

Three Tools to Visualize and Prevent Boilers and Furnaces Firebox Explosions

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Explosive incidents with harmful consequences continue to occur in boilers and furnaces (heaters) where fossil fuels are burned. Proper designs, proper maintenance, and proper operating procedures have been developed, backed by standards, codes, guidelines, and recommended practices. However, process knowledge (education) and appropriate operating and maintenance procedures (training) remain the essential tools for personnel to understand the circumstances leading to catastrophic consequences and thus be able to enhance the safety conditions of combustion processes. Tackling the root of this problem requires visualizing the associated concepts, rules, and cautions to fully understand the nature of combustion, foresee its hazards, and prevent incident outcomes and consequences. This article is intended to provide colleagues in the field, engineers, technicians, and operators—who, on a daily basis, live in close proximity to the risks of fossil-fired boilers, furnaces, gas turbines, heaters, and processes with flammable mixtures—three basic tools to allow them to visualize, and thus, find it easier to remember, the concepts associated with the hazards of combustion processes by reviewing the knowledge available to prevent explosive incidents. © 2017 American Institute of Chemical Engineers Process Saf Prog 36: 221–236, 2017

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We can benefit from nature if we understand and respect its inherent rules of behavior. (Eng. Roberto Fernández Blanco—DASIS Corp. [CCPS Member])

INTRODUCTION

Nature has a simple character and foreseeable behavior. Its truths are its “essence,” what is “inherent,” the stark “reality” that we should observe and appreciate with scientific objectivity, assimilate, and respect. Only if we understand the rules of its natural behavior will we be able to operate with it in a harmonious and productive manner. Such rules entail knowledge that we should learn to decipher, free from any preconceptions, for our greater safety

and benefit, describing them in straightforward and precise mathematical language. To those who worry about how difficult it is to lose weight, nature tells them that by merely traveling to interstellar space they will see their “weight” drop drastically, but their figure (“mass”) will remain unchanged. This evidences the fact that the “essence” of a body is its mass and that its weight is a consequence.

Similarly, it is key for plant personnel to understand the “essential nature” of any risk processes they live together with and the rules of their natural behavior to visualize the hazards and prevent the risks they are exposed to, as “You can’t prevent what you cannot imagine” (quoted from my presentation at fifth LACPS-2013—Cartagena, Colombia).

COMBUSTION: THE RULES OF ITS NATURAL BEHAVIOR

Boilers and furnaces generate heat for heating up process fluids and products through hydrocarbon combustion in large combustion chambers (fireboxes) capable of withstanding continuous temperatures well over 1,100°C and hold, at pressures close to atmospheric levels, the substantially expanded volume of gases resulting from combustion. Within a firebox, and close to its refractory material walls, floor, and roof, there is a grid of tightly mounted tubes through which the fluid runs that will be heated by the thermal radiation of inflamed fuels. The tubes come from a previous area—convection zone—where the fluid enters and is preheated by the residual heat contributed by the combustion gases flowing from the firebox toward the stack (Figure 1). However, nature will expose us to catastrophic explosion risks if we do not make sure that the fuel–air mixture combustion is performed observing and respecting the rules of its natural behavior.

What are these rules?

VISUALIZING THE CONCEPTS ON FUEL–AIR MIXTURES

Our knowledge and analysis of the rules of nature (reality) enables us to identify three useful and necessary tools to visualize and prevent the risk of explosions from flammable mixtures in the combustion chambers (fireboxes) of boilers and furnaces where fossil fuels (hydrocarbons) are burned. Flammable materials only burn in the gaseous state. Fuel–oxygen combustion reaction occurs in the gas phase. Thus, liquids and solids (with the exception of carbon) must vaporize and gasify before they can burn. This requires an initial source of heat to start their vaporization/gasification prior to combustion. Once the materials have ignited, a portion of the generated heat is transferred to the nearby flammable material, heating it up to the gaseous condition and

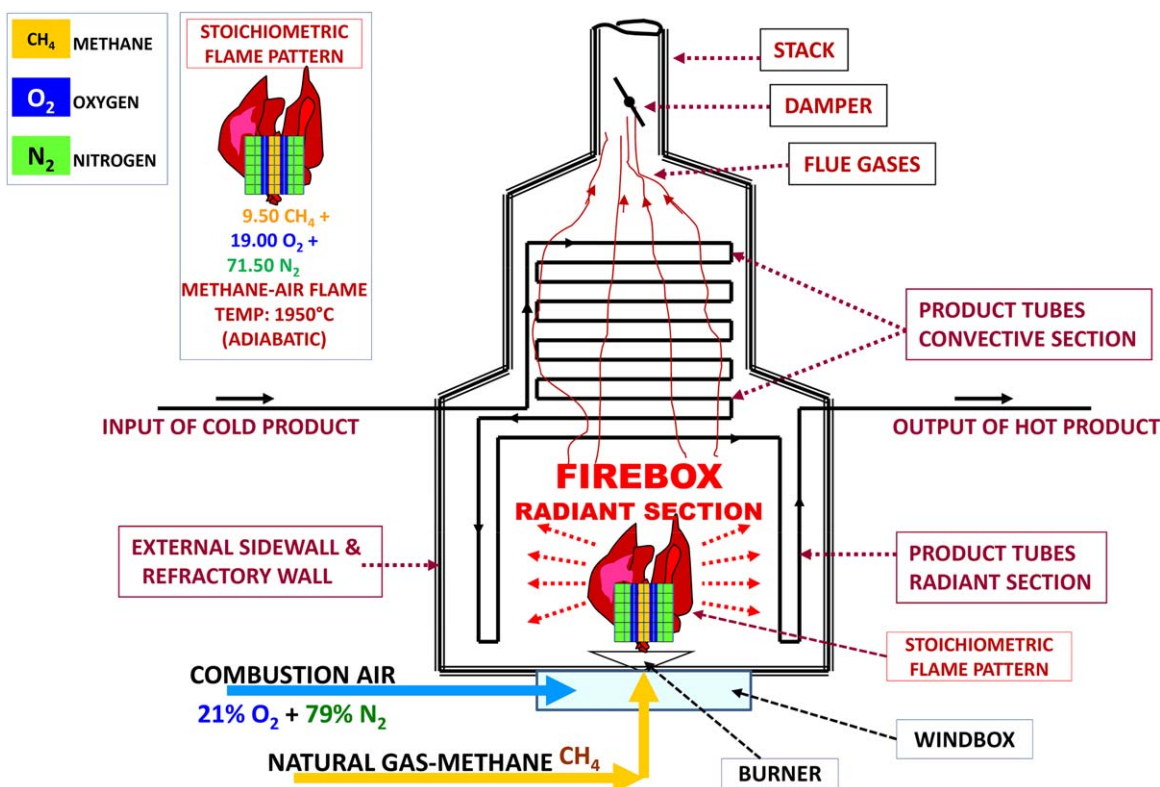


Figure 1. Furnace schematic. [Color figure can be viewed at wileyonlinelibrary.com]

sustaining the propagation of the combustion. Due to the rapid oxidation reaction, heat is generated much faster than it is dissipated, thereby causing a sharp rise of temperature with the emission of visible light (combustion with flame). Some heavier fuel oils (Fuel Oil #5 and #6) need to be pre-heated to reduce their viscosity and allow for an easier atomization—mechanical or steam assisted—to break them down into finely divided droplets (spray) for greater ease of vaporization, gasification, and ignition when they go into the fire-box to be burned. Similarly, solid fuels need to be pulverized first and then gasified through chemical decomposition (pyrolysis).

Combustion of most flammables occurs in the gaseous phase. Often, the mixtures are at low relative pressures (ca. atmospheric) and thus, the ideal gas law applies:

$$P_{\text{abs}} V = nRT_{\text{abs}}$$

Where,

P_{abs} is the absolute pressure (gauge plus the local barometric pressure), Pa

V is the volume of the system, m^3

T_{abs} is the absolute Temperature, K.

R is the ideal gas constant, which is $8.314 \text{ Pa m}^3/\text{mole K}$ in SI units.

n is the number of moles.

About Mole, as a fact of nature the molecular mass or molecular weight, M , of all ideal gases (being at the same pressure and temperature) occupies the same volume, referred as molar volume V_m , named V_{mole} or just “mole” (here represented by a V_m Box and chosen as a benchmark as shown in Figure 3). The mole contains equal amount of substance regardless of the specific molecular mass of any gas. That is why the above equation does not include any element that distinguishes one gas from another, it holds for

all gases and can thus be deemed “universal”: “Therefore, all gases are equal before the law... the Universal Law of Ideal Gases.”

At the reference condition of $t = 0^\circ\text{C}$ ($T_{\text{abs}} = 273.15 \text{ K}$) and $P_{\text{atm,abs}} = 1.01325 \text{ Pa}$, the molar volume of any ideal gas turn out to be $V_{\text{mole}} = 22.415 \text{ dm}^3$ (liters), containing the fixed quantity of substance of 6.022×10^{23} particles (called the Avogadro constant N_A).

To distinguish the molar volume for the different gases involved in combustion, we use different colors (Figure 4), bearing in mind that each box represents one molar volume and that every gas differs from the others by its molecular make up and molecular mass.

Combustion calculations involve transitions between moles, volumes, and masses.

The ideal gas law along with molecular masses assist in these conversions:

Example: To know how many kilograms of oxygen (O_2) are contained in a cylinder of 54 L at 140 barg and 27°C , we first need to find out the “ n ” number of moles contained there.

From the gas law: $n = P_{\text{abs}} V / RT_{\text{abs}}$, where:

$$P_{\text{abs}} (\text{Pa}) = 140 \cdot \text{barg} \times 10^5 \cdot \text{Pa/bar} + 1.01325 \times 10^5 \text{ Pa} = 141.01325 \times 10^5 \text{ Pa (absolute)} =$$

- $P_{\text{abs}} (\text{Pa}) = \sim 141 \times 10^5 \text{ Pa} = \frac{141 \times 10^5 \text{ N/m}^2}{}$
- $T_{\text{abs}} [\text{K}] = 273.15 + 27^\circ\text{C} = 300.15 \text{ K} \sim 300 \text{ K}$
- $V = 54 \text{ dm}^3 = \frac{54 \times 10^{-3} \text{ m}^3}{}$

Then,

$$n = P_{\text{abs}} V / RT_{\text{abs}} = 141 \times 10^5 \text{ N/m}^2 \times 54 \times 10^{-3} \text{ m}^3 / 300 \text{ K} \times 8.31434 \text{ N m/mole} \times \text{K} = \sim 305 \text{ moles}$$

As O_2 has a molecular mass of 32 g/mole, the total mass is

$$\text{Total mass } \text{O}_2 = n \times M_{\text{O}_2} = 305 \text{ moles} \times 32 \text{ g/mole} = \underline{9,760 \text{ g of } \text{O}_2}$$

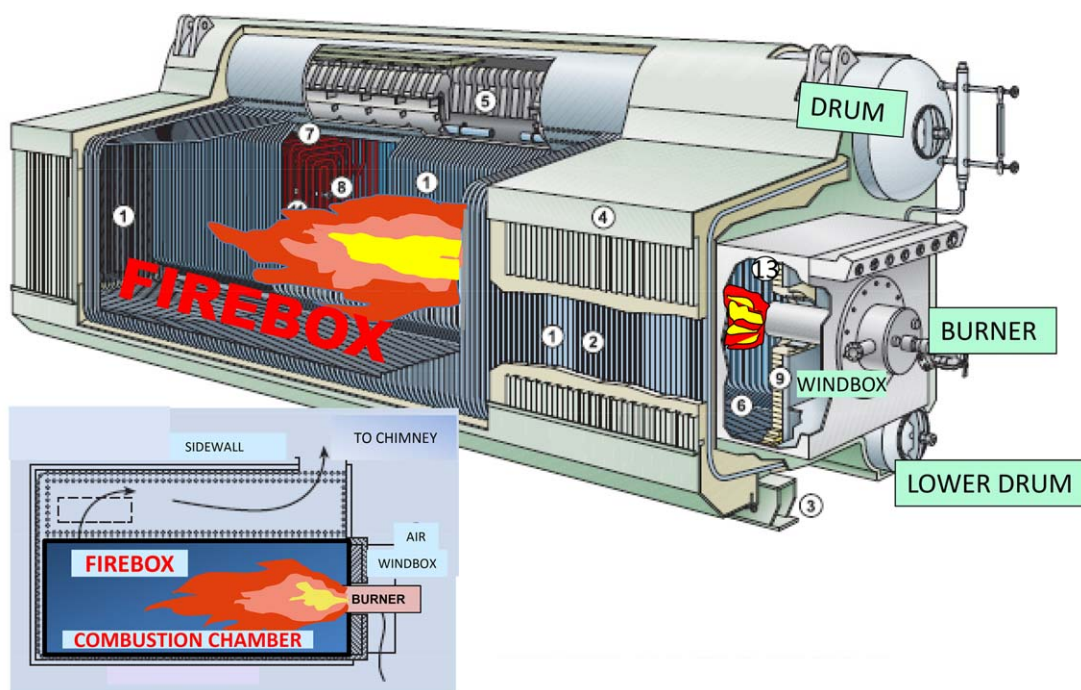


Figure 2. Boiler cross-sectional view. [Color figure can be viewed at wileyonlinelibrary.com]

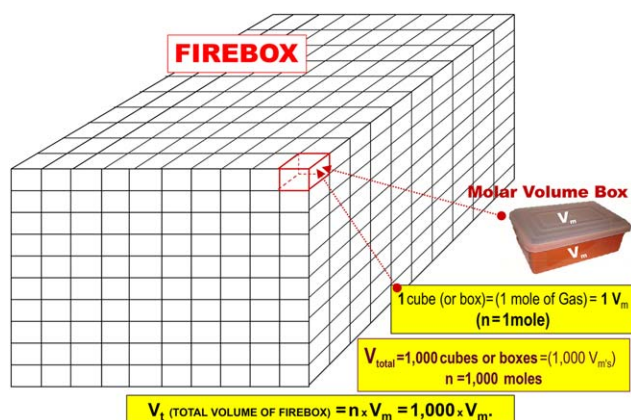


Figure 3. Combustion chamber represented by 1,000 moles. [Color figure can be viewed at wileyonlinelibrary.com]

FIRST TOOL—VISUALIZING THE FUEL-AIR MIXTURE IN THE COMBUSTION CHAMBER: INTRODUCING MOLAR VOLUME

Figure 2 shows a cross-sectional view of a single-burner boiler with its combustion chamber (firebox). A furnace has a similar arrangement (Figure 1). One or more burners supply fuel (fuel gas, fuel oil, and/or pulverized coal) and air into a combustion chamber large enough to accommodate—at close to atmospheric pressure—the passage of the hot, expanding flue gases produced by the combustion of the fuel-air mixtures. Since all fuels (gas, vapor, liquid, or solid) ignite once gasified, we will use, as a proxy for purposes of our analysis, a methane-air mixture. If the methane oxidation was performed exclusively with pure oxygen and at the exact stoichiometric proportions where the union of both components takes place without resulting in any excess or shortage of either one, the vigorous combustion carried out

at the burner outlet would reach an equilibrium temperature close to 2,760°C (3,033 K). However, if the combustion occurs with oxygen from atmospheric air, also at the perfect stoichiometric methane/oxygen proportions, the inevitable presence of inert nitrogen from the air would absorb some of the heat produced by the combustion, thus reducing the equilibrium temperature in the flame pattern zone to a value under 1,940°C (2,213 K).

With the fuel and the air entering at about 25°C–27°C (~300 K) through the burner into the firebox and being burned at a temperature of up to 2,213 K, the ideal gas law predicts that the flue gases expand at the proportion $V_2/V_1 = T_2/T_1 = 2,213/300$ or approximately 7.40 times, a fact that warrants the large size of the combustion chamber to accommodate the expanded flue gases at near atmospheric pressure. It is usually necessary to add some excess air flow, of approximately 5%–15%, to ensure complete combustion of methane-air to carbon dioxide and water vapor.

What takes place in the firebox is the combustion and the radiant transfer of heat from the burner's flame shape (or fire ball) to the processed product passing through the tubes (water or any other element), which requires the combustion chamber to have adequate dimensions to accommodate the expanded flue gases, while also providing space to fit the grid of heated product tubes along the firebox walls, roof, and floor *and* keep the grid far enough from the tongues of flame to prevent them from impinging on (i.e., touching or licking) it, in order to preserve and protect from overheating, both the heated product and the mechanical integrity of the tubes.

To simplify the visualization of the flammable mixture in any combustion chamber (firebox), we will start our analysis by assuming that the firebox is a symmetrical cubic cabin filled with a compact pile of bricks, cubes, or boxes that cover its entire volume (Figure 3). Each cube has the capacity of 1 mole of gas or 1 molar volume, V_m . Figure 3 shows $10 \times 10 \times 10$ molar volumes, all at the same pressure and temperature, totaling $1,000 V_m$ and $n = 1,000$ moles total.

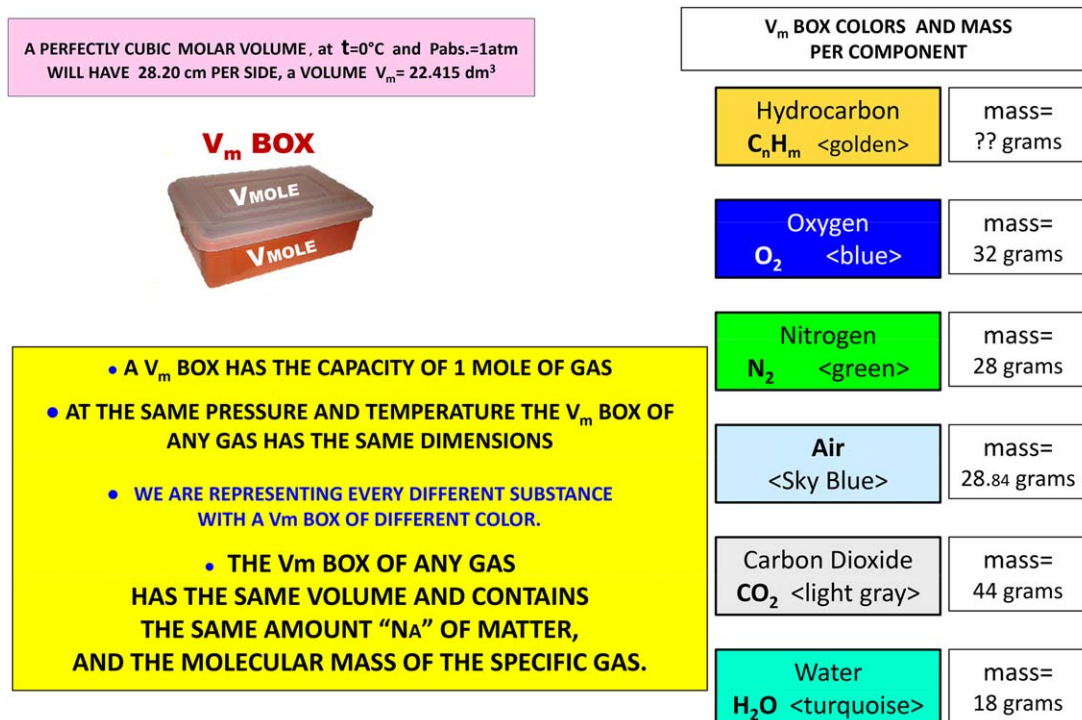


Figure 4. Colors of V_m BOX for different components. [Color figure can be viewed at wileyonlinelibrary.com]

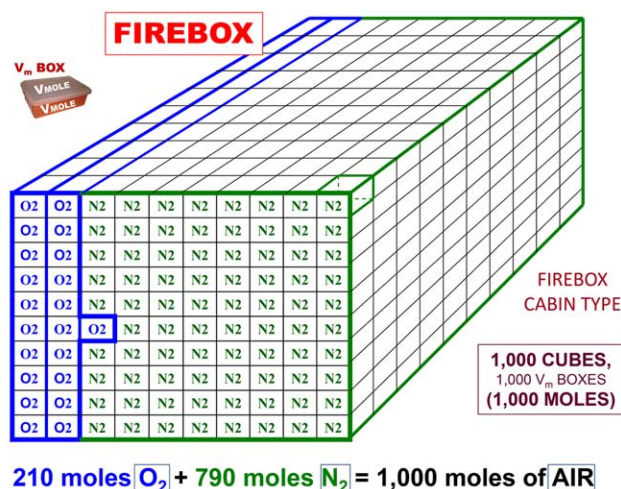


Figure 5. Firebox full of air (volumetric view). 210 moles O_2 + 790 moles N_2 = 1,000 moles of AIR. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 5 depicts our firebox full of air, that is, containing 210 molar volumes of oxygen (O_2) (blue) and 790 molar volumes of nitrogen (N_2) (green), totaling 1,000 molar volumes of air.

As at 1 atm and 0°C , every molar volume has a precise value of $22.415\text{ dm}^3/\text{mole}$, our 1,000 moles firebox has (at 1 atm and 0°C) a total volume of $22.415\text{ dm}^3/\text{mole} \times 1,000\text{ moles} = 22.415\text{ m}^3$, that is, it is a firebox of about $2.85\text{ m} \times 2.85\text{ m} \times 2.85\text{ m}$. At different temperatures, the molar volumes will change accordingly, increasing proportionally with the absolute temperature and decreasing inversely with the absolute pressure (see ideal gas law).

Now that we have achieved a clear, three-dimensional visualization of how the firebox is filled, for the sake of greater simplicity but with the same scientific rigor, we will proceed to visualize (represent) our specific firebox in two dimensions ($10 \times 10 = 100$), from a front or side view, an approach that will allow us to make calculations in percentage terms. Figure 6 depicts the firebox full of air, that is, with 21 moles of O_2 (blue) plus 79 moles of N_2 (green), totaling 100 moles of air.

Next, let us consider the addition of a fuel and the process of combustion. In our example, 1 mole of CH_4 (methane) reacts with 2 moles of O_2 to create 1 mole of CO_2 plus 2 moles of H_2O (as vapor); 802.62 kJ of energy of CH_4 is released in the process [9]. This energy is used to heat the exhaust gases, including the inert nitrogen, and heat the surrounding process fluid passing through the tubes. A perfect or complete combustion (a stoichiometric reaction) occurs when it involves the exact required pairs of flammable gas moles with oxygen moles (or grams) where both are consumed together without any shortage or excess left over.

The mass involved are as follows: Using methane CH_4 for a stoichiometric relationship with oxygen (O_2), every mole of carbon (12 g) will burn with 1 mole of O_2 ($2 \times 16 = 32\text{ g}$) producing 1 mole of carbon dioxide (CO_2) ($12\text{ g} + 2 \times 16\text{ g} = 44\text{ g}$ of CO_2) plus heat. Similarly, each of the two 2 moles of hydrogen (H_2) ($2 \times 1\text{ g}$ each) burns with 1 mole of oxygen (O_2) ($2 \times 16 = 32\text{ g}$) to engender two 2 moles of water (H_2O) ($2 \times 1 + 16 = 18\text{ g}/\text{mole}$ of water, total 36 g of H_2O) plus heat (Figure 7). Thus, to achieve its complete combustion, every mole of CH_4 relates with 2 moles of O_2 , exhaling 1 mole of CO_2 , sweating 2 moles of H_2O , and releasing heat (about $802.6\text{ kJ}/\text{mole}$ of CH_4). If this reaction happens with air (Figure 7), the inert presence of the non-participant nitrogen (N_2) should be included as a voyeur inert gas heated by the heat released by the $\text{CH}_4 + 2 \times \text{O}_2$ combustion.

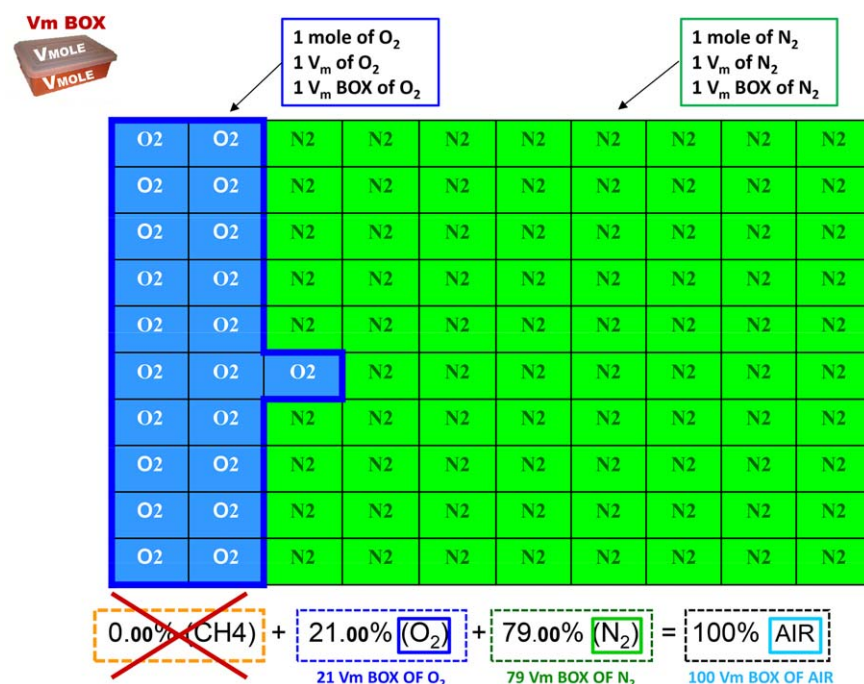


Figure 6. Firebox with Air only—lateral view. [Color figure can be viewed at wileyonlinelibrary.com]

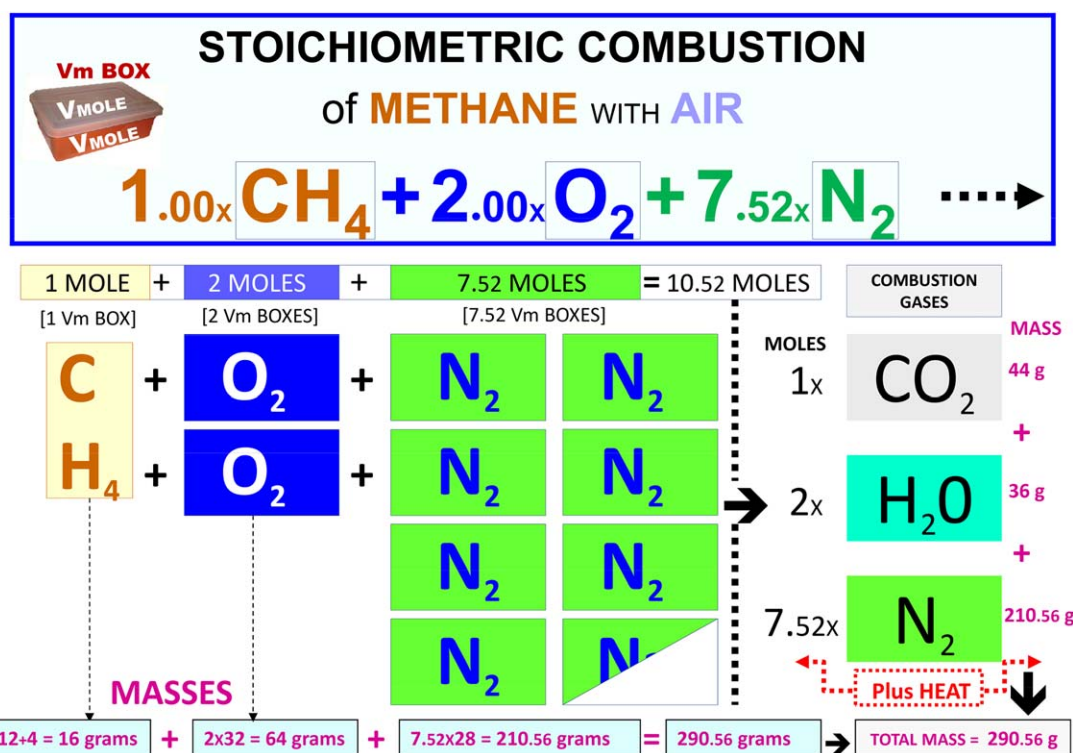


Figure 7. Methane–air stoichiometric combustion. [Color figure can be viewed at wileyonlinelibrary.com]

From the air composition, 21% O_2 + 79% N_2 = 100% AIR , we realize that for every mole of O_2 in the air introduced, $79/21 = 3.76$ moles of the burdensome moles of nitrogen (N_2) are added. To put this in percentage terms in order to visualize the composition of moles within the firebox of Figure 8, we proceed as follows:

Furnace feed 1 mole CH_4 + 2 moles of O_2 + 2×3.76 moles of N_2 = 10.52 moles of AIR .

Dividing everything by 10.52 and multiplying by 100, we get the equation in percentages:

$$9.50\% \text{CH}_4 + 19.00\% \text{O}_2 + 71.50\% \text{N}_2 = 100\% \text{gas-air mixture}_2$$

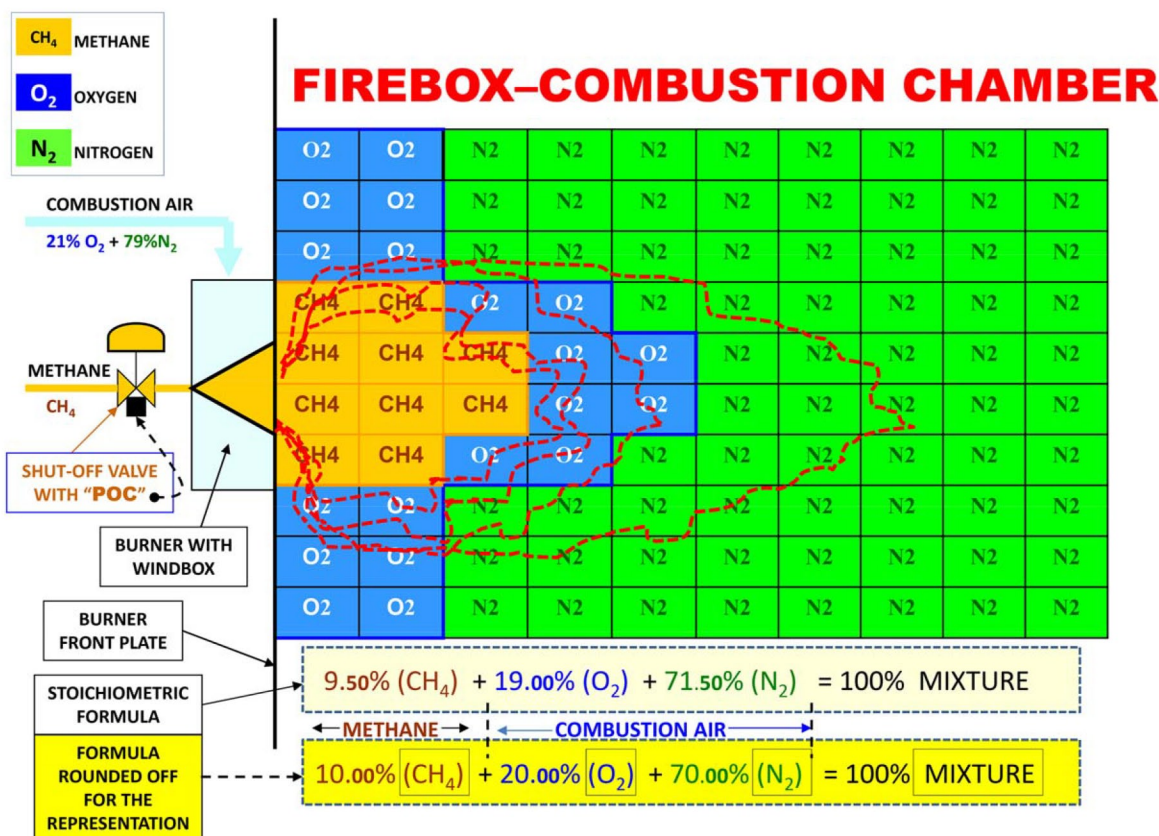


Figure 8. Stoichiometric mixture methane-air. [Color figure can be viewed at wileyonlinelibrary.com]

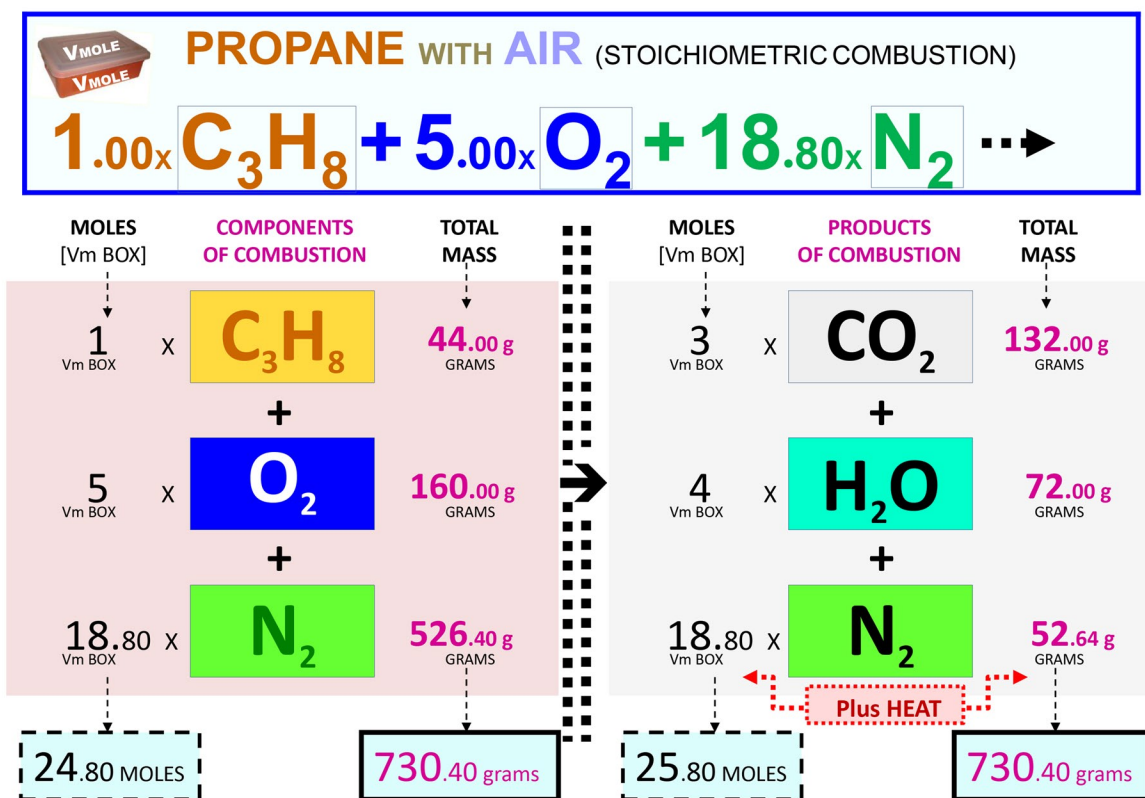


Figure 9. Propane-air stoichiometric combustion. [Color figure can be viewed at wileyonlinelibrary.com]

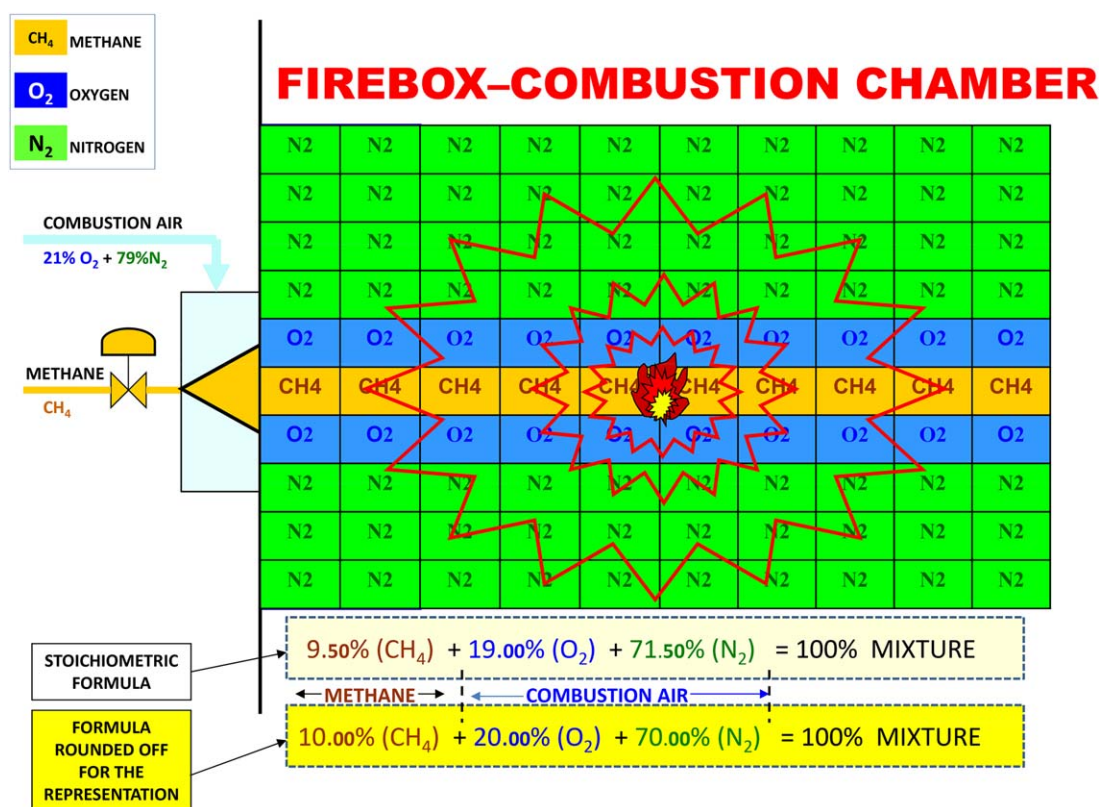


Figure 10. Inflammation and radiation of a stoichiometric methane–air mixture. [Color figure can be viewed at wileyonlinelibrary.com]

To make this visualization easier, we round up the percentages as follows:

$$10.00\% \text{ [CH}_4\text{]} + 20.00\% \text{ [O}_2\text{]} + 70.00\% \text{ [N}_2\text{]} = 100\% \text{ gas-air mixture}$$

This is the simplified equation we use for visualization in Figure 8, which allows us to realize—and be aware of—how little volume of methane in air is necessary to have a stoichiometric flammable mixture within the firebox ready to be ignited explosively.

In Figure 9, propane–air stoichiometric combustion is included to show and point out that the quantity of moles of the products of the reaction may or may not be equal to the quantity of moles participating as components in the reaction, but the total mass of the products will be always equal to the mass of the components of the reaction.

Figure 10 shows the ignition, inflammation progress, and radiation of a stoichiometric methane–air mixture. Starting from a stoichiometric union, if either one of the components is added, air (forming a lean mixture, i.e., without enough fuel) or methane (forming a fuel-rich mixture), the excess parts of the components will not participate in the combustion reaction, but will only absorb heat, reducing the overall temperature rise due to combustion. If one of the reactants too limited, combustion cannot be sustained. These limit points are the lower flammability level (LFL) and the upper flammability level (UFL). Figure 11 displays four different methane–air mixtures and situations within the firebox. Figure 11a reproduces the stoichiometric mixture shown in Figure 7. This is the optimal combustion mixture representing the normal continuous operation, where the burner causes the participants, methane and oxygen (air), to enter the

combustion chamber together in stoichiometric (or close) proportions, irrespectively of the flow being supplied but each keeping its due proportions, so that they both can enjoy a full and complete combustion. Figure 11b shows a methane–air mixture at the LFL, which means that, at a level under this low percentage of CH₄ volume in air (lean mixture), the participants in this poor oxidation process would release an unsatisfactory level of calories, resulting in such low body temperatures (less than 1,200°C) that they will not sustain the participants' interest in burning together. Thus, the combustion will not take place. In turn, Figure 11c shows a methane–air mixture at the UFL. This means that the high percentage of CH₄ volume in air leave methane without the company of enough oxygen (air) to satisfy its oxidation desire, so the combustion will be not accomplished.

Within these two limits (LFL and UFL), the combustion may be accomplished with part of the components not participating but absorbing heat and reducing the oxidation temperatures. Thus, a firebox full of any of these mixtures between the above two limits will result in an explosion of the entire volume of mixture if an ignition source triggers the oxidation act, with the obvious tragic consequences.

So, visualize and bear in mind how little volumes of methane in air (the same applies to other fuels) are needed to have a full firebox explosion! This clearly provides evidence about how important it is to implement appropriate operating procedures and layers of protection to prevent the accumulation of these explosive mixtures and the potentially ensuing firebox explosion. In fact, the safest condition (and more efficient combustion) actually occurs when methane and air harmonically consummate their oxidation act as closely as possible to their optimal relationship condition (stoichiometric). However, let us take a special look at Figure

VISUALIZING THE FIREBOX WITH METHANE FLAMMABLE MIXTURES

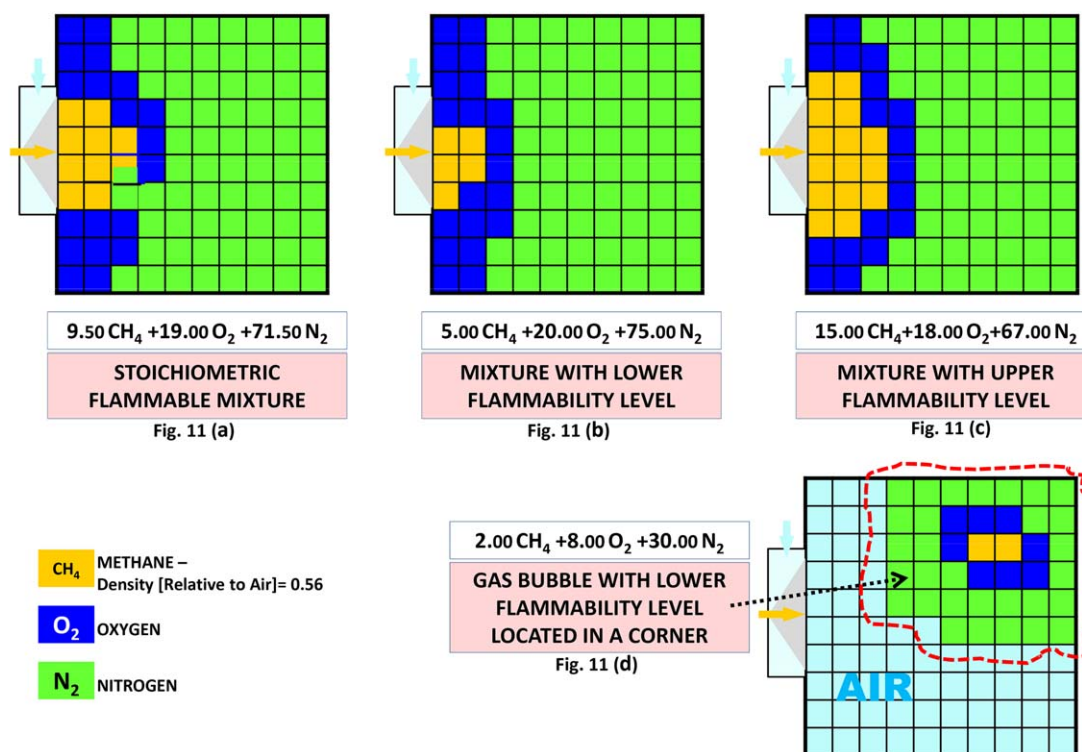


Figure 11. Flammable gas mixtures. [Color figure can be viewed at wileyonlinelibrary.com]

11d. The methane density is about half (~ 0.56) the density of air. This causes the unburned methane to float in air as a buoyant gas and move on to stay in any corner within the firebox or any other internal sections of the boiler or furnace, creating a small flammable bubble or cloud that, upon finding the necessary oxygen and any ignition source (or auto-ignition temperature [AIT] when the boiler or furnace is operating), will lead to an explosion of reduced intensity, from a minor “puff” level to any other bigger localized explosion with some destructive consequences.

Such explosions occur rather frequently as a result of various types of problems, like leakages through the methane shutoff valves into the firebox or when there is an inappropriate ratio between the incoming flows of methane and air, as any methane in excess over the stoichiometric oxidation, left with unsatisfied burning desires due to the lack of oxygen, moves to other areas in the firebox in search of more seductive oxygen to complete the pending ardent encounter.

FIRST TOOL SUM-UP

We have now clearly visualized the great affinity between fuels and oxygen. The visualization of the combustion mixtures with molar volumes allows operators to imagine, and be alert to, any potential explosive risk that may surround them. It also demonstrates how necessary it is to impose rules and limits to ensure safe and efficient oxidation reactions.

The key to a safe and efficient combustion reaction lies in the combustion chamber (firebox). Everything there should be “perfect,” namely, an appropriately designed burner operating in an “as good as new” (AGAN) condition, the fuel participating with its expected quality, and both fuel and air

entering the combustion chamber together, with the required total flow of fuel plus air necessary to supply the demanded degree of heat into the firebox but always maintaining the appropriate (stoichiometric or near-stoichiometric) proportions between them in order to become close to each other and consummate the most complete and satisfactory oxidation with the expected flame shape to supply the required heat with a regular distributing radiation profile within the firebox.

To ensure such safety and efficiency, it is necessary to have a proper fuel/air cross-metering Instrumented Combustion Control System (ICCS). The ICCS needs a high degree of reliability and integrity to keep the right fuel–air relationship for the continuously changing load of combustion (as demanded by the process). The ICCS needs to be capable of maintaining a steady flame throughout the burner turndown ratio (the ratio between its maximum and its minimum steady firing capability), and thus ensuring that under no circumstances will the fuel flow exceed the established air flow ratio and lead to a fuel-rich mixture. Why is this? Because, if the fuel–air relationship turns into a fuel-rich condition, the hot fraction of unburned fuel will seek for more oxygen anywhere, leading to a possibly wild completion of the oxidation process in an explosive way, which may range from a mere “puff” to a stronger explosion, particularly if the excess fuel builds up as a bubble or cloud in any area of the boiler or furnace when traveling with the flue gases to the stack.

Special recommendations are in order to address this hazardous, high-risk situation. The wrong and dangerous natural tendency of an improperly trained operator is to suddenly try to compensate for the “lack of air by adding air” when he or she realizes that there is an excess of fuel over the

stoichiometric ratio. The operator supplies the oxygen needed to complete its combustion, however, the result may be explosive because of accumulated unburned fuel within any place of the boiler or furnace. The magnitude or severity depends upon the accumulated surplus of unburned fuel.

So, *never add air when there is hot unburned fuel*. What the operator should do is just the opposite: reduce the fuel flow back to its proper relationship with air, thus causing the combustion to occur at its most satisfactory, complete condition, that is, stoichiometric. Only after restoring the proper fuel/air ratio will the operator be able to safely and efficiently increase both components in tandem—while at all times keeping the appropriate fuel/air ratio—to supply the heating calories the process is needing.

In addition to the explosive risk described above, another one may emerge. The lack of a proper amount of air causes the flames to lengthen, in response to the fuel's attempt to find the sought-after oxygen, until they can touch the tubes (flame impingement) and complete their combustion over the skin of the tubes, heating them up to temperatures of about 1,370°C that severely weaken their mechanical integrity and thus engender a high risk of triggering a huge fire if tube ruptures occur in furnaces that heat flammable products.

So, to sum up, to ensure a safe and efficient combustion, it is necessary to bear in mind that:

- a. The basic, key safety rule is “Never allow a boiler or furnace vessel to hold unburned fuel,” either when it is out of service or in operation. In other words, “No fuel should enter the firebox if it is not going to be immediately and totally burned.”
- b. The combustion chamber (firebox) and the burners of a boiler or furnace should be optimally designed to accommodate the fuels that are going to be burned. This includes the burners' fuel tips with their orifices of proper size, positions and alignments and the combustion air with adequate distribution, everything in order to obtain the proper flame pattern with a sufficiently smaller flame shape and volume (for faster concentrated combustion) and proper orientation within the firebox.
- c. Many factors may affect the operation of the burners, such as (a) poor quality of out-of-specification fuels, also with undesirable components (like hydrogen sulfide); (b) inappropriate fuel conditions (lack of cleanness, pressure, temperature, viscosity, and atomizing media); (c) inadequate velocity of the fuels exiting the tips due to mechanical degradation of the tips with orifice sizes damaged by oxidation, erosion and/or corrosion, also producing uneven flames; (d) tip problems resulting from dirt, debris, clogging, plugging, and/or coke buildup that narrow or block the tip fuel jets; and (e) also external failures in ancillary components like filters, pumps, fans, dampers, valves, and so forth.
- d. The first, critical prerequisite for a safe and efficient combustion is definitely to keep the burners in AGAN condition, operating with the fuels they are designed for and within the proper operating values as to quality and parameters.
- e. None of the above problems and concerns can be overcome with instrumented systems. No instrumented system could make the burners (and, hence, the boiler or furnace) produce what they are unable to do by themselves because of their poor design, the use of inappropriate fuels, fuels out of proper operating conditions (pressure, temperature, viscosity, purity, and atomization), and/or burner components mechanically degraded due to a lack of proper maintenance.
- f. Inefficient and risky combustions problems arise from inadequate fuel–air ratios; irregular flame patterns; flame impingement; leaks and spillages; flame instability; flame flashback; leaning-tilting flame; flame liftoff; smoky flames; water in fuel oil or liquids in fuel gases; dirty burner tip; eroded tips; tips improperly oriented; plugged or partially plugged tips; tips improperly placed, incorrectly positioned or turned toward a wrong orientation; windbox or plenum not correctly sized, causing some burners to have more combustion air while others are starved for it, and so forth. None of these problems may be overcome with control or safety instrumented functions.
- g. It is necessary to pay very special attention to the issue of fuel shutoff. We have seen above (Figure 11d) how little unburned fuel accumulated in the firebox or any other corner of the boiler/furnace is required to result in an explosive risk.
- h. To prevent explosive conditions, it is necessary to avoid unburned fuel accumulation when the boiler or furnace is out of operation due to a normal, safety, or emergency shutdown or when some burners go out of operation due to an operative (normal) burner shutdown or due to a flameout (burner safety shutdown). It is also helpful and strongly recommended to implement a fast lightoff of the pilot burners with one-shot ignition of proper heating power.
- i. Special care should be taken in selecting the manual supervised shutoff valves and the fast-closing automatic safety hermetic fuel shutoff valves to prevent any fuel leakage through the burner into the combustion chamber (see Codes and Standards NFPA 85, 86, and 87 for further details).
- j. The Burner Management System—which long ago my company dubbed Burner Management Safety Instrumented System (BMSIS)—is intended to protect the boiler or furnace by Monitoring (sensing, indicating and alarming), Supervising (sensing, indicating, alarming, and automatically acting as interlock and/or permissive) and executing the proper safe sequences for lightoff and normal or emergency shutoffs and shutdowns when dangerous conditions arise such as a flameout of burners.
- k. BMSIS must comply with the NFPA requirements (NFPA 85 and 86) and follow the recommendations stated in safety performance standards IEC 61508 and ANSI/ISA 84/IEC 61511.

SECOND TOOL: VISUALIZING AND UNDERSTANDING THE FLAMMABILITY TRIANGLE

The Flammability Triangle is a map that depicts—within an equilateral triangle—the areas where the fuel, oxygen, and nitrogen mixtures are and are not flammable. This regular triangle, with all three sides of equal length, is used as a perfect coordinate system to represent with one point any specific mixture of the three components, like the equations in Figures 7 and 9, but expressed in percentages as shown in Figures 8 and 10.

How Does It Work?

By looking at Figure 12, we will realize that any parallel sides of an equilateral triangle forms internal equilateral triangles like IPH, IFC, AEH, and FPG. The scale of any of the sides ranges from 0% to 100%. Any inside point “P” is identified by the three arrows or segments: IP (fuel, golden), GP (oxygen O₂, blue), and EP (nitrogen N₂, green).

Through geometrical comparisons, we can see that IP = AD (on the AB scale), GP = EB = CH (on the CA scale), and EP = DE = BF (on the BC scale). Then, Figure 12 shows us that IP + GP + EP = AD + EB + DE = AB = 100%.

$$IP + GP + EP = 100\%$$

Segment IP being equal to the percentage of the fuel in the mixture, segment GP equal to the percentage of the oxygen (O_2), and segment EP equal to the percentage of nitrogen (N_2), the addition of all three segments totals one side of the triangle, that is, 100%. So, any point "P" inside the triangle exactly represents the mixture of any fuel gas with oxygen and nitrogen, where $IP = AD\%$ is the percentage of fuel, $GP = CH\%$ the percentage of oxygen (O_2), and $EP = BF\%$ the percentage of nitrogen (N_2).

Of course, any distinct fuel will have its proper Flammability Triangle (or Flammability Map). We will perform the analysis drawing the Flammability Triangle of methane based

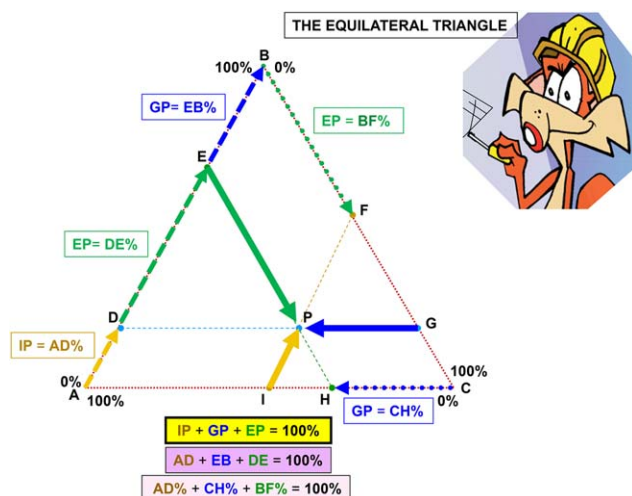


Figure 12. Identifying the mixture represented by point "P". [Color figure can be viewed at [wileyonlinelibrary.com](#)]

on the formula from Figure 7. The procedure for all other fuels is exactly the same.

Side AB% is the scale for methane (CH_4), side CA% the scale for oxygen (O_2), and side BC% the scale for nitrogen (N_2) (Figure 13).

As most combustions occur with air, we will draw the line that represents all the air points that will complete the mixture with any percentage of fuel. This air line starts at point K, where the percentage of fuel is 0% (which means that the mixture is pure air), the percentage of oxygen (O_2) is $CK = 21\%$ (point K) and the percentage of nitrogen (N_2) is $BL = 79\%$ (point L) (Figures 6 and 13). The air line ends at point B, where the mixture is pure fuel ($AB = 100\%$, $O_2 = 0\%$, and $N_2 = 0\%$). The KBL triangle clearly shows that any point P_i on air line KB meets the ratio of the air components, that is, $N_2/O_2 = 79/21$ (BL/CK).

The other important line, CE, represents all the possible stoichiometric oxidation reactions, all the points in a complete oxidation (combustion) of methane where every mole of CH_4 reacts with 2 moles of oxygen O_2 ($1CH_4/2O_2$) for any participating amount of inert nitrogen N_2 .

Point E represents the mixture of $1CH_4$ with $2O_2$ pure oxygen when $N_2 = 0\%$, that is, 33.33% of CH_4 (AE in the methane red scale) with 66.66% of O_2 (CM in the oxygen blue scale) with $N_2 = 0\%$, this denoted by point B in the green scale of nitrogen. The opposite point C represents a mixture of pure nitrogen N_2 ($100\%N_2$ with $O_2 = 0\%$ and $CH_4 = 0\%$).

Point S, where both lines (air line and stoichiometric line) intersect, represents the methane stoichiometric mixture with air (Figures (10 and 11)a, 13, and 14).

The arrow components of S are $SG = 9.50\%$, $SO = 19.00\%$ and $SN = 71.50\%$, that is,

$$9.50\% CH_4 + 19.00\% O_2 + 71.50\% N_2 = 100\% \text{ MIXTURE}$$

We are now ready to draw the Flammability Map of methane by testing successive laboratory samples representing all the combinations of mixtures to determine, on a point-by-point

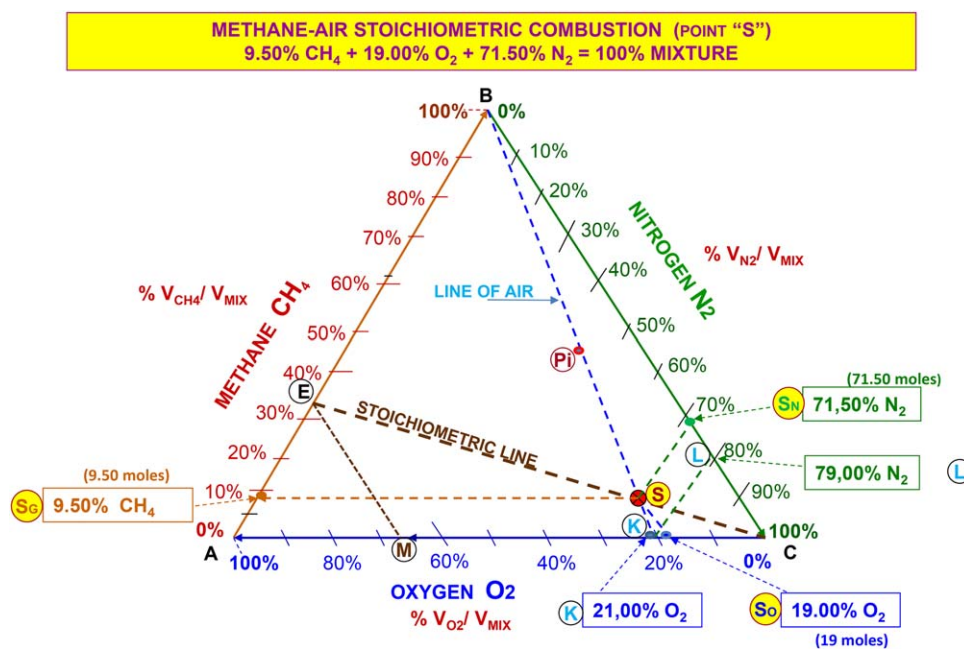


Figure 13. Methane Flammability Triangle. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

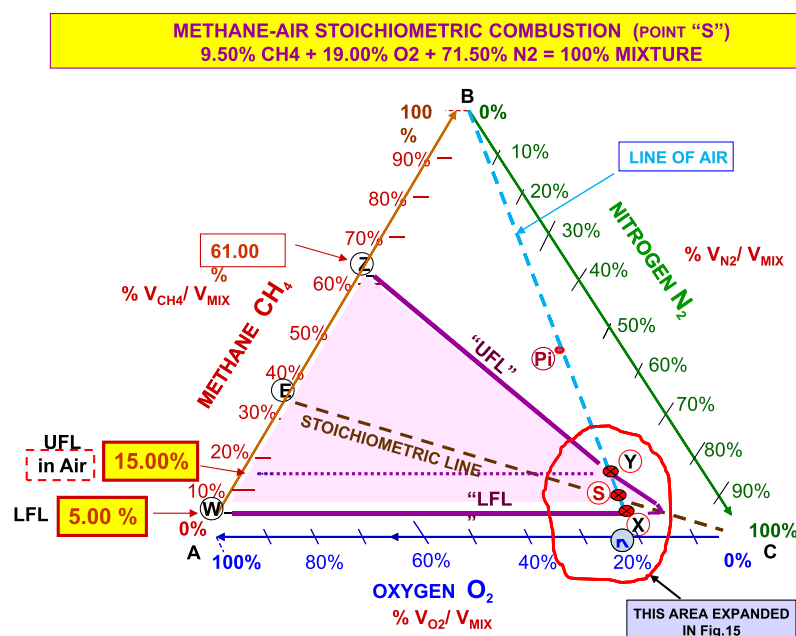


Figure 14. Methane Flammability Map. [Color figure can be viewed at wileyonlinelibrary.com]

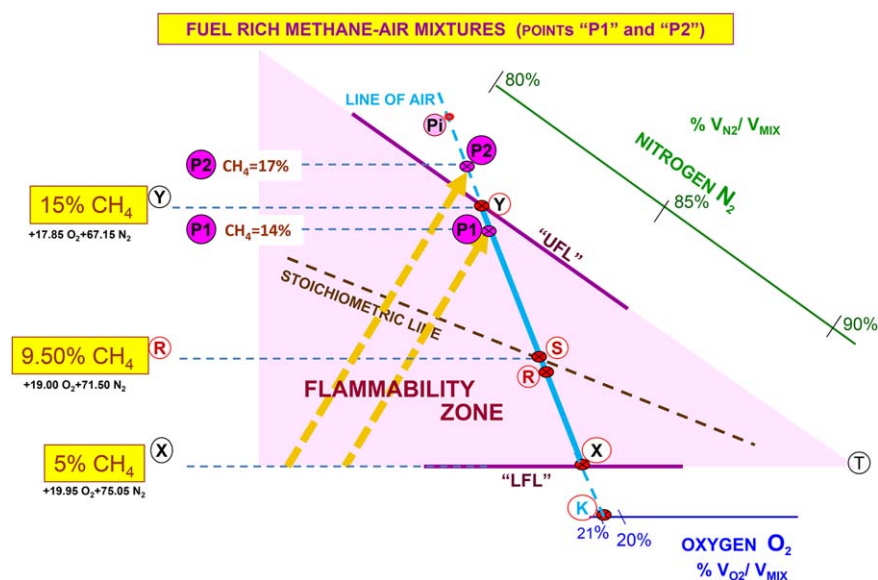


Figure 15. Expanded nose of the methane Flammability Map. Methane-air combustion. [Color figure can be viewed at wileyonlinelibrary.com]

basis, which mixtures are flammable and which ones are not.

The result is the methane Flammability Map in Figure 14, which depicts the boundary of the flammability zone (area shown in violet) that includes all the points (mixtures) at which the mixtures are flammable.

The upper bound is the UFL and the lower bound is the LFL.

All the mixtures represented by points outside the flammability zone are "not flammable."

Of particular interest is segment XY of the air line (see in amplified Figure 15 a representation of the nose of the Flammability Map), which includes point S (the stoichiometric mixture of methane and air), because methane combustions are usually mixtures of the fuel with atmospheric air. Point Y, where the air line and the UFL boundary intersect, represents the UFL of the flammable methane/air mixture, whose value is 15% methane volume in the 100% of the total volume of the mixture, as we visualized in Figure 11c.

Similarly, point X in Figures 14 and 15 represents the LFL of the flammable methane–air mixture, whose value is 5% volume of methane in 100% of the mixture, as we visualized in Figure 11b.

Once the Flammability Map is understood, it is very useful to visualize the combustion characteristics of different mixtures and to evaluate their level of risk in order to establish proper procedures and develop the proper layers of protection when operating with vessels (also boilers and furnaces), gas turbines, and fuel piping, so as to prevent destructive explosions.

We will now consider some different hazardous situations.

Assume that you are operating a one-burner natural gas (mostly methane) boiler having a high load demand. The normal, ideal and most efficient combustion condition is represented by point S in the Flammability Map (the stoichiometric methane–air mixture).

In real life, in order to ensure an appropriate methane–air mixture, it is necessary to operate with some excess of air of about 5%–15%, this mixture being represented by point R with the equation $4.975 \text{ CH}_4 + 19.95 \text{ O}_2 + 75.02 \text{ N}_2$.

A failure in the ICCS or an improper manual adjustment of the fuel/air ratio may cause the mixture to become fuel rich (an excess of fuel over the stoichiometric fuel/air ratio), shown as P1 in the Flammability Map. This means that there is not enough air for all the fuel to undergo a complete combustion. Thus, the surplus fuel anxiously looks for additional oxygen, and its unsatisfactory, incomplete combustion results in the presence of CO (carbon monoxide) in the flue gases and in soot formation.

If the surplus fuel suddenly finds, or is supplied with, extra air, as the combustion chamber and the next section of the boiler (or furnace) are at high temperatures (over 635°C, the methane/air AIT), the outcome will be an explosion of a magnitude ranging from a mere puff to a major explosion, depending on the size of the unburned fuel cloud.

Against this backdrop, all the more relevant is the special recommendation provided in the First Tool Sum-Up section, which we reiterate and highlight below:

- Special recommendations are in order to address the risk arising from a hazardous fuel-rich mixture. This situation usually leads to the spontaneous, but wrong and dangerous, natural tendency of an improperly trained operator to try to compensate for the “lack of air by adding air,” supplying the hot and anxious fuel with the oxygen needed to complete its combustion explosively, with a magnitude or severity depending on the accumulated surplus of unburned fuel.
- So, “never add air when there is hot unburned fuel.”
- What the operator should do is just the opposite: reduce the fuel flow back to its proper (stoichiometric or near-stoichiometric) relationship with air, ensuring that the combustion is accomplished in its most satisfactory, complete condition.
- Only after restoring the proper fuel/air ratio will the operator be able to safely and efficiently increase both components in tandem—while at all times keeping the appropriate fuel/air ratio—to supply the heating calories the process is needing.
- A similar hazardous situation may arise as a result of a sudden flameout of the burner, compounded by a delay in the closure of the fuel shutoff valve and/or an inappropriate closure and/or failure to shut off.

Particular attention should be paid to the selection and maintenance of the fuel shutoff valves because their plug and seat should close hermetically with Leakage Class VI

(FM7400) within 1-s response time, having an inaccessible Proof Of Closure (POC) switch to confirm its closure and having remote and local visual plug position indication. The shutoff valves must be chosen and assembled in accordance with the prescriptive requisites stated by NFPA 85 and 86, with a minimum SIL2 (capable SIL3) integrity level and being rigorously tested periodically at a frequency to be established according to the PFDavg resulting from a Layer Of Protection Analysis or a Quantitative Risk Analysis.

If the boiler or furnace is in a cold condition and there is a leakage in the shutoff valves, the combustion chamber may accumulate fuel up to a mixture concentration level within the flammability zone of the Flammability Map or above the UFL (like point P2 in Figure 15), thus being exposed to the Risk of a catastrophic explosion.

Being over the UFL limit (as point P₂), the mixture (if homogeneous) is not flammable, but when the operator starts to purge the boiler with air to clean up the combustion chamber, point P₂ starts to move down along the air line (KB in Figure 13 or XY in Figures 14 and 15), with the mixture proportions changing accordingly. As a result, point P moves into the flammability zone (now as point P₁), continues moving down from point Y to point X (the LFL limit), and drops further until it reaches point K. The purge is thus completed, with the total removal of any fuel from the boiler.

This firebox purging should also be done taking special care not to generate sparks (static sparks or those resulting from pushing metallic debris), with the forced draft fan blowing softly and sending the minimum (or over it) air flow recommended by NFPA 85 during the estimated necessary time to complete the established number of boiler volume removals to make sure that fuel has been cleaned out of the firebox.

But an additional precaution should be taken in view of the possibility that a shutoff valve is not functioning well, has a fuel leakage in spite of being hermetically closed, and, consequently, re-creates the explosive dangerous condition.

This precaution requires establishing a very short time frame between the end of the purge and the light-off of the burners (NFPA 85, 86, and 87) to prevent the accumulation of flammable mixture from a probable fuel leakage. In addition, it is advisable to implement a one-shot pilot burner light-off in order to avoid successive attempts of burner ignition that may rapidly lead to a new accumulation of a dangerous fuel–air mixture. Such attempts should be limited *both* as to the number *and* the total time of attempts, whichever occurs first.

INCIDENT

A highly illustrative incident to bear in mind was the 1979 explosion occurring in Argentina’s Necochea Power Plant.

One of a set of two water tube boilers, with membrane walls (2 × 70 MW), burning fuel Oil #6, was operatively shut down. As the fuel oil header supplied fuel to both boilers, one of the fuel oil shutoff valves of this out-of-service boiler had debris in its seat that prevented the plug from closing hermetically. The boiler was cold and the valve leakage caused it to slowly accumulate a pool of high-viscosity fuel oil #6 in its floor.

When the boiler was put back into operation, the operator performed the start-up initiating the sequence of purging followed by the light-off of the pilot burners and then of the main burners, all of which was accurately done. The boiler began to run in parallel with the other operating boilers and started to supply steam to the turbines to contribute to the generation of the electric power being demanded.

When the firebox reached its high temperature regime, the fuel oil from the floor pool started to heat up and vaporize. This additional vaporized fuel, being added to that supplied by the burners, changed the fuel-air mixture to a fuel-rich condition over the UFL limit, thus suffocating the flames and producing a flameout of the boiler.

And what do you think the worried boiler operator did, his mission being to supply the steam demanded by the steam turbines to satisfy public demand for electricity? He rapidly reinitiated the ignition sequence by purging with air, supplying—unaware of the risk—enough air into the fuel-saturated combustion chamber just to move the representative point P of the mixture below the UFL, into the flammability zone.

The next step in the ignition sequence was the ignition of the pilot burners, which provoked a tremendous explosion, fortunately without inflicting any injuries to the few people who were close to the boiler area. Nobody had anticipated the likelihood of this particular incident.

Lesson learned: If an operating boiler suddenly suffers a complete flameout, do not attempt to reignite it. Look for the causes.

THIRD TOOL: THE MINIMUM IGNITION ENERGY

Ignition is the beginning of the light-up (exothermic oxidation) at a point in a flammable mixture and its immediate propagation, by “contagion,” to all the surrounding moles of a flammable gas that react with the oxygen needed for combustion.

Upon light-up, such starting point generates enough heat to inflame all other nearby points and thus trigger a sudden and violent inflammation. The ensuing inflammation can be a controlled combustion (as in the case of burners in boilers, furnaces, fueled turbines and heaters) or an out-of-control inflammation (i.e., an explosion in the form of a deflagration or detonation, depending on the characteristics of the mixture and the degree of confinement of the area where it occurs). The mixture is ready to become inflamed, an impulse that increases with temperature. It only needs to gather enough thermal energy to reach the starting point of the exothermic link of fuel with luring oxygen (O_2). If the mixture has a degree of concentration represented by a “P” point within the flammability zone of its Flammability Map and is subject to external heating, it will reach a temperature where it suddenly ignites, an event that looks like a spontaneous ignition. This occurs at a temperature known as AIT.

This scenario may occur in an environment classified as Hazardous Zone when the flammable mixture comes into contact with a hot enough surface of some device of the process, such as a lamp, or the frame, or bearings case of an electrical motor, with a temperature high enough to heat the mixture to its AIT temperature level. Another appropriate example involves the flammable mixture of Carbon Disulfide (CS_2) with an AIT of $90^\circ C$, meaning that it just needs to make contact with a bare steam pipe to explode.

Of course, this may also happen if the mixture comes into contact with a flame or a spark or an electric discharge (static electricity or direct electric arc). Methane CH_4 has an AIT between $540^\circ C$ and $630^\circ C$ (depending on the research source). A match gets a temperature of about $870^\circ C$ and an electric arc may get temperatures up to $5,400^\circ C$. However, nature tells us that a spark of not very high energy may ignite flammable mixtures. So the question is, what is the Minimum Ignition Energy (MIE)? A spark heats up a very small volume of flammable mixture, a spot, transferring enough calorific energy to initiate its ignition and consequent explosion (Figure 10).

Laboratory tests and analyses have found that, for most of the common hydrocarbons mixtures close to their stoichiometric concentrations, the spark ignition energy required is about 0.25 mJ, with the particular exceptions of hydrogen (H_2) and acetylene (C_2H_2), which have an energy of 0.020 mJ, about 1/10 of the MIE of the other mixtures.

Methane (CH_4) has a MIE = 0.28 mJ, while ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10} , n pentane C_5H_{12} , and hexane C_6H_{14} have a MIE between 0.24 and 0.26 mJ (Figure 16). In short, all of these are in a range of about 1/4 of millijoule. Now the question is, how can we realize how much energy is 0.28 mJ? We will ask our friend Pedrito Skill, the fox, to help us visualize how much energy is 0.28 mJ (Figure 17). The potential energy of a coin or debris of 10 g (0.035 ounce) (like a half dollar which weighs slightly over 10 g) falling from a height of “few millimeters,” impacting the iron pipe and turning the kinetic energy into heat is almost equivalent to MIE = 0.28 mJ. The static spark a person can feel is about 20 mJ, about 70 times bigger than the above mentioned MIE.

When we realize that this so small—assumed as insignificant—amount of energy is enough to ignite an explosive mixture, we begin to worry, up to the point of being afraid of the energy a lightning bug flying close might release. In early 2009, in an industrial boiler of a hazardous oil processing plant, the height of a natural gas vent pipe of a shutoff manifold was extended. We were informally told that during the work (cutting or welding, not clearly confirmed) a minimum puff happened. This prompted us to explore the possible causes of this specific event, and—in addition—to delve deeper into the matter and relate it to NFPA 69 (Figure 18) so as to adapt its recommendations to fuel pipe cleaning and purging and the procedures to be followed for any task to be performed in any fuel pipeline.

The conclusions are depicted in Figures 17 and 19, recalling the 1939 detonation-type explosion of the underground sour crude oil pipeline in north Texas, when it was being cleaned with a scrapper plug forced through with compressed air. As a probable consequence of a spark or heating from friction, the detonation pressure front traveled back through the supposedly empty pipe (in all likelihood with flammable mixture clouds inside) destroying about 45 km of the line.

INCIDENT

About 8 months later, on February 7, 2010, this concern was definitely confirmed by a catastrophic explosion in the Kleen Energy Power Plant, located in Middletown, CT, that killed 6 workers and injured 50 others.

What is now considered a deadly practice, prohibited since then by the Chemical Safety Board (CSB) with the backing of NFPA 56 (Standard for cleaning and purging of Flammable Gas piping systems released in 2012 at the request of the CSB), was a reiterated, high-risk approach commonly used in the precommissioning phase of construction: blowing down the pipe to clean and remove debris using the high-flow and high-pressure natural gas (of 45 bar in this case) available for the turbines, and venting the gas into the atmosphere at an open end, which in this case stood at about 6 m above the ground and close to the area of the turbines and their respective Heat Recovery Steam Generators.

The blowdowns were performed intermittently (about 15 times) and, based on an analysis of what we visualized above, it is clear that this incident consequence was close to inevitable (very high probability). The gas pipe was successively filled with gas, and it naturally refilled with air when each blowdown was completed. Thus, between one blowdown and the next one, the concentration of the natural

MIXTURES IN AIR						
GASES		FLASH POINT-°C	AIT (°C)	LFL (%V/V)	UFL (%V/V)	MIE (mJ)
Acetylene	C ₂ H ₂		305 °C	2.50	81	0.020 mJ
Hydrogen	H ₂		400 °C	4	75	0.018 mJ
Methane	CH ₄	-222.50	632 °C	5	15	0.280 mJ
Butane	C ₄ H ₁₀	- 60.00	408 °C	1.80	8.40	0.260 mJ
Ethane	C ₂ H ₆	-130.00	472 °C	3	12.40	0.240 mJ
Hexane	C ₆ H ₁₄	- 23.00	487 °C	1.20	7.40	0.248 mJ
Pentane	C ₅ H ₁₂	- 40.00	579 °C	1.50	7.80	0.220 mJ
Propane	C ₃ H ₈	-104.40	493°C	2.20	9.50	0.250 mJ

Figure 16. Flammable gas mixtures values (approximate). [Color figure can be viewed at wileyonlinelibrary.com]

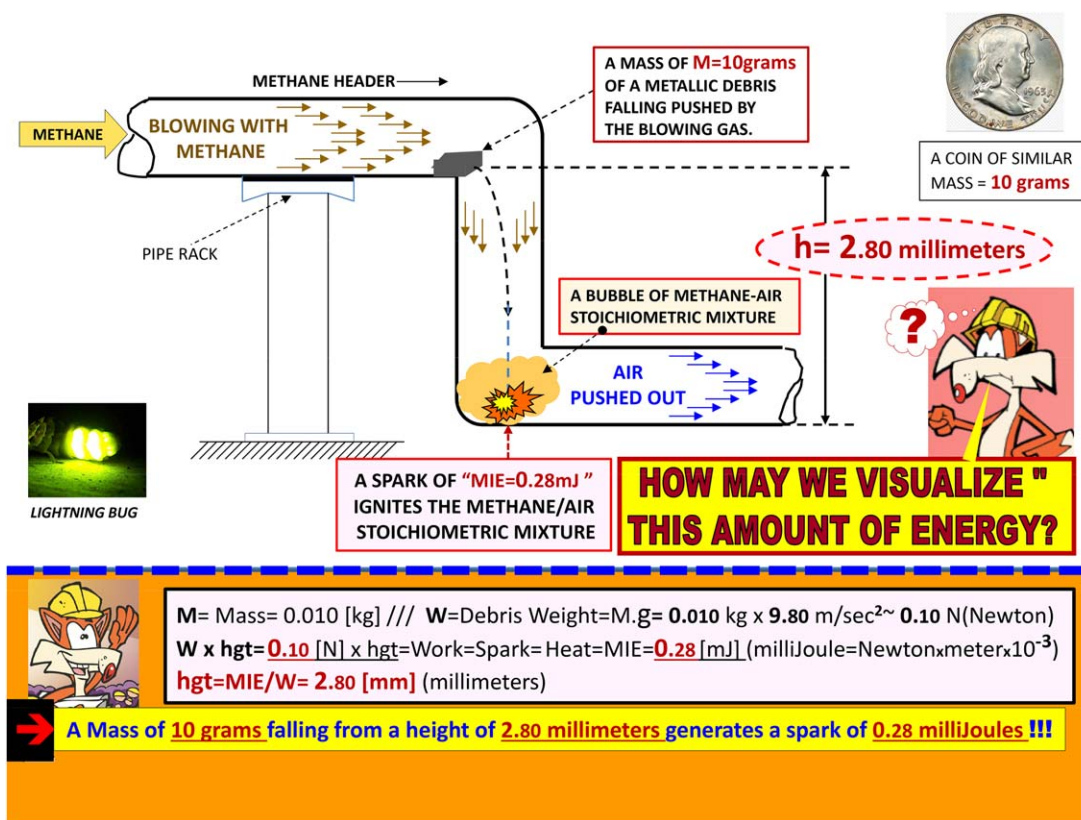


Figure 17. A spark of 0.28 mJ is produced by a 10 g steel coin falling in the steel pipe from a height of 2.80 mm. [Color figure can be viewed at wileyonlinelibrary.com]

gas-air mixtures in the pipe changed from full gas to close-to-full air, that is, moving back and forth (or up and down) within the flammable zone along the "air" line in the Flammability Map and crossing—in both directions—the UFL and LFL limits (Figures 14 and 15).

Simultaneously, the energy used to remove the debris largely exceeded the MIE values, causing the metallic debris particles to fly and generate sparks as they collided with the pipe walls, between themselves, inside and outside the pipe, and also with the external structures upon being expelled

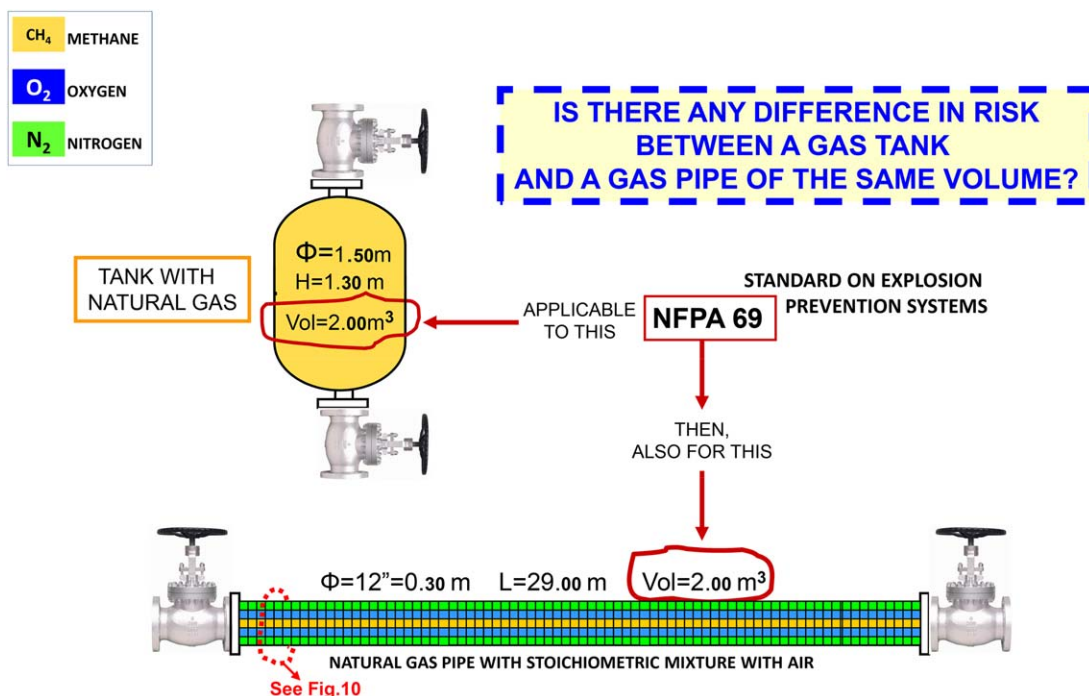


Figure 18. Explosion risk in a gas pipeline. [Color figure can be viewed at wileyonlinelibrary.com]

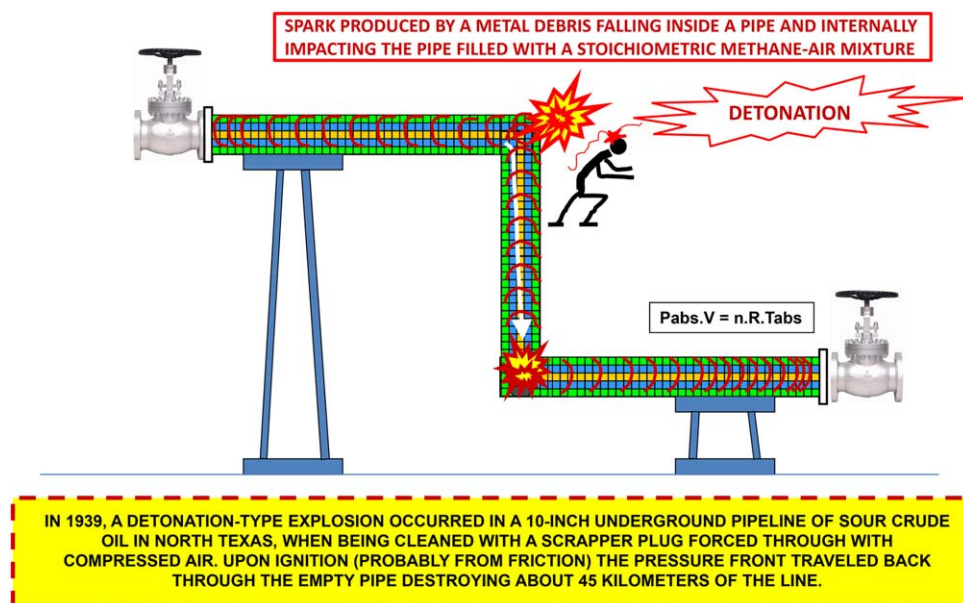


Figure 19. A spark generating a detonation within a pipeline. [Color figure can be viewed at wileyonlinelibrary.com]

from the open end of the pipe to the atmosphere in an area with some degree of confinement and high risk of accumulation of a natural gas-air mixture dancing within the flammable zone. The very likely ignition and explosion of the flammable mixture being vented eventually occurred, the outcome being six workers killed, at least 50 others injured, and massive losses. In my presentation at the 5th LACPS in Cartagena (2013), I described this incident as equivalent to a huge lighter ready to ignite the high-volume natural gas cloud being blown (Figure 20).

TO SUM UP

All three main tools for preventing fuel mixture explosions in boilers, furnaces, turbines, and heaters having been visualized, we may now conclude this article giving a more complete and synthetic form to the traditional Fire Triangle, by inserting the Flammability Map to make it clear that, for a fire or explosion to occur, all three components of the fire triangle sides and the flammable mixture with a concentration within the flammable zone (Figure 21) must be present.



Figure 20. Explosion at Klean Energy Power Plant in Middletown, CT. [Color figure can be viewed at wileyonlinelibrary.com]

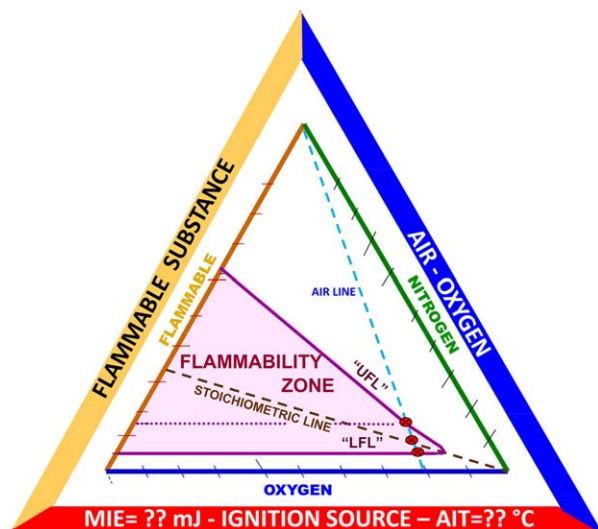


Figure 21. Fire Flammability Triangle. [Color figure can be viewed at wileyonlinelibrary.com]

The sole purpose of this article is to serve as a contribution to my colleagues in the field—those who live in close proximity to risk processes involving flammable products—by refreshing our understanding of these tools and

imprinting on our minds the vivid images of the problems and circumstances that may result in catastrophic explosions.

ACKNOWLEDGMENT

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FOR FURTHER READING

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