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Lecture No -52 Fires and Explosion: Flammability Characteristics

Welcome to lecture 52 of plant design and economics. In this module, we are talking about chemical process safety and in this lecture we will talk about flammability characteristics of fires and explosions.

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Three major types of chemical plant accidents are fire, explosion and toxic release. We have discussed the probability of occurrence of fire is highest. That of explosion is intermediate and probability of occurrence of toxic release is low. But the potential for fatalities for toxic release is highest and that for fire is lowest and explosion has intermediate potential for fatalities. Also, the potential for economic laws for fire, it is intermediate for explosion, it is high and for toxic release it is low.

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Now, we will talk about the flammability characteristics for fire and explosion. So, let us start with fire triangle. Fire or burning is the rapid exothermic oxidation of an ignited fuel. The fuel can be in solid form, it can be liquid form or it can be vapour form. But vapour and liquid first are generally easier to ignite compared to solid fuel. The combustion always occurs in the vapour phase, so the liquids will be first volatilized or the solids will be decomposed into vapour before combustion occurs.

And the essential elements for combustion to occur are fuel, an oxidizer or oxidizing agent and an ignition source such as heat. As we discussed fuel may be gas vapour liquids solid also solid in the form of a dust dispersed in a gas. So, solid in the form of a dust dispersed in a gas will also be a fuel. If you look at the fire triangle, the three sides represent oxygen, heat or ignition source and fuel.

So, when all are in place; when fuel oxidizer and ignition source are present at the necessary levels the burning will occur. If any of the side is missing no fire will occur. So, to eliminate fire you need to take away any of the one of this sides.

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So, let us just elaborate on these fuels ignition sources as well as oxidizing agents. The liquid fuels can be gasoline, acetone, ether, pentane etcetera. The solid fuels may be plastics, wood dust fibers, metal particles. The gases fluids may be acetylene, propane, carbon monoxide, hydrogen. The oxidizing agents or oxidizers may also be gases, liquids and solids. Oxygen, fluorine, chlorine, Liquids hydrogen peroxide, nitric acid, perchloric acid.

Solids as metal peroxides, ammonium nitrates, etcetera. Ignition sources it may be sparks, flames, static electricity, heat etcetera. So, these are the some of the common fuels which may be liquid solid gases. Some of the common oxidizers which may again be gases liquids and solids and some common ignition sources.

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What is the difference between fires and explosion? The difference lies in the rate of energy release. Both fires and explosions are associated with energy release. But the major distinction between fires and explosion is in the rate of such energy release. Fires will release energy relatively slowly whereas explosion release energy very rapidly typically on the order of microseconds. Fire can also result from explosions and explosion can also result from fires.

Now the consequences of energy release on the accidents can be understood from a simple example of a standard automobile tire. Let us consider a standard automobile tire where there is compressed air. So compressed air contains enough energy. Now if this energy is slowly released through a nozzle. The tire will simply deflect and nothing will happen. However, if the tire suddenly ruptures and all the energy within it release rapidly it will result in a dangerous explosion.

So, the rate with which energy is released is important and that is the major difference between fires and explosion.

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Now, let us introduce an important definition known as flammability limit. Before that, we will introduce another definition known as autoignition temperature. The autoignition temperature of a gas or vapour is the temperature at which it will ignite spontaneously in air, without any external source of ignition. So, as the name suggests autoignition temperature of a gas or vapour refers to that temperature at which the gas or vapour will ignite spontaneously, it will not require any external source of ignition.

Now a flammable gas or vapour will burn in air only over a limited range of composition. So, any composition of gas or vapour will not burn in air it will not burn below certain composition and it will not burn above certain composition. It will only burn in air over a limited range of composition. So below a certain concentration of the flammable gas the mixture can be considered to be very dilute and it will not burn, we call it the mixture is too lean to burn.

This lower concentration is known as lower flammability limit or LFL. Similarly, there is a higher side concentration. So above a certain concentration the mixture will be considered to be extremely concentrated that it cannot burn. We call it the mixture is too reached to burn. This high concentration is known as upper flammability limit or UFL. So, concentrations of gas or vapour which will lie within the lower flammability limit and upper flammability limit will only burn.

That means the flammable range of the gas or vapour mixture will be within lower flammability limit and the upper flammability limit.

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Combustion of a flammable gas-air mixture occurs if the composition of the mixture lies in the flammable range and if there is a source of ignition. Alternatively, the combustion of the mixture occurs without a source of ignition if the mixture is heated up to its autoignition temperature. The most flammable mixture is usually the stoichiometric mixture for combustion, it is often found that the concentration of the lower and upper flammable limits are approximately one-half and twice of the stoichiometric mixture, respectively.

We will see more about it in next few slides. Let us now introduce another definition known as Flash Point, the flash point of a liquid is the lowest temperature at which it gives off enough vapour to form an ignitable mixture with air. The flash point generally increases with increasing pressure. So the flash point of a liquid is the lowest temperature at which it gives of enough vapour to from a mixture that will ignite with air. The flash point generally increases with increases with increases with increases with a mixture that will ignite with air. The flash point generally increases with increasing pressure.

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Now, let us look at this figure, where the concentration of flammable vapour is plotted against temperature. So, all the flammability limits such as lower flammability limit, upper flammability limits are shown we also show the flash point we also show the autoignition temperature. Now, this curve represents the saturation vapour pressure curve. This is the flash point. So, beyond this temperature only the mixture can burn.

This represents the lower flammability limit LFL. And this represents the upper flammability limit or UFL. So, and this temperature represents autoignition temperature. Now note that, the gas mixture is neither flammable here nor flammable here because they are outside the lower flammability limit or upper flammability limit and it is only flammable here. And since this represent autoignition temperature this represents autoignition region.

These flammability limits, this lower flammability limit as well as upper flammability limit they are affected by pressure. However, how the pressure will affect this flammability limit depends on that particular mixture. In some cases, are decrease in pressure can narrow the flammable range; that means this will cause. What will cause a decrease in pressure. In some cases in some systems are decrease in pressure will narrow the flammable range by bringing down this upper flammable limit and increasing this lower flammable limit.

So ultimately these two will collapse and there will not be any flammable region. So it will be the gas mixture will be non flammable. Whereas an increase in pressure can do the reverse that means it can widen the flammable range. Well this has been noticed in certain systems the opposite effect as also been observed in some other systems, so this phenomenon is system specific.

The flammable limits are also affected by temperature and increase in temperature usually widens the flammability range.

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How to compute the flammability limit of vapour mixtures? Note that you are not going to handle only pure gas or vapour will be a mixture of various components. We can compute the flammability limit of a vapour mixture of say n components if we know the flammability limit of these components in fuel and air. This can be done by using Le Chatelier equation. For example consider that we have an n component mixture, so there are n numbers of combustibles species.

And let yi be the mole fraction of component i on a combustible basis. And LFLi represents the lower flammable limit for component i in volume percent in fuel and air. So, that is the case this equation will tell me the lower flammability limit of the mixture. So is basically take the mole fraction of the component i and divide that quantity by the lower flammability level. So, the mole fraction of component i divided by lower probability limit of component i.

Such quantities you add for all the components present. Add it up take the reciprocal of it that becomes the lower flammability limit of the mixture. Similarly, you can also find the upper flammability limit of the mixture which can be obtained from the upper flammability limit for each component in the mixture.

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So, consider this problem. Let us say we have a mixture of hexane, methane and ethylene. The volume percents are given. Total combustible is 3.3 is expressed as volume percent. So remaining is air. So, 96.7% is air volume percent. So, mole fraction of hexane, methane and ethylene on combustible basis are given. How do you obtain 0.24? And say the volume percent of hexane is 0.8 and total combustible is 3.3.

So, mole fraction of hexane on combustible basis will be 0.8 by 3.3. And this will be 0.24. Similarly, compute per methane 2 by 3.3 which is 0.61. And you also compute for ethylene. So, the mole fraction and combustible basis are given and the lower flammability limit and the upper flammability limit of all the components are given. Now, you make use of the formula. So, this is 0.24 by 1.2.

That means the mole fraction of hexane by LFL of hexane plus mole fraction of hexane divided by LFL of hexane plus mole fraction of ethylene divided by LFL of ethylene and then if you do this computation, it will be 2.65 expressed as volume percent. Exactly the same way you compute the upper flammability limit of the mixture and you obtain is 3. So, LFL is 2.65 UFL is 13%. Total combustible is 3.3 so it is lying within this. So we conclude that the mixture of hexane, methane, ethylene has given is flammable.

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The flammability limits of these vapour mixtures functions of temperature and pressure and if you know say the flammability limit lower flammability limit or upper flammability limit. At say heat temperature 25 degree Celsius we can compute it in other temperatures by making use of these correlations. What delta H c terms is the net heat of combustion in the unit of kilo calorie per mole and T represents temperature in unit degree Celsius.

So this is about knowing the flammability limit at 25 degree Celsius, I can compute the flammability limit or some other temperatures. However, pressure, pressure does not have much effect on the lower flammability limit expect at very low pressure. At very low pressure flames do not propagate. But, the upper flammability limit increases significantly as the pressure is increased. And it then widens the flammability range.

And this volume also can be computed using this correlation. So, this correlation can be used to find out the LFL and UFL at other temperatures of pressure given the LFL and UFL values at some other temperature say 25 degree Celsius or some other pressure P.

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Estimation of Flammabil Flammability limits can be easily measu	ITTY LIMITS red and experimental determination is always
function of the stoichiometric concentra	stion (C _{st}) of fuel:
$LFL = 0.55C_{st}, UFL = 3.50C_{st}$	where C _{st} is volume % fuel in fuel plus air.
For most organic compounds:	$C_{\mu} = \frac{\text{Moles of fuel}}{\text{Moles of fuel} + \text{Moles of air}} \times 100$
$C_m H_y O_y + z O_2 = m C O_2 + \frac{x}{2} H_2 O$	$\Rightarrow C_{ii} = \frac{1}{1 + \frac{\text{Moles of air}}{1 + \frac{1}{1 + 1$
Then, $z = m + \frac{x}{4} - \frac{y}{2}$ ==	$O_{p} = \frac{1}{(1)(1)(1)(1)} \times 100$
Here z has units of moles O ₂ /mole fuel.	$1 + \left(\frac{1}{0.21}\right) \left(\frac{\text{Moles of } O_1}{\text{Moles of fuel}}\right) \leftarrow \mathbf{z}$

Now more about estimation on flammability limits. Note that it is not very difficult to measure experimentally the flammability limit. Flammability limits can be easily measured experimentally and experimental determination of flammability limit is always recommended because estimated values can never match the accuracy of the experimentally obtained values accuracy as well as the authenticity or the reliability dependability.

Experimental values are always more reliable then estimated values. So, whenever it is possible to do experiments will do experiments unless, there is reason not to do experiment. Such as extremely dangerous to do experiments or extremely expensive or is really not required. Some amount of inaccuracy is there with the estimation it does not matter much we can follow standard we can follow the correlations for estimation of quantities.

But whenever it is possible to perform experiments, the experimental data are always more reliable. For many hydrocarbon vapours the lower flammability limit and the upper flammability limit are a function of the stoichiometric concentration of fuel. Stoichiometric concentration of fuel is volume percent of fuel in fuel plus air; that means total combustible. And for several hydrocarbons, it is possible to estimate the LFL and UFL values if we know the stoichiometric concentration.

So LFL is 0.55 multiplied by stoichiometric concentration and EFL is point 3.50 multiplied by stoichiometric concentration. So, how will you compute the stoichiometric concentration? For most organic compounds, we can write this equation as combustion. Let us consider this well C mHxOy +zO2 gives me mCo2 + x by 2 H2O. So do an oxygen balance, which will be 2z = 2m + x by 2 and here you also have Y.

So, y + 2z = 2m + x by 2. So, z you compute it will be m + x by 4 - y by 2. So, this z has unit moles oxygen per moles fuel. So now the stoichiometric concentration is volume percent fuel in fuel plus air. So replacing these volume percent by moles we can write CST as moles of fuel divided by moles of fuels plus moles of air multiplied by 100. So, divide numerator and denominator by moles of fuel. We can write like this.

And then if we consider that air contains 21 percent oxygen. We can write stoichiometric concentration as 1 by 1 + 0.21 into moles of oxygen by moles of square and then multiplied by 100. Note that this quantity is nothing but this z. So, this way we can find out the stoichiometric concentration of the fuel. We have given the steps for the fuel CmHxOy. So, once you have the stoichiometric concentration, you can estimate LFL and UFL.

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Next, we introduce another definition known as limiting oxygen concentration or minimum oxygen concentration. The lower flammability limit measures the lowest concentration that will

allow combustion of a vapour air mixture. However, oxygen is the key ingredient and there is a minimum oxygen concentration required to propagate a flame. Below that there will not be any propagation of flame.

So, explosion and fires can be prevented by reducing the oxygen concentration regardless the concentration of minimum quantity of oxygen is required for propagation of a flame. So, an effective measure to stop explosions and fire will be the reduction of oxygen concentration. It does not matter in what concentration fuel present if you take away the oxygen. It will be equivalent to taking 1 side of this fire triangle.

And we can prevent explosion of fires. This concept is the basis for a common procedure called inerting. So, you just reduce the concentration of oxygen. Below the limiting oxygen concentration the reaction cannot generate enough energy to heat the entire mixture of gases including the inert gases to the extent required for the self-propagation of the flame. So, this is how the procedure called inerting works.

You just reduce the oxygen concentration below the limiting oxygen concentration. We can add inert to do that. We will see this later only talk about prevention of fire and explosion in next lesson.



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The limiting oxygen concentration depends on the inert gas species. So, whether; you are using nitrogen or carbon dioxide as inert gas. Depending on that a particular gas or vapour will have different limiting oxygen concentration below, which they are will not be propagation of flame. The limiting oxygen concentration or minimum oxygen concentration as it is also called has the units of percentage of moles of oxygen in total moles.

Total moles means air plus fuel that is total combustibles. If experimental data are not available the limiting oxygen concentration can be estimated using the stoichiometry of the combustion reaction and the lower flammability limit. Here in the table, you see certain values for the limiting oxygen concentration for methane, ethane, propane and N-butane, benzene. You can notice that the LOC or the MOC values are higher when carbon dioxide is taken as inert compared to the case when nitrogen is considered as inert.

So it is always better to have experimental data on the limiting oxygen concentration or minimum oxygen concentration, but in absence of data if you have to estimate the LOC or MOC you can do that using the stoichiometry of the combustion reaction and the knowledge of lower flammability limit. For example consider this reaction, this is the combustion reaction. Consider the stoichiometry and the LOC will be moles of fuel divided by total moles multiplied by moles of oxygen divided by moles of fuel.

So, this is nothing but LFL. So, LOC becomes LFL multiplied by moles of oxygen divided by moles of fuel. So, this is how we can estimate.

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Limiting oxygen concentration of a dust: The limiting oxygen concentration of a dust is the minimum concentration of oxygen capable of supporting combustion of dust that is dispersed in the form of a cloud. We discussed that the fuel can be in the solid dust form which is dispersed in a gas. A mixture with oxygen concentration below the limiting oxygen concentration is not capable of supporting combustion and hence cannot support a subsequent dust explosion.

The minimum ignition temperature of a dust is the lowest temperature at which dust that is dispersed in the form of a cloud can ignite. Note that this is an important factor in evaluating the sensitivity of a task to ignition sources such as hot surfaces. Decreasing particle size of dust and decreasing moisture content both lower the minimum ignition temperature.

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Now let us introduce this flammability diagram which is useful to understand the flammability envelope or the favorability region for three component system such as fuel, oxygen and nitrogen, which is inert. Now since we have a 3 component system we can make use of typical triangular diagram to express their concentrations. So, a typical triangular flammability diagram can be used to present all possible mixtures of a three component systems.

So, three apex represents three pure components. Let us say this one represent 100% fuel. This represent 100% oxygen and this represents 100% nitrogen. Now, there are several lines, let us say this is air line and this is stoichiometry line. So, we will understand what we mean by air line and we will understand what is stoichiometric lines soon. Before that let us look at the point A. The point A represents a mixture of 3 component.

Because in a triangular diagram this point A is located within the diagram. So, we represents a mixture of three components. Note that point on the sides will represent a 2 component mixture. Up ends represent 100% pure component and point within the triangular will represent three component mixture. So, point A represents the component mixtures with 10% nitrogen. Why 10% nitrogen?

Because the nitrogen content of point A will be indicated by this line. Note that all these parallel lines are shown. So, this is 10% nitrogen. Nitrogen is increasing in this direction. Similarly point

A represents 70% fuel. Why 70% fuel? Because this is 70% fuel and then similarly it represents 20% oxygen. Now, you also see that LFL, UFL minimum oxygen concentration. These are all indicated and a region is shaded which is the flammability limit or probability region will see how to obtain this.

But what we want to point out here is since this point A is outside the region the mixture given by point A is not flammable. So, flammable zone will represent all mixtures that are flammable. And mixtures outside the flammable region are not flammable.

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Now, let us see what this air line and stoichiometric line means. The air line represents all possible combinations of fuels plus air. How do you obtain this air line? Airline is obtained by joining two points one, which is representing pure air which is nothing but a mixture of 79% nitrogen and 21% oxygen. So it is lying on this side, it is a binary mixture. So, I join this point with a point where there is no oxygen no nitrogen that means 100% fuel.

So that is this point. So, joining these 2 points by straight line I obtained the air line. So, every point on this line represents various combinations of fuel plus air. Similarly the stoichiometric line represents all stoichiometric combinations of fuel plus oxygen.

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Now to obtain the flammability region or the flammability envelope, let us first locate the upper flammability limit. And the lower flammability limit on this air line. We also locate the minimum oxygen concentration and when we also locate the lower flammability limit in pure oxygen. And the upper flammability limit in pure oxygen. Now if I consider these points and join these points what I obtain is flammability zone.

So, join lower limit in pure oxygen LFL minimum oxygen concentration and then minimum oxygen concentration upper flammability limit and the lower limit in pure oxygen. Then the region we obtained is the flammable region. Any mixture lying within this region is flammable. Any mixture outside this region is non flammable. So, thereby by putting inert in my system I can control this flammable zone and this diagram will help mean doing that.

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	un ignition the	ergy and a solution
Chemical	Minimum ignition energy (mJ)	The minimum ignition energy (MIE) is the minimum energy input required to
Acetylene	0.020	initiate combustion
Benzene	0.225	
1,3-Butadiene	0.125	
n-Butane	0.260	All flammable materials (including dusts)
Cyclohexane	0.223	have MIEs
Cyclopropane	0.180	nove miest
Ethane	0.240	
Ethene	0.124	The MIE depends on the specific
Ethylacetate	0.480	chemical or mixture, the
Ethylene oxide	0.062	
n-Heptane	0.240	concentration, pressure, and
Hexane	0.248	temperature.
Hydrogen	0.018	
Methane	0.280 Many hydr	ocarbons: MIEs = 0.25 mJ (approx)

So here are presented the minimum ignition energy of various chemicals. The minimum ignition energy is the minimum energy input required to initiate combustion. All flammable materials thus will have a minimum ignition energy. The minimum ignition energy depends on the specific chemical or mixture of chemicals the concentrations as well as pressure and temperature.

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Here are list of certain ignition sources note that the fire triangle has 3 sides; fuel, oxygen and ignition source. It is indicated heat here. The number of ignition sources are quite large. So it is very difficult to eliminate all. And note that electrical and smoking these are two major ignition sources representing 23% and 18% respectively. Then comes friction, which accounts for 10% (**Refer Slide Time: 44:42**)



Static electricity is generated when mists or sprays pass through orifices. A charge may accumulate and discharge in a spark. If flammable vapours are present, a fire or explosion will occur. Mists and sprays also affect flammability limits. For suspension with drop diameters less than 0.01 millimeter, the LFL is practically same as substance in vapour form; this is true even at low temperatures where the liquid is non-volatile and no vapour is present.

Mist of this type of formed by condensation. When sprays are drop diameters between 6 millimeter and 1.5 millimeter flame propagation is not possible. So when you have drop diameters, much larger in the range of 0.6 millimeter to 1.5 millimeter flame propagation is not possible. However, if small drops are formed let us say by collapse of these large drops. This may create a hazardous condition. So, with this we will stop our discussion here and in the next class we will talk about how to prevent fires and explosion.