

Flammability limits

During a fire, a smoke layer is formed. A smoke layer is a fairly complex composition of different gases. At some point, flames will appear in the smoke layer. Why is it, that ignition occurs at that specific time? And why does it occur at that location? The simple answer is that at that time a “complete fire triangle” is formed. The mixture of (gaseous) fuel and oxygen has reached the right temperature to auto ignite. Many firefighters struggle with this concept. How does it really work? Why is a certain mixture too lean at first and then later too rich? The article below tries to explain all of this in a comprehensible way.

1.1 Flammability limits or explosive limit

The flammability limits or explosive limits are an important concept to fully understand fire behavior. During a fire, gaseous fuel is formed due to pyrolysis. These pyrolysis gases can mix with other gases in the surroundings. When sufficient flammable gases have been formed, the *lower explosive limit* is reached. Lower explosive limit (LEL) and *lower flammability limit* (LFL) are two different wordings for the same principle. Many firefighters will probably have seen the abbreviation LEL on a multi gas detector (“explosion meter”). In this article, I will be using the term lower flammability limit because it better fits the intended meaning. The moment a mixture of smoke gas and air passes this lower limit, it can be ignited. As it happens a mixture, in a room such as a bedroom, that is just above the lower limit will not explode. At the most, a slow combustion will occur. An important fact to keep in mind is that this article in essence is about fire and fire gases. Fire gases contain less energy than methane, the gas that is further used in this article to illustrate the principles of flammability limits.



Figure 1 Ignition of a mixture of gas and air. On the left-hand picture, ignition has just occurred. The flame front is moving in a circular way into all directions. The right-hand picture shows an increase of the volume of flames. (Photo's: Karel Lambert)

When afterwards, the amount of flammable gases increases, the percentage of flammable gas in the mixture will rise. At some point, there will so much flammable gases that the mixture can no longer be ignited. This is called the *upper explosive limit* (UEL), or rather the *upper flammability limit* (UFL).

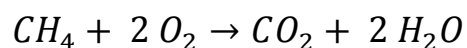
Mixtures of oxygen and fuel that are located between these two limits are flammable. They can be ignited (see Figure 1 and 2). Somewhere in between these two limits is the ideal

mixture. This is the mixture that causes the most violent explosion. The article will now expand on the explosive limits of methane. The smoke formed in a fire however, is made up of many different fire gases. Still, methane is a good substitute for describing the principles of flammability limits.

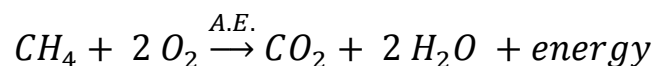


Figure 2 These photos show the rest of the reaction process illustrated in Figure 1. The left-hand photo shows the flame spreading further. This is also shown in the right-hand photo. That way, the flames are spreading along the entire volume in which the mixture is inside the flammable range. (Photo's: Karel Lambert)

Below, the chemical equation which describes the combustion of methane, is given. Methane (CH₄) is the scientific name for natural gas. This gas is used for instance in a kitchen stove. Methane can be ignited when oxygen (O₂) is present. Usually, both components are gaseous. In this specific equation, there is one molecule of methane that reacts with two molecules of oxygen. After the reaction has taken place, there no longer is any methane or oxygen. One molecule of carbon dioxide (CO₂) and two molecules of water (H₂O) have been formed. A mixture in which all the oxygen as well as all the fuel is burned, is called the *stoichiometric mixture*. This is another name for the ideal mixture.



However, these two substances aren't the only products of the reaction. The combustion of methane is an *exothermic* reaction. This means that energy is produced as well. Suppose a mixture is formed of methane and oxygen. In this mixture there are two oxygen molecules for every molecule of methane. Imagine a total of one kilogram of methane is being burned. This will produce 50 MJ (MegaJoule) worth of energy. Literary works on fire physics will offer in depth information on this subject if needed.



The reaction will not start by itself however. If you were to turn open the gas of the kitchen stove at home, natural gas will start flowing out. The gas will mix with the air, but it will not spontaneously combust. That requires an ignition. The oxygen and the natural gas both have a temperature of about 20 °C. The ignition energy will cause temperature to rise at a specific location, so that it will be high enough to start the reaction: the ignition temperature. The higher the initial temperature of both gases, the lower the ignition energy needed will be. In other words, it will require more energy outdoors during winter with a temperature of -20 °C to ignite the mixture, than it will in the summer with an outdoor temperature of 30 °C. After all, the mixture will need to be heated for an extra 50 °C during winter. This is an important factor, because the smoke which provides the fuel

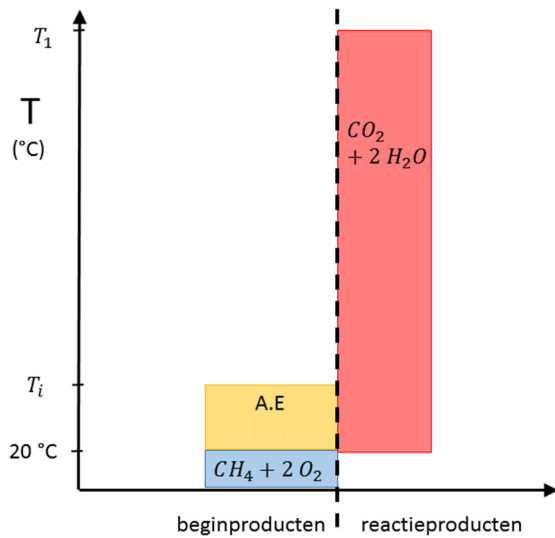


Figure 3 Graphic illustration of the ideal combustion of methane in pure oxygen. The two products (methane and oxygen) are approximately at room temperature (20 °C). A certain amount of activation energy is added and the reaction will start. The reaction products are heated to their end temperature. (Drawing: Karel Lambert)

during a fire, can differ immensely in temperature. The higher the temperature of the smoke, the less energy will be needed to ignite the smoke. This energy is called *activation energy* (AE).

The energy that is produced during the chemical reaction, will cause the temperature of the reaction products to be higher than the initial temperature of the gases that started the reaction. The chemical energy contained within the methane has been converted into thermal energy. Actually, it is more correct to state that energy is released during the reaction. Before the reaction process takes place, energy is stored in the methane gas. In everyday speech, we simply say energy is produced. This wording is also used in this article.

The energy that was released, is distributed amongst the reaction products: CO₂ and water.

When ignition occurs somewhere in the mixture, heat is produced. This heat will spread out towards neighboring molecules. The produced heat will serve as activation energy for neighboring molecules. This will cause a chain reaction. The flame will form and spread throughout the mixture (see Figure 1 and Figure 2).

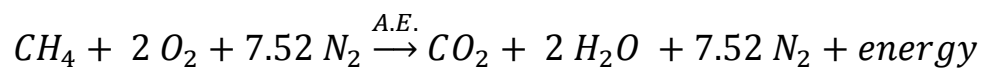
It's possible to illustrate this in a drawing. Figure 3 shows temperature on the vertical axis. The initial products are listed in blue: CH₄ and oxygen. In this particular case, the initial products have a temperature of 20 °C. This is also the initial temperature of the reaction. The area surface of the blue rectangle depicts the energy stored within the two gases. This means it's not the X-axis that represents energy. Energy is illustrated as a surface area size. The X-axis has the initial products on the left of the dotted line. On the right of the dotted line are the reaction products.

As stated above, a certain amount of activation energy needs to be added to the gases. For this we need an ignition source. This can be a spark, a match, a heated surface, ... The amount of energy that needs to be added, is illustrated by the orange rectangle. Energy

will have to be added until the initial products have reached a certain temperature: the *ignition temperature* T_i . The reaction itself is illustrated by the black dotted line. Again, to the left of the dotted line are the initial products, to the right are the products formed during the reaction. Also during the reaction, an enormous amount of energy is produced. This energy is used to heat up the reaction products. Figure 3 shows that the end temperature of the CO_2 and the water is considerably higher than the initial temperature. The temperature of the reaction products is illustrated by T_1 on the drawing.

The energy produced by the reaction is depicted by the surface area of the red rectangle. This is the thermal energy that is the result of the combustion process. It needs to be said that vertical axis is not in full scale. If the red rectangle was to be drawn in true size, it would be several meters high instead of the few centimeters that are drawn now. This does mean that all of the following illustrations actually show a temperature of the reaction products that's "too low".

When we look back at our kitchen stove, something different than described above is happening. In the kitchen, methane does not burn in pure oxygen. The actual mixture also contains nitrogen (N_2) next to methane and oxygen. The air in our surroundings is made up of 21% oxygen and 79% nitrogen. This means that for every molecule of oxygen, there are 3,76 molecules of nitrogen present. The chemical equation for the combustion of methane in air is now as follows:



The drawing of this reaction has also changed. At both ends, an extra element is added. Figure 4 shows the nitrogen as two green rectangles. The nitrogen is present before combustion takes place. And even though it does not participate in the chemical reaction, it will still need to be heated up to T_i . After all, nature strives to keep everything equally warm or cold. If we want to ignite the mixture (or put differently: if we want to heat up the mixture to the ignition temperature), then we will have to add more energy than was the case in an oxygen-methane mixture. This is clearly shown in the drawing. The surface area size of the orange rectangle has increased substantially. A mixture of methane and air will require a more powerful ignition source than a mixture of methane and oxygen.

The result of the combustion will also be different. The nitrogen does not participate in the chemical reaction and can be found again afterwards. A mixture of CO_2 , water and nitrogen is formed. The heat produced is exactly the same as in the previous situation. After all, an equal amount of methane is being burned. However, the amount of heat being produced now has to be distributed amongst three different end products. The nitrogen will absorb a large amount of heat. Figure 4 also shows that the end temperature of the reaction process is lower than that of Figure 3: $T_2 < T_1$. The combined surface area size of the red and green rectangles in Figure 4 is equal to the surface area size of the red rectangle in Figure 3. This can be clearly seen on the drawing.

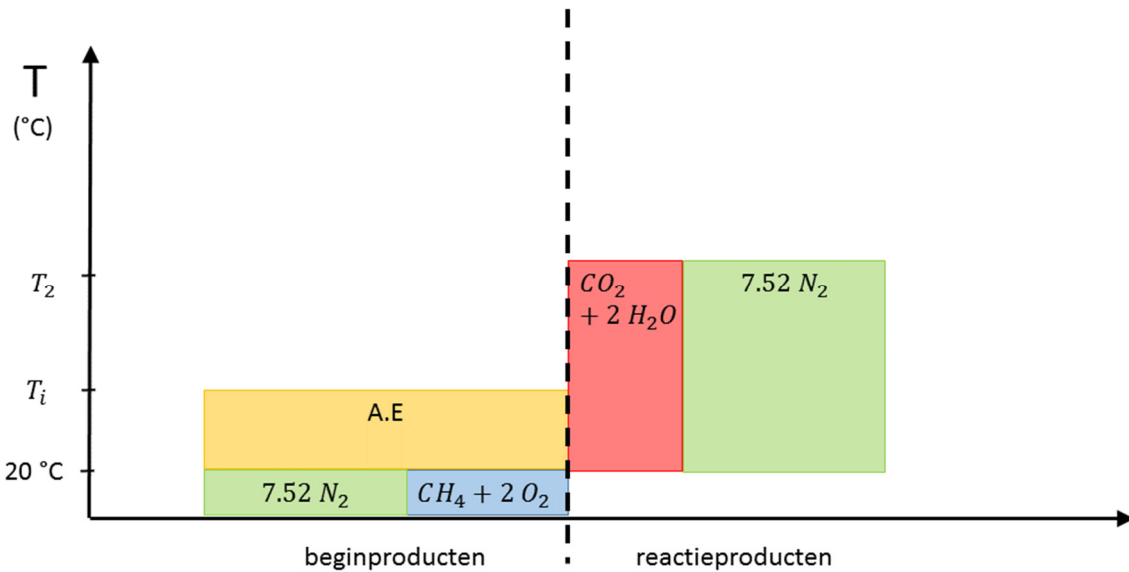
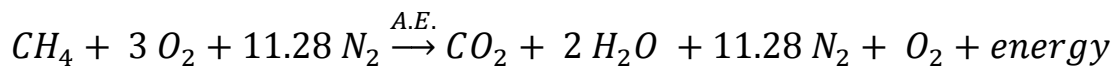


Figure 4 The graphic illustration of the ideal combustion of methane in air. The green rectangles depict the nitrogen which does not participate in the combustion process. The temperature of the reaction products on the right of the dotted line is lower than in the previous drawing. The surface area size of the red and green rectangles on the right of the dotted line, represents the thermal energy. (Drawing: Karel Lambert)

Both of the reactions described above are dealing with ideal mixtures. In reality, an ideal mixture will rarely be present. Either there will be too much fuel, or there will be too much oxygen. This will affect the reaction. Suppose there now are three molecules of oxygen available instead of two. Then the reaction will go as follows:



Aside from extra oxygen, there is also extra nitrogen in the mixture. For each molecule of oxygen there are 3,76 molecules of nitrogen in the mixture. This means that now, there are 11,28 molecules of nitrogen present. The reaction will change once more. Amongst the reaction products, we can now see the excess oxygen molecule. And again, this will change the graphic illustration.

Left of the dotted line in Figure 5 are the initial products. The blue rectangle still represents the products that will take part in the combustion process: the methane and the oxygen needed to burn that amount of methane. The green rectangle depicts the nitrogen. However the amount of nitrogen has increased and therefore the green rectangle is now wider. The purple rectangle indicates the excess oxygen molecule. We are dealing with a *lean mixture* here. This means that there is less fuel present than in an ideal situation. The orange rectangle has increased in size once more. After all, all the initial products have to be heated to T_i . This includes the oxygen that does not participate in the chemical reaction.

To the right of the dotted line in Figure 5, are the end products of the reaction. The red rectangle depicts the products that are the result of the combustion process. These are the same as in the previous drawings. Aside from these, there is the nitrogen (green rectangle) and the oxygen (purple rectangle) that does not participate in the reaction process. The energy that is being produced, is equal to that in the previous situations. The surface area size of the red rectangle in Figure 3 is equal to the combined surface area size of the red,

green and purple rectangles in Figure 5. When comparing all the drawings, it becomes clear that the temperature of the reaction products decreases further as more elements need to be heated up: $T_3 < T_2 < T_1$.

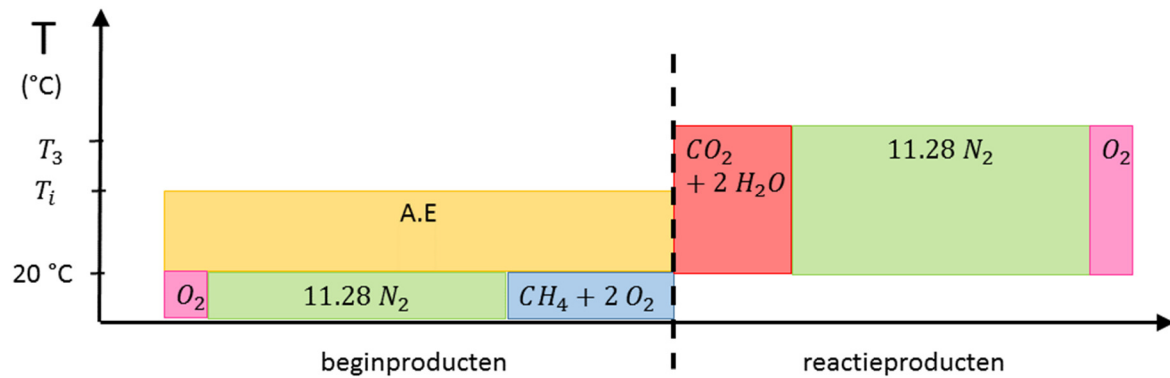


Figure 5 The graphic illustration of the combustion of methane in a surplus amount of air. The purple rectangles depict the excess oxygen. The green rectangles have widened in comparison to the previous drawing. The end temperature of the reaction products, to the right of the dotted line, is again lower than in the previous drawing. The combined surface area size of all the rectangles illustrating the reaction products, is equal to the thermal energy produced by the combustion. (Drawing: Karel Lambert)

The temperature of the reaction products acts as an ignition source for neighboring gases. This means the reaction products have to provide the activation energy to ignite gases next to them. The drawings above show that the ignition energy (AE) needed, is increasing each time. But at the same time, we can see that the end temperature of the combustion is decreasing in each drawing ($T_3 < T_2 < T_1$). At some point, there will be so much excess oxygen (and nitrogen), that the reaction products will no longer be hot enough to act as an ignition source for neighboring gases. It will then no longer be possible to form a flame front. For a mixture with too much air for the amount of fuel, this is where the lower explosive limit or the lower flammability limit has been reached.

After Figure 4, it is possible to add extra CH_4 instead of extra oxygen. At the end of the reaction process there will be an excess of methane instead of oxygen. Next to that, the amount of nitrogen remains the same. The excess methane will need to be heated by the activation energy. Again, this process will require more activation energy as more methane is present beforehand. The excess methane that does not burn, will also absorb some of the produced energy. This will cause the overall temperature of the reaction products to decrease. At some point, this will lead to a mixture with so much methane, that a flame front will no longer be formed. That point equals the upper explosive limit or the upper flammability limit.

Explosive limits are expressed in volume percent. The lower explosive limit (LEL) indicates how much percent fuel needs to be added to air in order to form a combustible mixture. The upper explosive limit (UEL) indicates how much percent fuel needs to be added to cause the mixture to no longer be combustible.

Substance	LEL or LFL (Vol %)	UEL or UFL (Vol %)
Hydrogen	4	75
Carbon monoxide	12,5	74
Methane	5	15
Ethane	3	12,4
Propane	2,1	9,5
Butane	1,8	8,4
Methanol	6,7	36
Ethanol	3,3	19
Acetone	2,6	13

Methane is the gas more commonly known as natural gas. The lower explosive limit is 5%. This means that a mixture with just enough natural gas to ignite is made up of: 5% methane and 95% air or, in other words, 5% methane, 19,95% oxygen and 75,05% nitrogen. The upper explosive limit is 15%. The values for both limits are rounded figures. Sometimes in literature, numbers can be found that are a bit further apart.

1.2 Thermal ballast

When we look at the different drawings above, we can see that the amount of gases, which do not participate in the combustion process, becomes greater and greater. These gases act as freeloaders. They do not contribute, but they do want to be heated by the activation energy. This means more activation energy is needed to ignite a mixture. Subsequently, they want to be heated by the energy that is being produced as well. This will lead to lower end temperatures.

This effect is also described as *thermal ballast*. The molecules that do not participate are a ballast in the chemical process. They make it harder and harder to achieve a decent combustion. When there is sufficient ballast, combustion becomes impossible.

Thermal ballast is an important concept for the fire service. One example of this, that is not mentioned in the section above, is adding steam. When firefighters start an interior attack, they will have to cool the gasses. To achieve this, fine water droplets are directed in a fog pattern into the smoke layer. The water droplets will absorb energy by extracting it from the smoke layer. Next, steam is also formed. Steam is a gas that will mix with the smoke. This means that an extra rectangle will need to be added at the right-hand side in the drawings above. Steam does not participate in the reaction process, but it will absorb part of the activation energy and part of the energy produced by the reaction. By inserting steam into a mixture, that mixture can be rendered inflammable.

Actually, the ballast extracts heat in the combustion process. All of the heat that is absorbed by molecules which don't participate in the combustion, is "lost" to that combustion process.

It is interesting to look at where the produced energy is being directed. In a fire or a combustion reaction (like for instance a candle flame), energy is being produced at the exact place where the combustion takes place. Next, this energy is spread through conduction, convection and radiation. When too much energy disappears from the reaction zone, then the combustion will stop.

This effect can be studied with the help of a candle. A candle burns with a laminar diffusion flame. This means that oxygen and fuel are being constantly mixed on the flame surface. This also means that the top end of the flame is "ignited" by the energy produced at the bottom end of the flame. When a piece of metal gauze is held in the middle of the flame, the flame is cut off. This is because the metal gauze absorbs and redirects the heat of the flame. Flammable gases continue to rise through the mesh, but transfer their heat to the metal gauze. The gauze will then transfer the heat to the surroundings. Above the gauze there is still a mixture of oxygen and fuel, but there is no longer enough energy to ignite the mixture. This phenomenon, where a flame cannot propagate because energy is being directed away, is called *quenching*.

In a compartment fire, this effect plays a part in several different ways. The walls of the room in which there is a fire for instance, will partially act as the metal gauze. Their influence on the fire is more complex however. In the beginning of the fire, the walls will absorb heat. The exact amount will depend on the structural properties of these walls. After some time, the surface of the walls will become very hot. The heat absorption will then decrease. This is not the same for the metal gauze. Metal has fantastic heat conducting properties. Most materials used in construction do not have these properties. That is why the heat absorption of the walls changes after some time.

A second way in which this effect is present in compartment fires is when firefighters flow water droplets into flames. Each individual droplet can absorb a certain amount of energy. When two droplets are close to each other, so much energy will be absorbed that a flame will have a hard time passing through the droplets. A fog of water droplets moving through a flame front will act as a metal gauze going through a candle flame. The fog of droplets can cool sufficiently to stop the flame.

Thermal ballast also works the other way around. Figure 4 illustrates the combustion of methane in air. Both gases are at room temperature upon ignition. The activation energy needs to heat the gases enough in one specific location to start the reaction.

In the text above, methane is used to illustrate the flammability of smoke. Smoke is rarely at room temperature. The temperature of smoke is determined by the heat release rate of the fire. When hot smoke rises and moves away from the fire, it mixes with air. This causes smoke to cool down. Figure 6 illustrates the ideal combustion of methane and air. Opposed to Figure 4, the mixture of gas and air is now at a temperature higher than room temperature. The temperature of the mixture is 200 °C. When we look at Figure 6 in comparison to Figure 4, we now see that less activation energy is needed. The surface area size of the orange rectangle is smaller. On top of that, the end temperature of the products will be 180 °C higher. After all, an equal amount of energy is still being produced during the combustion. Since the initial temperature is 180 °C higher than in Figure 4, the end temperature will be 180 °C higher as well. This is shown by the green and red rectangles reaching higher on the axis in Figure 6 than in Figure 4: $T_4 > T_2$.

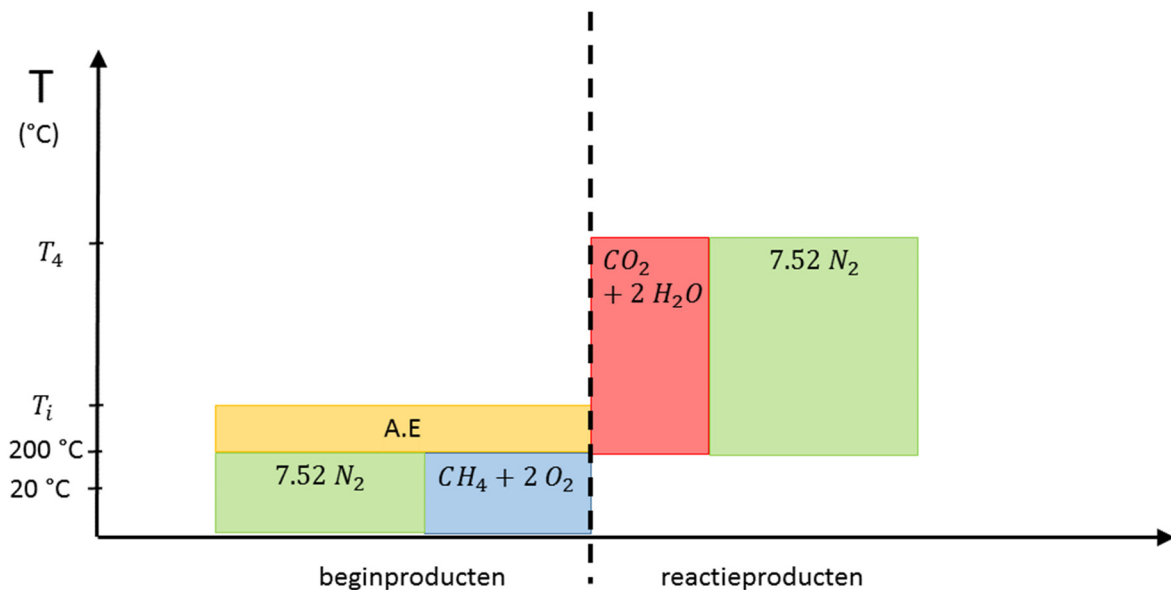


Figure 6 Graphic illustration of the ideal combustion of methane in air. Both elements have an initial temperature of 200 °C. This means that the activation energy needed will be less than that needed to ignite a mixture at room temperature. This is depicted by the orange rectangle having a smaller surface area size than in Figure 4. (Drawing: Karel Lambert)

Another important aspect of a higher initial temperature, is that the flammable range widens. The amount of activation energy needed has become less.

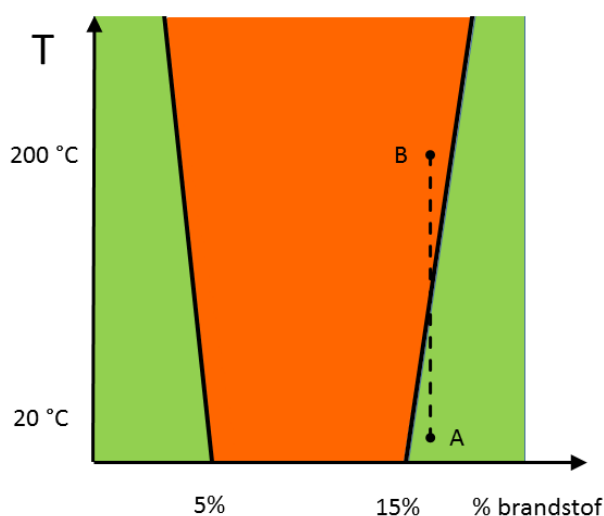


Figure 7 The explosive limits of methane drawn out in relation to temperature. The mixture in point A is inflammable. When the mixture is heated from 20 °C to 200 °C, it enters point B. Point B is inside the flammable range. (Drawing: Karel Lambert)

is heated up, it will become flammable at some point. We can clearly see that point B is inside the flammable range while point is outside of it. The only thing that has changed, is the temperature.

In the paragraphs above, we explained that certain mixtures could no longer be ignited because the combustion did not provide enough activation energy for other molecules. A mixture that cannot be ignited at 20 °C, because the activation energy needed is higher than the energy produced, may well be ignited at 200 °C. The amount of energy produced has remained the same, while the activation energy required has become less. This means that the flammable range expands when the temperature rises. This is especially important during firefighting operations. After all, firefighters are typically working in exceptionally high temperatures. Figure 7 shows how a mixture with more than 15% methane (point A) is not flammable at a temperature of 20 °C. When the mixture

1.3 Closing remarks

Lastly, we need to emphasize that the paragraphs above are a simplified representation of reality. Methane is used because it serves as an easy substitute. On top of that, methane is the gas used in household kitchens for cooking. Everyone knows natural gas.

During a fire, the flammable mixture is not formed by methane and air. The mixture is formed by both fire gas and pyrolysis gas mixing with air. Fire gases are made up of many different components aside from CO₂ and water. Gases like CO and HCN are being produced along with a range of other gases. Each of these gases has their own flammable range and auto ignition temperature. On top of that, a large amount of pyrolysis gas is being produced. The less air there is for combustion, the more of these gases will be formed. Pyrolysis gases behave differently than methane and the various fire gases.

So in reality, the situation is far more complex than described above. Still, the simple illustration using methane can suffice to help explain flammability limits. These limits in turn, are very important to clarify rapid fire progress such backdraft, flashfire and smoke explosion. That is why it is worthwhile for firefighters to study explosive limits a bit more in depth.

2 Bibliography

- [1] *Introduction to fire dynamics 2nd edition, Dougal Drysdale, 1999*
- [2] *CFBT-instructor course for the Attack Cell, Karel Lambert, 2016*
- [3] *International fire behavior and suppression course, Lars Ågerstrand, Zweden, 2016*

Karel Lambert