

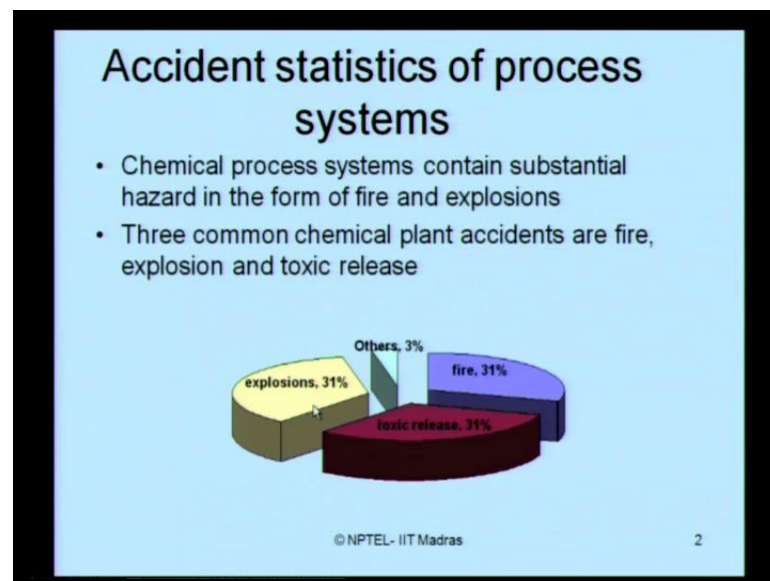
**Health,Safety and Environmental Management in Petroleum and offshore
Engineering**
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Module No. #03
Lecture No. #07

Fire and explosion modeling

Ladies and gentleman good morning, now under brace of NPTEL, IIT Madras, we are continuing with the lectures on HSE – Health, safety and environmental management. We are now through module one. We are now understanding, how to make QRA estimate based on module three. Today, we will discuss lecture seven on fire and explosion modeling.

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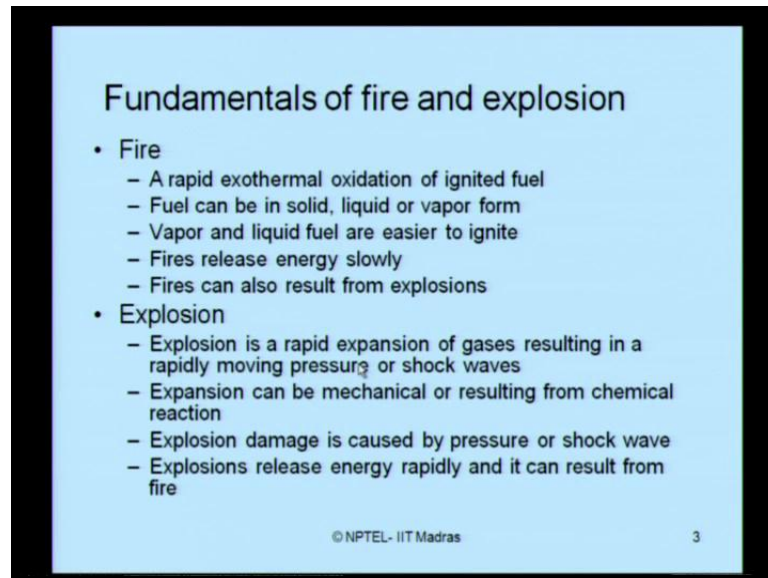


Let us look at quickly the statistics of process systems like petroleum engineering industries. A chemical process system contains substantial hazard in the form of fire and explosions. Three common chemical plant accidents are generally considered as fire, explosion and toxic release. If you look at the percentage division of these kinds of accidents in the process industry, fire accidents contribute about 31 percent of the total accidents in the process system. Toxic release contributes about 31 percent again and explosion contributes about 31 percent again. We have already understood, how to handle

the toxic release modeling using chemical exposure index methodologies in the last lecture.

In the current lecture, we will discuss about how to model fire and explosion accidents.

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The slide is titled "Fundamentals of fire and explosion" and contains two main sections: "Fire" and "Explosion".

- Fire
 - A rapid exothermal oxidation of ignited fuel
 - Fuel can be in solid, liquid or vapor form
 - Vapor and liquid fuel are easier to ignite
 - Fires release energy slowly
 - Fires can also result from explosions
- Explosion
 - Explosion is a rapid expansion of gases resulting in a rapidly moving pressure or shock waves
 - Expansion can be mechanical or resulting from chemical reaction
 - Explosion damage is caused by pressure or shock wave
 - Explosions release energy rapidly and it can result from fire

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Before we look into the detailed modeling of the fire and explosion, let us try to understand certain fundamentals related to fire and explosion. Basically how do you define or what do you understand by fire? Fire actually is a rapid exothermal oxidation of ignited fuel. The fuel can be solid liquid or in vapor form. Vapor and liquid fuel are easier to ignite whereas, solid is not that easy to get ignited, fire releases energy slowly. Fires can also result from explosions.

On the other hand, what is an explosion? Explosion is a rapid expansion of gases resulting in a rapid moving pressure or shock waves. So, one has to go to understand, what do we understand by shock waves or pressure waves. We will discuss that subsequently in this lecture. So, explosion is a rapid expansion of gases resulting in rapid moving pressure or shock waves. The expansion can be mechanical or it can result from chemical reactions. Explosion damage is essentially caused by pressure or a shock wave. Explosions release energy rapidly and it can result from fire.

So, ladies and gentleman, there is a strong interlocking between fire and explosion. Fire can result from explosion or explosion can result from fire. Fire is a rapid exothermal

oxidation of an ignited fuel, whereas explosion is a rapid expansion of gas resulting from rapidly moving pressure or shock waves. Fire releases energy slowly, whereas, explosion release energy rapidly. So, though there are fundamental differences between fire and explosion, the commonness is there is an interaction between these two; they are interlinked strongly between each other.

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Fire element	Type	examples
Fuel	Liquid	Gasoline, acetone, ether, pentane
	Solid	Plastics, wood dust, fibers, metal particles
	Gases	Acetylene, propane, CO, Hydrogen
Oxidizers	Gases	O ₂ , Fluorine, Cl ₂
	Liquids	Hydrogen peroxide, HNO ₃ , perchloric acid
	Solids	Metal peroxides, ammonium nitrite
Ignition sources	Sparks, flames, static electricity, heat	

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Let us look at some three classical fire elements like fuel, oxidizers, and ignition sources. If you look at the fire element as a fuel then, you can also have types as a liquid, solid or gases. I can give some examples here to make you to really familiar with different kinds of fuel. Look at for example gases - hydrogen gas, carbon monoxide, propane acetylene. Look at some solids which can be a fuel for on fire element – plastics, wooden dust, fibers, metal particles. If you look at liquid as fuel for on fire element then we can talk about gasoline, acetone, ether, pentane etcetera.

Now, look at the oxidizers as fire element again they can be sub classified as different types like solids, liquids, or gases. Look at gases – oxygen, fluorine, chlorine. Look at liquids examples can be hydrogen peroxide, HNO₃- nitric acid, and perchloric acid. If you look at solids as examples there can be metal peroxides, ammonium nitrite etcetera. If you look at the ignition sources as one of the fire element, then you can see some examples as sparks, flames, static electricity, heat all can be sort of an fire element can be considered as ignition sources.

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Accident prevention

- Fire and explosion accidents can be prevented using knowledge of the following
 - Fire and explosion characteristics of materials
 - Nature of fire and explosion process
 - Procedures to reduce fire and explosion hazards
- Fire Triangle
- Fire and explosion can be prevented by removing any one arm of the fire triangle



The diagram illustrates the Fire Triangle as a red equilateral triangle. The word "FIRE" is written in the center of the triangle. The three vertices of the triangle are labeled: "FUEL" at the top-left, "AIR (O₂)" at the top-right, and "Ignition source" at the bottom. The triangle is set against a light blue background.

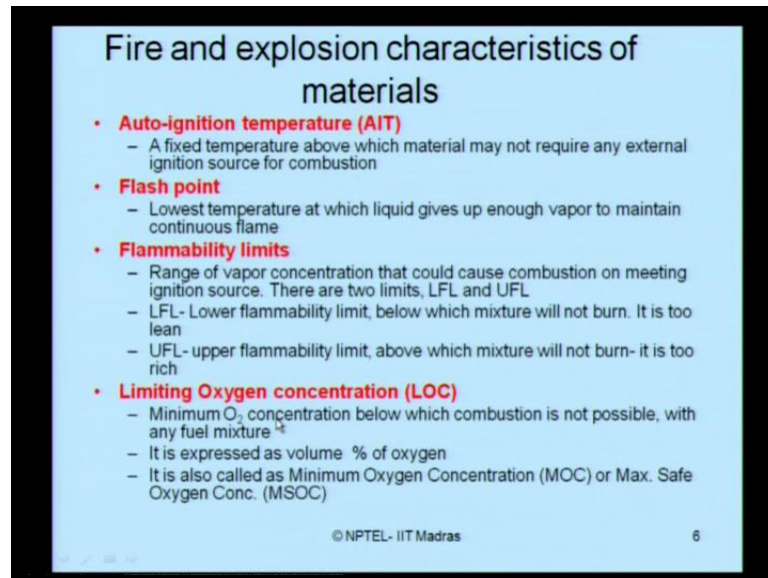
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Now, the question comes, if at all I encounter an accident because of fire or explosion, how can we prevent such accidents? So, the fire and explosion accidents can be prevented using knowledge of the following things. Number one - fire and explosion characteristics of the material should be thoroughly understood. The nature of fire and explosion process must be understood. The procedures to reduce fire and explosion hazards should be understood.

Now, famously the fire accidents can be indicated as what we call as a fire triangle. The fire triangle essentially has three arms - one is what we call as an oxygen arm; other is what we call as a fuel arm; the third one is what we call as an ignition source. So hypothetically, if you want to prevent fire accident, make anyone of these arms absent in your scenario. On the other hand, do not try to have any ignition source or do not have inventory of fuel that can catch fire or limit oxygen content. So, that the fuel does not catch fire, so easily.

So, fire triangle ladies and gentleman is represented by three arms namely oxygen arm, fuel arm, and ignition source. So, fire and explosion can be easily prevented by removing any one of the arm of this fire triangle.

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Fire and explosion characteristics of materials

- **Auto-ignition temperature (AIT)**
 - A fixed temperature above which material may not require any external ignition source for combustion
- **Flash point**
 - Lowest temperature at which liquid gives up enough vapor to maintain continuous flame
- **Flammability limits**
 - Range of vapor concentration that could cause combustion on meeting ignition source. There are two limits, LFL and UFL
 - LFL- Lower flammability limit, below which mixture will not burn. It is too lean
 - UFL- upper flammability limit, above which mixture will not burn- it is too rich
- **Limiting Oxygen concentration (LOC)**
 - Minimum O_2 concentration below which combustion is not possible, with any fuel mixture⁴
 - It is expressed as volume % of oxygen
 - It is also called as Minimum Oxygen Concentration (MOC) or Max. Safe Oxygen Conc. (MSOC)

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Let us look at some characteristics of materials which can cause fire or which can result in explosion. As I told you, to prevent accidents from fire or explosion, one should understand the characteristics of materials in detail. The top most characteristic of importance is what we call as auto ignition temperature. It is defined as a fixed temperature above which material may not require any external ignition source for combustion. It is very interesting. Every material has a fixed temperature above which, on the other hand during operation by any chance, if the operating temperature exceeds the auto ignition temperature of that material then in that case the material does not actually require any external ignition source for combustion. It will ignite on its own; that is what we call as auto ignition.

So, there is a fixed temperature above which the material catches combustion or gets combusted automatically. So, in our own interest, if you know what is an AIT of the inventory material which you have stock on board, try to see that your operating temperature does not exceed this fixed temperature of AIT of the material.

The second important characteristic of material is that is flash point. What is a flash point? Flash point is the lowest temperature at which the liquid gives up enough vapor to maintain a continuous flame. On the other hand, if the operating temperature in your present situation goes below the value of the lowest temperature at which the liquid has a

flash point. Then the liquid can give enough vapor to maintain continuity of the flame. And continuity of the flame means the fire is burning continuously.

Flammability limits or some essential characteristics of igneous materials. There are two flammability limits - what we call as lower flammability limit and upper flammability limit. The range of vapor concentration that could cause combustion on meeting ignition source is what we call as flammability limits. Basically, it is a range of vapor concentration between the two respective limits namely lower flammability limit and upper flammability limit.

Then the question comes subsequently, what do you understand by lower flammability limit? LFL is that limit below which the mixture will not burn because the mixture will be considered as too lean to burn. Upper flammability limit is that limit above which the mixture will not again burn it is considered to be too rich to burn. So, it is between these two ranges of limits the vapor concentration could cause combustion on meeting or in the presence of ignition sources.

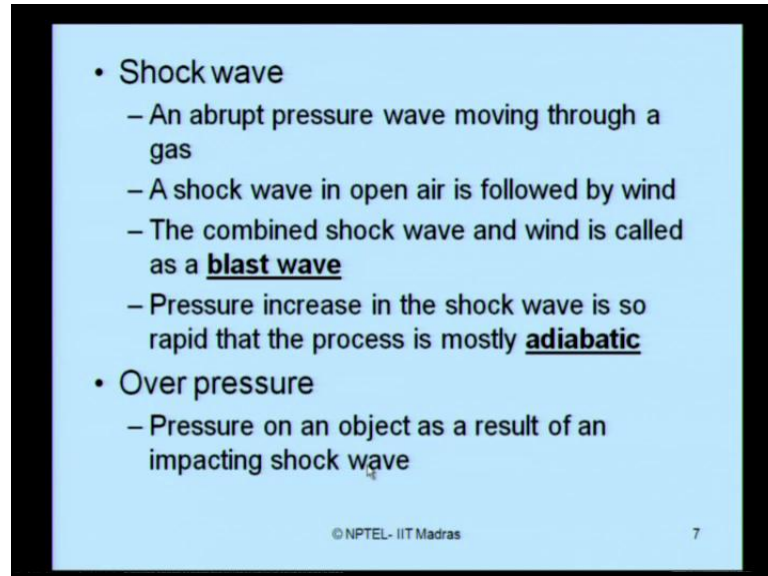
So, ladies and gentleman, by any chance if your operating temperature in the process plant like petroleum industry is between the LFL and UFL of the material. And if you have unfortunately an ignition source present on board, then there is a probability that the material or the mixture can catch fire.

Most interestingly, we have one more essential characteristic, what we call as limiting oxygen concentration; otherwise famously referred as LOC in the literature. What do we understand by the term limiting oxygen concentration? Ladies and gentleman, in the previous slide as we saw the fire triangle, we have all understood the presence of oxygen is very vital to cause fire for a given mixture. So, the limiting term as you have understood correctly quantifies the minimum oxygen concentration below which combustion is not possible. Let the fuel mixture be of any kind, if the oxygen concentration present in the scenario is lower than a minimum value then the combustion will not be possible.

Generally, LOC is expressed as volume percentage of oxygen. Some literatures refer this value as minimum oxygen concentration - MOC, or maximum safe oxygen concentration as - MSOC. Both of them refer to virtually the same meaning of limiting oxygen concentration. It is a minimum oxygen concentration expressed in volume percentage of

oxygen which is required to cause combustion. If the oxygen present in a scenario is lower than this combustion will not be possible.

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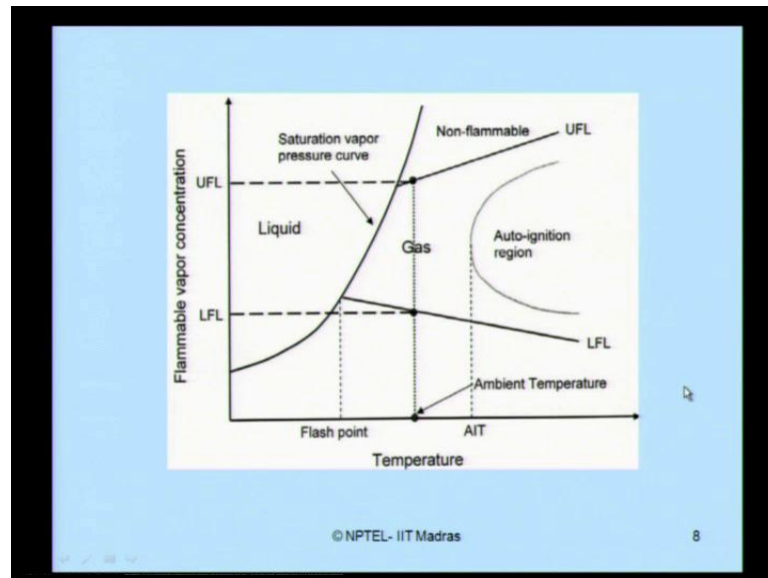
- Shock wave
 - An abrupt pressure wave moving through a gas
 - A shock wave in open air is followed by wind
 - The combined shock wave and wind is called as a **blast wave**
 - Pressure increase in the shock wave is so rapid that the process is mostly **adiabatic**
- Over pressure
 - Pressure on an object as a result of an impacting shock wave

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As we discussed in the last slide, we spoke something about what we call as a shock wave. Let us try to explain or define what is a shock wave? A shock wave is an abrupt pressure wave moving through a gas; there is a gas media. If an abrupt pressure wave move through this gas media what we call as a shock wave. A shock wave in open air is generally followed by wind. The combined shock wave and wind is what we understand as a blast wave. That is what the literature refers as a blast wave as a result of a blast wave pressure increases, so rapidly that the process is mostly adiabatic.

What do we understand by a term over pressure? Over pressure is that pressure on an object as a result of an impacting shock wave. For example, I have an object the shock wave creates an additional pressure. So, the pressure on an object which results from impacting shock wave is what I call as an over pressure.

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This figure explains the variation of temperature with the flammable vapor concentration on the y axis. On the y axis, I have marked the lower flammability limit and the upper flammability limit. Now, the characteristic of these two limits are very interesting. The two limits after the ambient temperature, the upper flammability limit keeps on increasing and the lower flammability limit keeps on decreasing, as far as the flammable vapor concentration is concerned with increase in temperature.

Flash point is the point beyond which, for increase in temperature the vapor concentration decreases. Now, the region between the LFL and UFL is what we call as a gaseous region and it is at that temperature this happens is what we call as an ambient temperature.

The autoignition temperature, as we discussed in the previous slide is indicated in the temperature arm as here. So, any region between the flammable limits and the temperature exceeding AIT is what we call as auto ignition region. Any region about upper flammable limit is what we call as a non-flammable region. And of course, any limit below lower flammable region is also non-flammable.

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Flammability characteristics of liquids

- Liquids
 - Experimentally determined by open cup or closed method
 - Mathematically it is calculated using boiling point relationship (a,b,c are constants; T_f is flash point, T_b is boiling point in Kelvins)

$$T_f = a + \frac{b \left(\frac{c}{T_b} \right)^2 e^{-\left(\frac{c}{T_b} \right)}}{\left(1 - e^{-\left(\frac{c}{T_b} \right)} \right)^2}$$

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Now interestingly, I want to estimate the flammability characteristics of liquids. How are they obtained? Liquids can be experimentally analyzed using an open cup or a closed method to obtain the flammable characteristics. Ladies and gentleman what on the flammability characteristics we saw in the last slide. For example, AIT, limiting oxygen concentration, upper flammability limit, lower flammability limit; these are all different flammability characteristics of a mixture which can cause a flame.

For example, the mixture which I am considering now is a liquid. If you want to estimate these flammability characteristics for a liquid, then I can do this experimentally by what I understand as an open cup method or a closed method. On the other hand, you can also mathematically estimate the flammability characteristics using the following equation. The flash point is what we will be interested as a flammability characteristic of the liquid. This is given by a simple expression here. Where the expression has constants of a, b and c; T_f is what I understand as a flash point and of course, T_b what I use here what we understand as a boiling point given in Kelvin.

So, for a liquid if I know the boiling point and the constants a, b and c using this relationship, I can easily estimate the flash point for this liquid.

Now, you may be wondering the obtaining a boiling point for a given liquid is very simple. And you can easily obtain using experimental investigations. Now, where we get the constants of a, b and c, which I have got to use in this equation.

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Chemical group	a	b	c
Hydrocarbons	225.1	537.6	2217
Alcohols	230.8	390.5	1780
Amines	222.4	416.6	1900
Acids	323.2	600.1	2970
Ethers	275.9	700.0	2879
Sulfur	238.0	577.9	2297
Esters	260.5	449.2	2217
Halogens	262.1	414.0	2154
Aldehydes	264.5	293.0	1970

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For example, for different chemical group a, b and c constants or available in the open literature or in standard text books. I have clubbed up some examples for your understanding. The hydrocarbons, alcohols, amines, acids, ethers, sulfur, esters, halogens, and aldehydes have different constants values available or taken from the open literature.

Now, it is very easy for us to estimate for an alcohol the flash point if I know the boiling point of this liquid. Using the relationship which I shown you in the previous slide, because for alcohol chemical group I already have the - a value, the b value and the c value from the open literature.

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Flammability characteristics of vapor and gases

- Flammability limits for vapors are determined experimentally in a specially closed vessel apparatus
- Flammability limits for mixture of gases and vapors are given by:

$$L_{FL,mixture} = \frac{1}{\sum \frac{y_i}{LFL_i}} \quad UFL_{mixture} = \frac{1}{\sum \frac{y_i}{UFL_i}}$$

- LFL_i is LFL for i^{th} component (in volume %) of i^{th} component in fuel and air; y_i is the mole fraction of i^{th} component on a combustible basis; n is the number of combustible species

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The next flammability characteristics which will discuss is for vapor and gases. Flammability limits for vapor are determined experimentally in a specially closed vessel apparatus. Flammability limits for mixture of gases and vapor are given by these two expressions. The lower flammability limits for a given mixture of gas and vapor is given by this equation. The upper flammability limits for a mixture of gas and vapor is given by this relationship. Where LFL_i is the lower flammability limit for the i^{th} component, which is expressed in volume percentage of the i^{th} component in fuel and air.

Y_i is the mole fraction of that i^{th} component on a combustible basis and you sum up this for n where n is a number of such combustible species. So, if you have different mixtures, if you have the mole fraction of any component on a combustible basis and if you know what is the volumetric composition of that in percentage in fuel in air, using this relationship of LFL and UFL for any given mixture can easily obtain the flammability limits of upper and lower respectively for that mixture.

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Flammability limit behavior

- Temperature dependencies
 - As temperature increases, UFL increases, LFL decreases
 - Flammability range increases

$$\text{LFL}_{\text{range}} = \text{LFL}_{25} - \frac{0.75}{\Delta H_c} (T - 25)$$
$$\text{UFL}_{\text{range}} = \text{UFL}_{25} + \frac{0.75}{\Delta H_c} (T - 25)$$

– ΔH_c is net heat combustion (kcal/mole), T is temperature in C

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Now, flammability limits also depends on temperature. As temperature increases, ladies and gentlemen, in the previous slide, you saw that upper flammability limit keeps on increasing whereas the lower flammability limit keeps on decreasing. On the other hand, I can say that the flammability range keeps on increasing with increase in temperature.

LFL range, can be now given as LFL at 25 minus 0.75 of delta H c T minus 25; where T is the temperature at which you are evaluating the study in degree Celsius. And delta H c is the net heat combustion of that mixture or liquid in kilocalorie per mole. So, if you want really find the lower flammability limits in range, you can use this expression directly to find the flammability range.

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Flammability limit behavior

- Pressure dependencies
 - As pressure increases, UFL increases
 - Pressure has little effect on LFL

$$UFL_p = UFL + 20.6(\log P + 1)$$

- P is absolute pressure in Mega Pascal

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Flammability limit behavior depends on pressure. As pressure increases, upper flammability level increases, as pressure has very little effect on the lower flammability limits. The upper flammability limit is given by the simple equation as a function of pressure. If you know the conventional upper flammability limits of the liquid at any pressure p then you can always find any pressure p on the flammability limit using this simple expression where P is absolute pressure expressed in megaPascal.

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Estimation of flammability limits using stoichiometric balance

- For many hydrocarbon vapors, LFL and UFL are function of stoichiometric concentration (C_{st}) of the fuel
- For a general combustion reaction,
$$C_m H_x O_y + z O_2 \rightarrow m CO_2 + (x/2) H_2O$$

$$C_{st} = \frac{21\%}{0.21 + z}$$
$$z = m + \frac{1}{4}x + \frac{1}{2}y$$
$$LFL = 0.55 C_{st}$$
$$UFL = 3.5 C_{st}$$

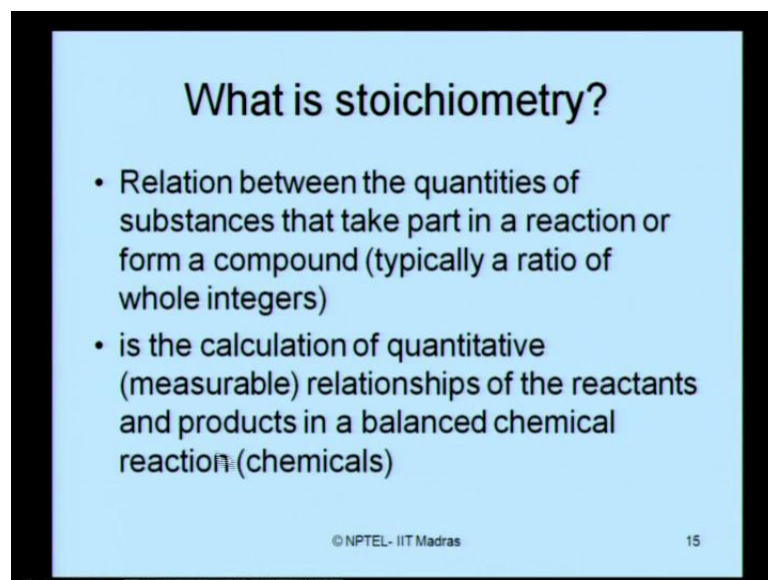
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You can also estimate the flammability limits using stoichiometric balance. For many hydrocarbon vapors, the lower limit and upper limit of flammability are essentially function of stoichiometric concentration of the fuel. The stoichiometric concentration, C_{st} , is given by a simple equation as expressed here.

Let us say for example, I take a general combustion reaction, where I have got some moles of carbon hydrogen and oxygen expressed as m , x and y and some amount of oxygen concentration present in the reaction. And if I know the chemical reaction as a combustion reaction exit of this combination then, on the other hand if I know the oxygen concentration I can find the stoichiometric concentration using this relationship, where z is given by m (the concentration of carbon) plus one-fourth of x (the concentration of hydrogen) and half of y (concentration of oxygen).

If I know this concentration present in the reaction, we can easily find the stoichiometric concentration C_{st} of the fuel. The moment I know the stoichiometric concentration of the fuel, I can find a LFL and UFL using this simple empirical relationship that LFL is 0.55 of C_{st} and UFL is 3.5 of C_{st} .

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What is stoichiometry?

- Relation between the quantities of substances that take part in a reaction or form a compound (typically a ratio of whole integers)
- is the calculation of quantitative (measurable) relationships of the reactants and products in a balanced chemical reaction (chemicals)

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This we make you to wonder to understand what is stoichiometry? Stoichiometry is a relationship between the quantities of substances that take part in a reaction or form a compound - typically it is a ratio of the whole integers. Actually, it is a calculation of quantitative relationship of the reactants and the products in a balanced chemical reaction.

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$$\text{LFL} = \frac{55}{4.76m + 1.19x - 2.38y + 1}$$
$$\text{UFL} = \frac{350}{4.76m + 1.19x - 2.38y + 1}$$

- Using heat combustion, LFL and UFL can be determined

$$\text{LFL} = \frac{-3.42}{\Delta H_c} + 0.569 \Delta H_c + 0.0538 \Delta H_c^2 + 1.8$$
$$\text{UFL} = \frac{350}{4.76m + 1.19x - 2.38y + 1}$$

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For example, LFL and UFL can also be given alternatively by another expression if you know the concentration of m, x and y separately. In the previous equation, directly we expressed to give you the C s t in terms of z value which is also a function of m, x and y. And based on the C s t value we obtain LFL and UFL subsequently. If one is interested to find our LFL, UFL directly one can use this expression which is derived from the previous equation.

Now, also using heat combustion relationship the flammability limits can be ascertained using the following equations for LFL and UFL respectively.

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Estimation of LOC (limiting oxygen conc.)

- LOC has units of percentage of moles of oxygen in total moles
- For hydrocarbons, LOC is estimated using stoichiometry of the combustion reaction and the LFL
- Fuel (hydro carbons) + (z) × O₂ → combustion products
- LOC ~ z × (LFL)

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One is also interested to estimate the limiting oxygen concentration of the given fuel. LOC has units of percentage of moles of oxygen present in total moles. For hydrocarbons, LOC is estimated using stoichiometry of the combustion reaction and the LFL. Let us say for example, if I take hydrocarbon as a fuel and combine this mixture with oxygen which can give you combustion products. Then, LOC is approximately equal to the product of z concentration of oxygen with LFL.

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Flammability diagram for hydrocarbon

- Determines whether a mixture is flammable or not
- Required for control/prevention of flammable mixtures
- Depends on chemical species
- Function of Temperature and Pressure

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After understanding the characteristics of the fuel or the mixture that can be flammable, we expressed this graphically in a diagram what we call as flammability diagram for a hydrocarbon. The flammability diagram has basically had three arms - one is what we call as a fuel arm; other is what we call as an oxygen arm; other is, third one is what we call as a nitrogen arm.

Remember this is similar to what we understand as a fire triangle. Now, interestingly the flammability diagram determines whether a given mixture is flammable or not. Before we understand, explain a flammability diagram and to plot a flammability diagram for a given mixture or given fuel. Let us tightly closely examine this diagram once again. The diagram has three arms as explained just now. This arm is called a fuel arm; the value of arm concentration of fuel varies from 0 to 100. Oxygen arm varies from again 0 to 100. And nitrogen arm varies from 0 to 100.

Ladies and gentleman, this is got a specific order. This is anticlockwise starting from fuel oxygen, nitrogen, and fuel. The concentration also varies anticlockwise, 0 to 100, 0 to 100, and 0 to 100. So, this is in essential format of what we call as a flammability diagram. Now, if you have any mixture or any fuel whose concentration of these three components lies in a region which is not shaded then we can say that the mixture or the fuel is not flammable. On the other hand, if the concentration of the fuel lies in the shaded area then we can say the fuel is flammable. So, a flammability diagram for any hydrocarbon mixture will tell you whether the fuel or the mixture is flammable or not.

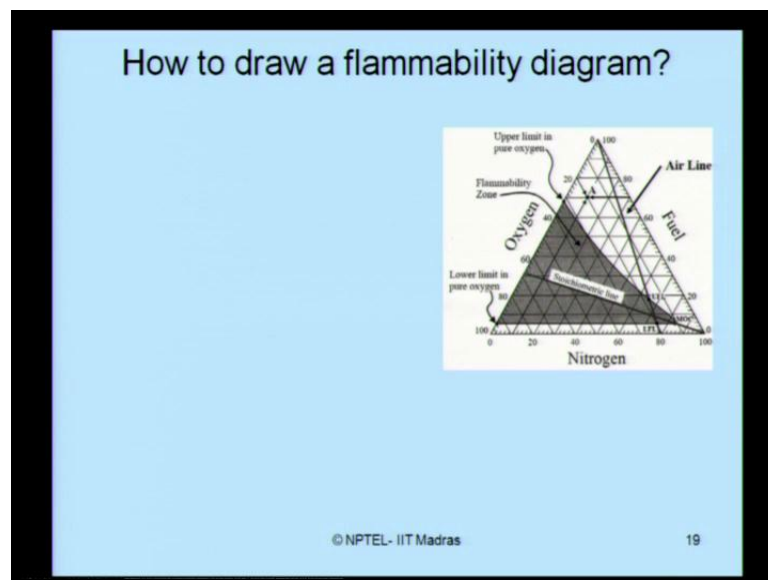
On the other hand, a combination of three arms of a fire triangle indirectly tells me whether the given mixture is flammable or not. Once you understand, the mixture is in which region flammable or non-flammable, they can always devise some control and prevention methods or techniques to prevent fire occurring from these flammable mixtures. Therefore, flammability diagram is an essential requirement of a process industry to really know whether the chemical being manufactured or the mixture being process is at any given point of time is flammable or not.

And of course, the flammability diagram depends on the chemical species. It is not unique and common for all species depending upon the chemical process, depending upon the mixture of these three arms, the point of concentration will lie either on the flammable region or not on the flammable region. So, it is interesting for one to

understand, how to plot a flammability diagram for given hydrocarbon mixture or for a given standard fuel.

We will take up an example to explain how we can plot the flammability diagram. Ladies and gentleman, understand very carefully that flammability diagram or function of temperature and pressure as well. Though, there is no arm being indicating here as a function of temperature and pressure, because all your flammable characteristics depend on temperature and pressure. Remember the shock waves, remember the upper and lower flammability limits, or remember the flammability range which is a function of temperature. Therefore, flammability diagram is a function of temperature and pressure.

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Now, the fundamental question comes, how to draw a flammability diagram? We will explain this, after a break in the next lecture. By giving you a suitable example, how to draw flammability diagram by taking or illustrating in example for one of the fuel what we call as methane.

Thank you.