:

- fuel;
- oxygen (or an oxidizer); and
- heat (or energy).

These three components can be represented as the three sides of a triangle, stating that as long as the triangle is not complete, that is, the legs are not touching each other to form

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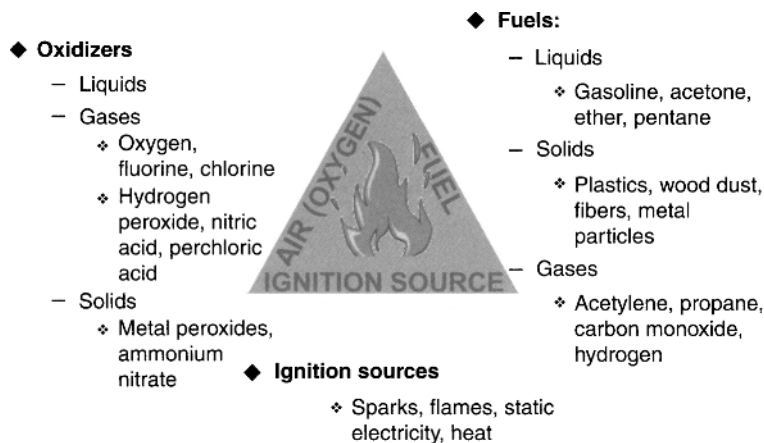


Figure 1.1 The fire triangle.

the closed or completed triangle, combustion cannot take place. See Figure 1.1.

The theory or explanation, as stated, is correct. Without fuel to burn, there can be no fire. If there is no oxygen present, there can be no fire (technically, this is not correct, but we can make the fire triangle theory technically correct by changing the oxygen leg to an oxidizer leg). Finally, without heat or a source of energy, there can be no fire. This last statement must also be brought up to date. The fact is that heat is just one form of energy: it is really energy that is necessary to start a fire. This difference is mentioned because there are some instances where light or some other form of energy may be what is needed to start the combustion reaction. It is best to change the “heat” leg of the fire triangle to the “energy” leg. Therefore, our fire triangle has three sides representing fuel, oxidizer, and energy.

A fuel is anything that will burn. Fuels may be categorized into the following classes:

- Elements (which include the metals, and some non-metals such as carbon, sulfur, and phosphorus);
- Hydrocarbons;

- Carbohydrates (including mixtures that are made up partially of cellulose, like wood and paper);
- Many covalently bonded gases (including carbon monoxide, ammonia, and hydrogen cyanide); and
- All other organically based compounds.

We are only concerned with gaseous and vapor streams that include hydrocarbons, covalently bonded gases, and of course organically based waste gas streams when it comes to flaring operations.

The list of materials that will combust is quite long, and one must not forget that the list includes not only the pure substances such as the elements and compounds that make up the list, but mixtures of those elements and compounds. Examples of mixtures would include natural gas, which is a mixture of methane (principally), ethane, and a few other compounds, and gasoline, which is a mixture of the first six liquid alkanes (pentane, hexane, heptane, octane, nonane, and decane), plus a few other compounds.

The oxidizer leg of the triangle usually refers to air, since it is the most common oxidizing agent encountered and is readily available. Oxygen does not burn. It is consumed during combustion.

The third leg of the fire triangle, the energy leg, provides the source of energy needed to start the combustion process. This energy can be provided in one or more of several ways. The energy can be generated chemically by the combustion of some other fuel, or it can be generated by some other exothermic chemical reaction. An exothermic reaction is defined as the emission or liberation of heat (or energy). This is the opposite of endothermic, which is defined as the taking-in or absorption of heat (or energy).

Energy may also be generated by mechanical action, that is, the application of physical force by one body upon another. Examples of this are the energy created by the friction of one matter upon another or the compression of a gas. The force of

friction in one case may produce energy that manifests itself as heat, while friction in the other case may result in a discharge of static electricity. Static electricity is created whenever molecules move over and past other molecules. This happens whether the moving molecules are in the form of a gas, a liquid, or a solid. This is the reason why leaking natural gas under high pressure will ignite. This is also the reason why two containers must be bonded – connected by an electrical conductor – when you are pouring flammable liquids from one container to another. In any case, the amount of energy present and/or released could be more than enough to start the combustion reaction.

A third method of generation of energy is electrical, which is the preferred method of igniting flares. This method manifests itself as heat, produced from an electrical circuit in combination with a gas pilot.

The second popular explanation combustion is the tetrahedron theory. This theory encompasses the three concepts much like the fire triangle theory, but adds a fourth side to the triangle to make up a pyramid or tetrahedron. This fourth side is referred to as the chain reaction of combustion. The explanation states that when energy is applied to a fuel like a hydrocarbon, some of the carbon-to-carbon bonds break, leaving an unpaired electron attached to one of the molecular fragments caused by the cleavage of the bond, thus creating a free radical. This molecular fragment with the unpaired electron, or “dangling” bond, is highly reactive, and will therefore seek out some other material to react with in order to satisfy the octet rule. The same energy source that provided the necessary energy to break the carbon-to-carbon bond may have also broken some carbon-to-hydrogen bonds, creating more free radicals, and also broken some oxygen-to-oxygen bonds, creating oxide radicals. This mass breaking of bonds creates the free radicals in a particular space, and in a number large enough to be near each other, so as to facilitate the

recombining of these free radicals with whatever other radicals or functional groups may be nearby. The breaking of these bonds releases the energy stored in them, so that this subsequent release of energy becomes the energy source for still more bond breakage, which in turn releases more energy. Thus the fire "feeds" upon itself by continuously creating and releasing more and more energy (the chain reaction), until one of several things happens: either the fuel is consumed, the oxygen is depleted, the energy is absorbed by something other than the fuel, or this chain reaction is broken. Thus, a fire usually begins as a very small amount of bond breakage by a relatively small energy (ignition) source and builds itself up higher and higher, until it becomes a raging inferno, limited only by the fuel present (a fuel-regulated fire) or the influx of oxygen (an oxygen-regulated fire). The earlier in the process that the reaction can be interrupted, the easier the extinguishment of the fire will be.

Finally, the last explanation is the life cycle theory. According to this theory, the combustion process can be categorized by six steps, rather than the three of the fire triangle or the four of the tetrahedron of fire theory. Three of the steps in this theory are the same as the only three steps in the fire triangle theory. The first step is the input heat, which is defined as an amount of heat required to produce the evolution of vapors from a solid or liquid. The input heat will also be the ignition source and must be high enough to reach the ignition temperature of the fuel; it must be continuing and self-generating and must heat enough of the fuel to produce the vapors necessary to form an ignitable mixture with the air near the source of the fuel.

The second part of the life cycle of fire theory is the fuel, essentially the same as the fuel in the tetrahedron of fire and the fire triangle. It was assumed without so stating in the fire triangle theory, and is true in all three theories, that the fuel must be in the proper form to burn; that is, it must have

vaporized, or, in the case of a metal, almost the entire piece must be raised to the proper temperature before it will begin to burn. The third part is oxygen, in which the classical explanation of this theory only concerns itself with atmospheric oxygen, because the theory centers around the diffusion flame, which is the flame produced by a spontaneous mixture (as opposed to a pre-mixed mixture) of fuel gases or vapors and air. This theory concerns itself with air-regulated fires, so air-flow is crucial to the theory; this is why only atmospheric oxygen is discussed. Ignoring oxygen and the halogens that are generated from oxidizing agents should be viewed as a flaw in this theory. The fourth part of the theory is proportioning, or the occurrence of intermolecular collisions between oxygen and the hydrocarbon molecule (the "touching" together of the oxidizer leg and the fuel leg of the fire triangle). The speed of the molecules and the number of collisions depend on the heat of the mixture of oxygen and fuel; the hotter the mixture, the higher the speed. A rule of thumb is used in chemistry that states the speed of any chemical reaction doubles for roughly every 18°F rise in temperature. The fifth step is mixing; that is, the ratio of fuel to oxygen must be right before ignition can occur (flammable range). Proper mixing after heat has been applied to the fuel to produce the vapors needed to burn is the reason for the "backdraft" explosion that occurs when a fresh supply of air is admitted to a room where a fire has been smoldering. The sixth step is ignition continuity, which is provided by the heat being radiated from the flame back to the surface of the fuel; this heat must be high enough to act as the input heat for the continuing cycle of fire. In a fire, chemical energy is converted to heat: if this heat is converted at a rate faster than the rate of heat loss from the fire, the heat of the fire increases; therefore, the reaction will proceed faster, producing more heat faster than it can be carried away from the fire, thus increasing the rate of reaction even more. When the rate of conversion of chemical energy falls below the rate

of dissipation, the fire goes out. That is to say, the sixth step, ignition continuity, is also the first step of the next cycle, the input heat. If the rate of generation of heat is such that there is not enough energy to raise or maintain the heat of the reaction, the cycle will be broken, and the fire will go out. The life cycle of fire theory adds the concepts of flash point and ignition point (heat input) and flammable range.

1.3 Physical Gas Laws

We begin our discussion with the subject of physical gas laws which deal with pressure-volume-temperature (PVT) relationships. These relationships are important in determining material balances for any gaseous system and in calculating certain parameters when determining whether a flare is meeting compliance as stipulated on a permit. In most cases, one can assume *ideal gas behavior* and define the initial (1) and final (2) states of a gas as follows:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad (1.1)$$

where T_1 and T_2 refer to absolute temperature, such as in Kelvin ($^{\circ}\text{K}$). The generalized form of the ideal gas law is given by the following:

$$PV = nRT = \frac{W}{M}RT \quad (1.2)$$

Or

$$P = \frac{W}{V} \frac{RT}{M} = \rho \frac{RT}{M} \quad (1.3)$$

where n , W , M , and P are the moles, weight, molecular weight, and density of the gas, respectively; R is a universal gas constant equal to 1.987 cal/(K•mol), 0.08205 L•atm/(K•mol), or 8.314 J/(K•mol) depending upon the P-V units.

As shown by the ideal gas law, the volume of gas will vary directly with absolute temperature and inversely with total pressure. In calculating the moles of gas, it is useful to know that the *molar volume* of any ideal gas will occupy 22.414 L at 1 atm and 273 K (0°C).

For mixtures of ideal gases, the total pressure (P_t) is equal to the sum of the component partial pressures ($P_t = P_1 + P_2 + \dots$) and proportional to the total number of moles ($N_t = n_1 + n_2 + \dots$). Hence, the mole fraction (X) of a gaseous component (i) is:

$$X_i = n_i/N_t = p_i/P_t \quad (1.4)$$

100 X_i gives the mole or volume percent. For the vapors of ideal liquids, one may apply Raoult's law:

$$X_i(\text{liquid}) = n_i/N_t(\text{liquid}) = p_i/p_i^\circ(\text{vapor}) \quad (1.5)$$

where P_i is partial pressure of the i^{th} component in solution, p_i° is the vapor pressure of the pure component, and X_i is its mole fraction in solution.

Real gases deviate from ideal behavior, particularly when subjected to high pressures or cryogenic temperatures. In such cases, other equations must be used to determine the P-V-T relationships, such as:

$$PV = nZRT \quad (1.6)$$

where Z is a compressibility factor that depends upon the critical properties of the gas (P_c , T_c , and V_c). A fair approximation of the Z factor can be obtained for most gases from the generalized compressibility curves¹ in terms of reduced pressure ($\pi = P/P_c$) and reduced temperature ($\theta = T/T_c$). Gases that are difficult to liquefy, such as hydrogen, give a more complex behavior.

Critical states and vaporization properties of common gases and liquids can be obtained from well-known references like *Perry's Chemical Engineer's Handbook* and the *CRC Handbook of Chemistry and Physics*.

¹ *Thermodynamics for Chemists*, Van Nostrand, 1947, 522 pp.

1.4 Stoichiometric and Thermodynamic Considerations

Combustion material balances vary with the composition and concentration of the reactants and the nature of the products at the reaction and combustion conditions. Theoretically, the maximum heat release should occur at the *stoichiometric concentration* (C_{st}) that defines the optimum molar concentration of combustible for complete reaction with the particular oxidant; fuel-lean mixtures suffer from oxidant dilution and fuel-rich mixtures from incomplete reaction.

Knowledge of thermodynamic properties is essential in calculating the energy balance of a given system. The energy change may be in the form of work performed or heat transferred relative to the system surroundings. The first law of thermodynamics (known as energy conservation) states that the energy change (ΔE) is:

$$\Delta E = Q - W \quad (1.7)$$

where Q is the heat absorbed (positive) and W is the work done by the system (positive). Heat evolved or work on the system would be negative.

For an *isothermal process* ($\Delta E = 0$), the total mechanical work ($W = \int P dV$) of expansion or compression of an ideal gas is

$$W = nRT \ln(V_2/V_1) = nRT \ln(P_1/P_2) \quad (1.8)$$

$$P_1 V_1 = P_2 V_2 \quad (1.9)$$

For an *adiabatic process* ($Q = 0$), the total work ($W = \int C_v dT$) is:

$$W = nC_v T_1 [1 - (P_2/P_1)^{R/C_p}]; P_1 V_1^\gamma = P_2 V_2^\gamma \quad (1.10)$$

where C_v and C_p are molar heat capacities; γ is C_p/C_v ratio, and their subscripts refer to constant volume (V) or constant pressure (P).

In the adiabatic process, the temperature change is expressed as follows:

$$T_2/T_1 = (V_1/V_2)^{R/C_v} = (P_2/P_1)^{R/C_p} \quad (1.11)$$

Reactions can occur at constant volume or constant pressure. Under constant volume, where no mechanical work is performed ($W = 0$), the heat change would be $Q_v = \Delta E$; at constant pressure, the heat change is $Q_p = \Delta E + P \Delta V$. And since the heat content or enthalpy (H) of a system is defined as:

$H = H_2 - H_1 = Q_p$, then the change at constant pressure is:

$$\Delta H = \Delta E + P \Delta V = \Delta E + \Delta n RT \quad (1.12)$$

Note that Δn is the change in the moles of gas after reaction of the system.

In a chemically reactive system, the reaction may evolve heat (i.e., exothermic) or absorb heat (endothermic). The heat of reaction (ΔH) is denoted by the enthalpy change of the reactants from their initial state to the final or product state. Enthalpy change can be calculated by use of the heats of formation (ΔH_f - kcal/mol) of each specie; the standard values are defined at 25°C (298°K) and 1 atm.

1.5 Ignition

Ignition is a vapor-phase combustion reaction with the evolution of heat and emission of light that may or may not be visible to the naked eye. Such reactions are most often associated with the rapid oxidation of a combustible in air or oxygen. They may also occur with other oxidants, such as the halogens and nitrogen oxides, as well as without any oxidant when the combustible is capable of highly exothermic decomposition.

Many or most combustible-oxidant systems are not capable of sufficient self-reaction at ambient temperature to produce ignition. Generally, they require heating to some critical level by an external temperature or energy source. Figure 1.2 allows

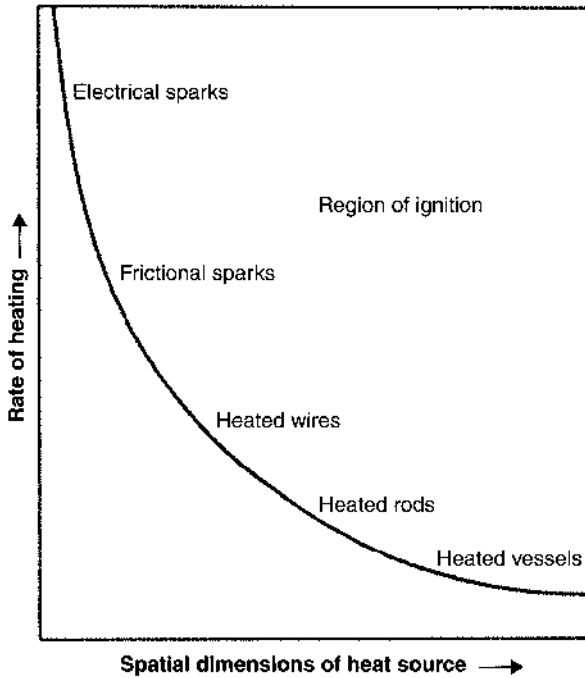


Figure 1.2 Generalized plot illustrating temporal and spatial characterization of various ignition sources.

the reader to consider the sources in terms of their spatial and temporal characteristics. At one extreme (electrical sparks), the source is infinitesimally small and very high in temperature and heating rate; here, one is primarily concerned with energy density and the ignition energy. At the other extreme (heated vessels), the source is large, heating rate is very low, and temperature is also relatively low; here, one is concerned with ignition temperature.

The simplest form of electrical ignition is a thermal process in which excessive surface heating is produced by the resistance to current flow in an electrical circuit. Other electrical ignitions involve sparks or arcs in which the energy approximates a point source and the heating duration may be as little as a fraction of a microsecond. These can be classified as a

high-voltage or electrostatic type and low-voltage or break spark type.

1.6 Flammability and Flammable Mixtures

A flammable gaseous mixture of combustible and oxidant is one that, when ignited, will propagate flame beyond the influence of the ignition source. All combustible gases and combustible vapors of liquids or solids form flammable mixtures over a limited range of combustible concentrations, depending upon temperature, pressure, and nature of the oxidant.

The critical combustible concentrations are known as the *limits of flammability* or explosion limits of the system and are defined as the fuel-lean or *lower limit* (L) and the fuel-rich or *upper limit* (U). These are also called the Lower Explosion Limit and the Upper Explosion Limit. These limits are usually expressed in volume percent and refer to homogeneous combustible vapor-oxidant mixtures. Since the flammability limits vary with temperature, and since the vapor formation of a combustible in its liquid or solid state is strongly dependent on temperature, it is useful to construct a flammability concentration-temperature diagram of the type shown in Figure 1.3. A three-dimensional plot to include the pressure effect would be required to completely define the flammability domains.

As shown in Figure 1.3, the flammable mixtures of a combustible liquid-air system may consist of mists (droplets + saturated vapor + air), saturated vapor-air mixtures (vapor pressure curve), or neat vapor-air mixtures (region beyond saturated vapor temperatures). The temperature range over which the liquid can form flammable vapor concentrations is defined by its *temperature limits of flammability* (T_L and T_U); intersections of these temperature limits with the vapor pressure curve define the *concentration limits of flammability* (L and U) at liquid-vapor equilibrium conditions.

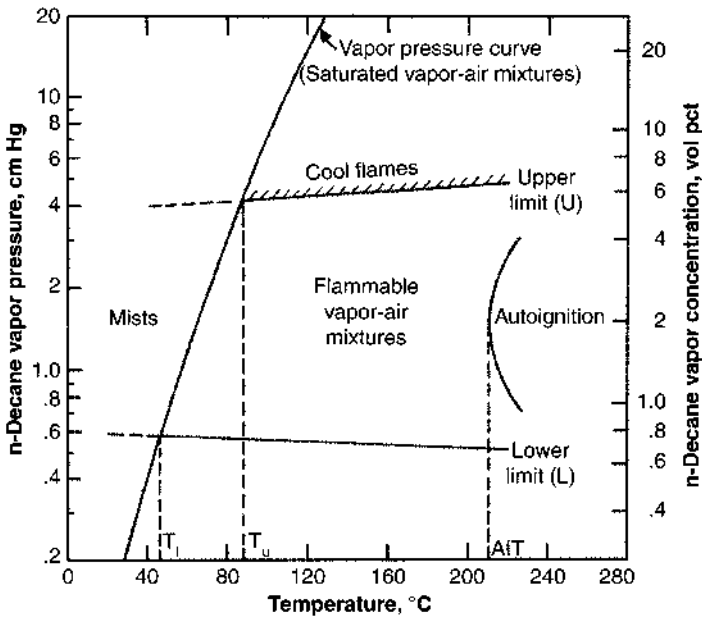


Figure 1.3 Flammability and vapor pressure diagram a hydrocarbon (non-specific) vapor-air system at various temperatures and atmospheric pressure. Note, AIT stands for autoignition temperature.

At higher temperatures, flammability domains for the neat vapor-air mixtures become widened, particularly on the fuel-rich side. Eventually, the temperature can be sufficient to produce autoignition of the mixtures, as illustrated in Figure 1.3. The lower temperature limit (T_L) is of interest because it defines the minimum temperature to which a combustible liquid or solid must be heated to form a flammable vapor-air mixture, i.e., the lower limit of flammability (L). In practice, this temperature corresponds approximately to the *flashpoint* of the combustible, which is determined under less ideal conditions (downward flame propagation and nonuniform mixtures) than those used in flammability limit determinations (upward propagation and uniform mixtures). *Closed cup flashpoints* are the most reliable values.

Flammable mists, sprays, or foams can form below the flashpoint or T_L of the combustible. However, their ignition energy requirements are much more severe than for neat vapor-air mixtures.

A variety of flammability diagrams have been proposed and relied on over the years to present complete limit of flammability data for combustible vapor-oxidant-inert systems. Usually the data are presented in the form of a rectangular plot. Figure 1.4 is an example for the gasoline vapor-air-nitrogen system. The graphical representation depicts the flammability limits as the oxidant alone (air) found on the ordinate (1.3 and 7.1 pct combustible); also, the variations of these limits with added inert (N_2) are indicated by the lower and upper boundaries defining the complete range of possible flammable mixtures for the total system.

The variation of a composition by the addition or reduction of any mixture component is shown for a composition outside the flammable zone. Additions of air to this composition point could result in the formation of flammable mixtures (dashed line), but that additions of combustible or inert could not form mixtures that fall into the flammable zone.

The *minimum oxygen concentration* (minimum O_2) and *critical combustible inert ratio* (critical C/I) below which flammable mixtures cannot form are noted in Figure 1.4. The minimum O_2 is obtained by drawing a constant oxidant tangent line of negative slope ($dC_f/dI = -1$) to the nose of the flammability diagram, whereas the critical C/I is found by constructing a tangent line from the origin to the lean side of the nose of the curve. The former is important in determining inerting requirements, and the latter in assessing fire extinguishing requirements.

As a general rule, limits of flammability widen with increased temperature, pressure, oxygen concentration, and energy of the ignition source. The limits are also widened by turbulence and buoyancy effects, which increase the flame propagation rate.

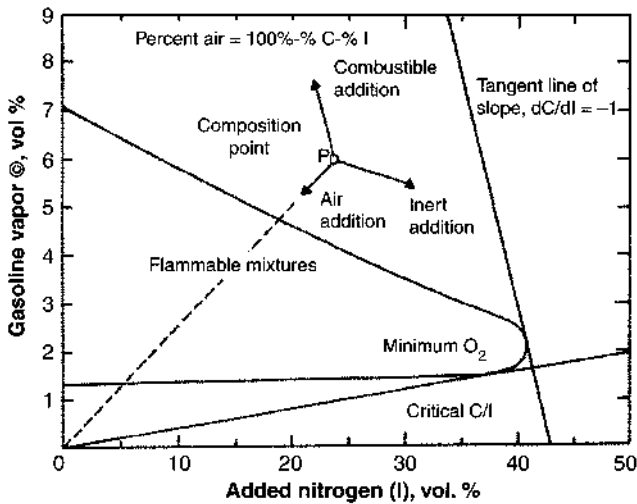


Figure 1.4 Generalized flammability diagram for gasoline vapor.

Flammability limits may be classified according to their propagation mode, upward or downward. *Upward limits* have the greatest practical value because they include the buoyancy effect and reflect the maximum flammability hazard; *downward limits* exclude buoyancy and are of greater fundamental significance. In addition to buoyancy, the differences between molecular diffusivities of the combustible and oxidant can contribute to the wide variations often observed between these limits.

As with ignition limits, flammability limits are narrowed by heat losses to vessel walls, and propagations can become impossible at some *quenching diameter*.

As an aside note, safety procedures are generally concerned with detecting flammable gas before it reaches its lower explosive limit. There are two commonly used standards which define the 'LEL' concentration for flammable substances: ISO10156 (also referenced in the superseded standard EN50054), and IEC60079-20:2000 (also referenced in BS EN61779-1:2000). The IEC (International Electrotechnical Commission) is a worldwide organization for standardization.

Historically, the flammability levels have been determined by a single standard: ISO10156 (Gases and gas mixtures-Determination of the fire potential and oxidizing ability for the selection of cylinder valve outlets).

IEC and EU (European) standards (IEC60079 and EN61779) define LEL concentrations measured using a 'stirred' concentration of gas (in contrast to the 'still' gas method employed in ISO10156). Some gases/vapors have proven to be more volatile when stirred, and the resultant LELs vary between the two standards for some gases/vapors.

The following table 1.1 reports LEL values as reported by the two standards. Note that the 50% LEL of methane in EN61779 calculates to a 2.2% volume concentration in air, as opposed to 2.5% volume as stated in ISO10156.

Stable combustion conditions require the proper amounts of fuels and oxygen. Combustion products are heat energy, carbon dioxide, water vapor, nitrogen, and other gases (excluding oxygen). In theory, there is a specific amount of oxygen needed to completely burn a given amount of fuel. In practice, burning conditions are never ideal. As such, more air than ideal must be supplied to burn all fuel completely. The amount of air more than the theoretical requirement is referred to as *excess air*.

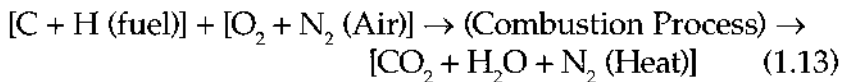
Determining the excess air at which the combustion system will operate requires knowledge of the **stoichiometric** air-fuel ratio (commonly referred to as the perfect or ideal fuel ratio or the stoichiometric combustion).

Stoichiometric or Theoretical Combustion is the ideal combustion process where fuel is burned completely. A complete combustion is a process burning all the carbon (C) to (CO_2), all the hydrogen (H) to (H_2O), and all the sulfur (S) to (SO_2). With unburned components in the exhaust gas, such as C, H_2 , CO, the combustion process is uncompleted and not stoichiometric.

Table 1.1 LEL values as reported by different standards.

Chemical	% Vol. at 100% LEL ISO10156	% Vol. at 100% LEL IEC60079-20-2000/BS EN61779-1:2000	Flash point °C	Ignition TEMP °C	Molecular weight (AIR = 28.80)	Vapor density (Air = 1)
Acetylene	2.40%	2.30%	–	305	26	0.9
Ammonia	15.00%	15.00%	–	630	17	0.59
Benzene	1.30%	1.20%	–11	560	78.1	2.7
Butane	1.80%	1.40%	–60	372	58.1	2.05
Iso-Butane	1.80%	1.30%	–	460	58.1	2
Ethane	3.00%	2.50%	–	515	30.1	1.04
Ethanol	4.30%	3.10%	12	363	46.1	1.59
Ethylene	2.70%	2.30%	–	425	28	0.97
Hexane	1.10%	1.00%	–21	233	86.2	2.97
Hydrogen	4.00%	4.00%	–	560	2	0.07
Methane	5.00%	4.40%	–	537	16	0.55
Methanol	7.30%	5.50%	11	386	32	1.11
Pentane	1.50%	1.40%	–40	258	72.2	2.48
Propane	2.10%	1.70%	–104	470	44.1	1.56
Toluene	1.20%	1.10%	4	535	92.1	3.2
Xylene	1.00%	1.00%	30	464	105.4	3.66

The combustion process can be expressed as:



where

C = Carbon

H = Hydrogen

O = Oxygen

N = Nitrogen

During stoichiometric combustion, there is a chemically correct mixing proportion between the air and the fuel. During the stoichiometric combustion process, no fuel or air are left over.

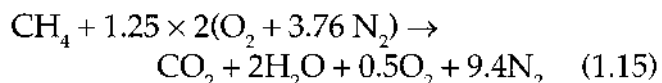
To determine the **excess air** or **excess fuel** for a combustion system, we need to know the stoichiometric **air-fuel ratio**. If the air content is higher than the stoichiometric ratio, then the mixture is said to be **fuel-lean**. But if air content is less than the stoichiometric ratio, the mixture is **fuel-rich**.

Taking methane as an example, the chemical equation for stoichiometric combustion is:



If more air is supplied, some of the air will not be involved in the reaction. The additional air (the *excess air*) will be used along with the *theoretical air* during the combustion. 200% theoretical air is 100% excess air.

The chemical equation for methane burned with 25% excess air can be expressed as



1.7 Gas Mixtures

If the flammability limits of the components of a mixture are known, the limits of the mixture may be calculated by

Le Chatelier's law. The form of this law for lower limits of complex mixtures in air is:

$$L = 100 / (C_1/L_1 + C_2/L_2 + \dots C_i/L_i) \quad (1.16)$$

where $C_1, C_2 \dots C_i$ are the proportions of each combustible gas in the mixture, free from air and $L_1, L_2 \dots L_i$ are the lower limits of each combustible gas in air, and L is the lower limit of the complex mixture in volume percent.

Although Le Chatelier's rule predicts fairly reliable lower limits for mixtures of many common fuel gases, it tends to be less reliable for upper-limit calculations because of the more complex reactions. Also, its application to limits of upward propagation that are greatly influenced by preferential diffusion (H_2 -air) and to limits of materials that involve chemical flame inhibition (extinguishing agents) presents uncertainties.

