Fundamentals of Combustion (Part 2)
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Lecture – 80
Combustion Modification Methods

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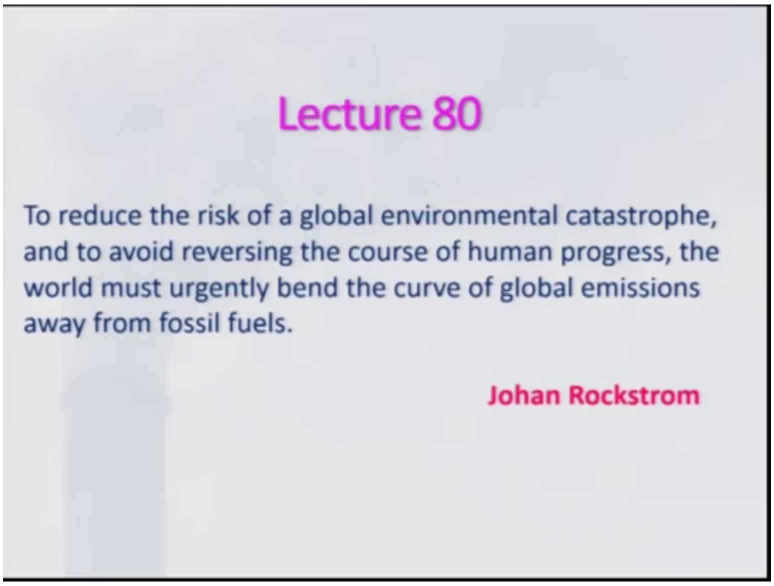

Lecture 80

To reduce the risk of a global environmental catastrophe, and to avoid reversing the course of human progress, the world must urgently bend the curve of global emissions away from fossil fuels.

Johan Rockstrom

Let us start this lecture with a third process by Johan Rockstrom. He says, “To reduce the risk of a global environment catastrophe, and to avoid reversing the course of human progress, the world must urgently bend the curves of global emissions away from the fossil fuels”. Now this is a very great statement and which really we need to look at, but; however, we need to also look at how to device the combustion systems such that it will be meeting our need while polluting the air the list.

In the last lecture, we discuss about how to control the CO x emission and also how to control the SO x emission level in the combustion system. And today we will be looking at very briefly NO x emission control and also the particulate matter control.

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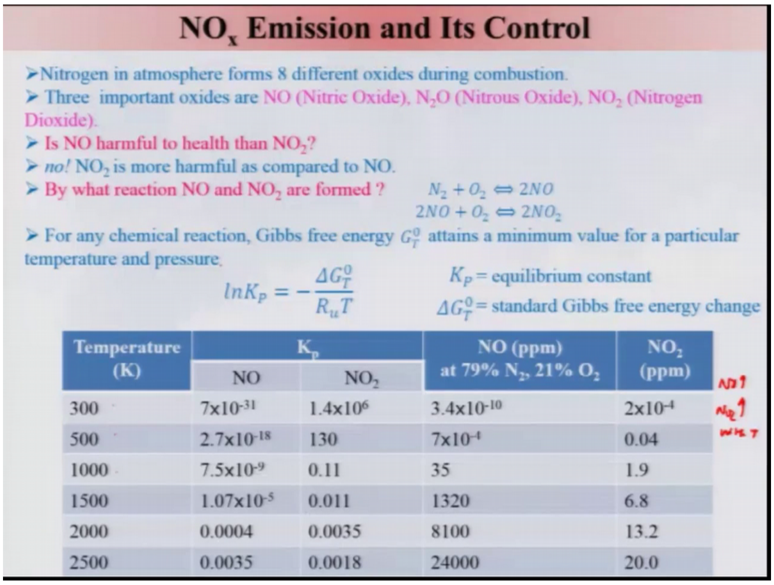

NO_x Emission and Its Control

- Nitrogen in atmosphere forms 8 different oxides during combustion.
- Three important oxides are NO (Nitric Oxide), N_2O (Nitrous Oxide), NO_2 (Nitrogen Dioxide).
- Is NO harmful to health than NO_2?
- *no!* NO_2 is more harmful as compared to NO.
- By what reaction NO and NO_2 are formed? $N_2 + O_2 \Leftrightarrow 2NO$

$$2NO + O_2 \Leftrightarrow 2NO_2$$

- For any chemical reaction, Gibbs free energy G_T^0 attains a minimum value for a particular temperature and pressure.

$$lnK_p = -\frac{\Delta G_T^0}{R_u T}$$

K_p = equilibrium constant

ΔG_T^0 = standard Gibbs free energy change

Temperature (K)	K_p		NO (ppm) at 79% N_2, 21% O_2	NO_2 (ppm)
	NO	NO_2		
300	7×10^{-31}	1.4×10^{6}	3.4×10^{-10}	2×10^{-4}
500	2.7×10^{-18}	130	7×10^{-4}	0.04
1000	7.5×10^{-9}	0.11	35	1.9
1500	1.07×10^{-5}	0.011	1320	6.8
2000	0.0004	0.0035	8100	13.2
2500	0.0035	0.0018	24000	20.0

$NO \uparrow$

$NO_2 \uparrow$

w.r.t. T

So, NO x emission control, if you look at is very important because of fact that it causes a lot of health issues as we are discuss particularly, the pharynx and then nostrils and other parts get affected very easily. Nitrogen in atmosphere forms 8 different oxides during the combustion; however, we will be only considering 3 of them as they are important and those are nitric oxide, nitrous oxide and nitrogen dioxide. So, this three will be considering.

And is NO harmful to health than NO 2? Certainly no rather NO 2 that is nitrogen dioxide is more harmful has compared to the nitric oxide. By what reaction NO, NO 2 are formed? NO 2 will be reacting with oxygen that is available in air and will be leading to the 2 moles of NO of course, that will be occurring at a high temperature and 2 moles of a N O can react with oxygen to form 2 N O 2 that is nitrogen dioxide. And for any chemical reaction the Gibbs free energy attains a minimum value for a particular temperature and pressure that we have already deal to with at length.

Just to again the recapture the essence what we are learnt that is lnK p is equal to minus delta G T divided by R u T and K p is the equilibrium constant and delta G naught is basically standard Gibbs free energy change that is occur during the chemical reaction at equilibrium. And if you do this computation at different temperature which is being shown here, 300, 500, 1000, 1500, 2000 and 2500 Kelvin, you can see that N O that is in ppm. Ppm basically parts per million at 79 percentage of nitrogen and 21 percent of oxygen corresponding to air. And this is at 300 Kelvin, this is a very very low value that is 3.110, 10 power minus 10. So, also the N O 2 which is also low, but little bit more than the N O and as the temperature increases this is N O values are increasing at rapidly and a very higher value that 2500 is 2400 p p m. Of course, the N O 2 also increasing trend; that means, we temperature increase with temperature this N O 2 increases with temperature and so, also N O level; that means, it is basically dependent on temperature what it says from the equilibrium point of view.

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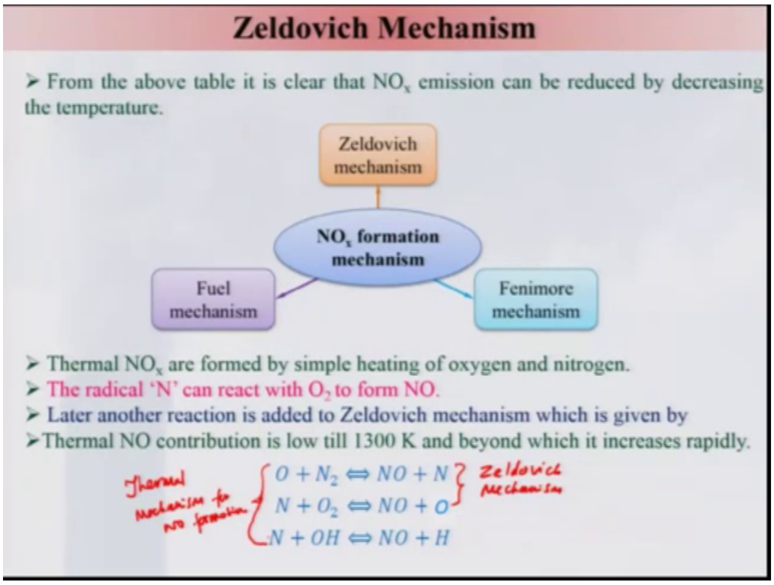

Zeldovich Mechanism

- From the above table it is clear that NO_x emission can be reduced by decreasing the temperature.

Zeldovich mechanism

NO_x formation mechanism

Fuel mechanism

Fenimore mechanism

- Thermal NO_x are formed by simple heating of oxygen and nitrogen.
- The radical 'N' can react with O_2 to form NO.
- Later another reaction is added to Zeldovich mechanism which is given by
- Thermal NO contribution is low till 1300 K and beyond which it increases rapidly.

Thermal mechanism for NO formation

$$O + N_2 \Leftrightarrow NO + N$$
$$N + O_2 \Leftrightarrow NO + O$$
$$N + OH \Leftrightarrow NO + H$$

Zeldovich Mechanism

And therefore, one can get the clue that N O x emission can be reduced by decreasing the temperature and particularly when we are using the air as a medium. So, N O x formation mechanism one can think of a Zeldovich mechanism and there is another way of fuel mechanism and the Fenimore mechanism. The thermal NO is basically comes from the Zeldovich who was proposed that one and thermal N O x are formed by simple heating of oxygen nitrogen as I told earlier.

And so, that this is basically it is O plus N 2 going to the N O plus N and the radical N is being formed in this reaction can react with the oxygen to form N O. And these 2 reaction is basically given by in the beginning are proposed by the Zeldovich. Therefore, this is known as Zeldovich mechanism, but later on people gave another reaction which is added to the Zeldovich mechanism that is N is reacting with O H going to the N O plus H. And this is three together is known as thermal mechanism for N O formation and thermal N O contribution is quite low till it attains the temperature of around 1300 kelvin, but beyond which it increases a rapidly that we will see by looking at how it is.

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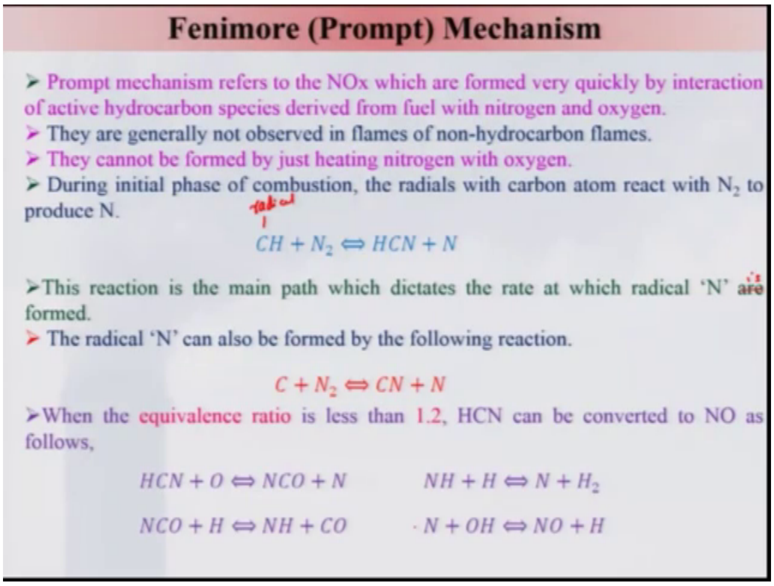

Fenimore (Prompt) Mechanism

- Prompt mechanism refers to the NOx which are formed very quickly by interaction of active hydrocarbon species derived from fuel with nitrogen and oxygen.
- They are generally not observed in flames of non-hydrocarbon flames.
- They cannot be formed by just heating nitrogen with oxygen.
- During initial phase of combustion, the radials with carbon atom react with N_2 to produce N.

radical

$$CH + N_2 \Leftrightarrow HCN + N$$

- This reaction is the main path which dictates the rate at which radical 'N' ~~are~~ is formed.
- The radical 'N' can also be formed by the following reaction.

$$C + N_2 \Leftrightarrow CN + N$$

- When the equivalence ratio is less than 1.2, HCN can be converted to NO as follows,

$$HCN + O \Leftrightarrow NCO + N \qquad NH + H \Leftrightarrow N + H_2$$

$$NCO + H \Leftrightarrow NH + CO \qquad N + OH \Leftrightarrow NO + H$$

But before that let us look at the prompt mechanism refers to the N O x formation which are formed very quickly by interaction of active hydrocarbon species particularly derived from the fuel with nitrogen and oxygen. So, they are not generally observed in the flames of non hydrocarbon flames, but if the hydrocarbons such there then naturally the Fenimore or the prompt mechanism will be there.

They cannot be found by just heating the hydrogen with oxygen that we had seen earlier and which is basically different than Fenimore mechanism and that is the basically the thermal mechanism. During initial phase of combustion, the radicals with the carbon atom react with nitrogen to produce the N as per the following reaction. Let us say C H is the radical which will be reacting with nitrogen and forming the H C N and again the radical N or the N atom and this reaction is the main path which indicates the rate at which the radical N is formed.

And the radical N can also be formed by the following reaction C will be reacting with N 2 getting into product of C N and N. And when equivalence ratio is less than 1.2 the H C N can be converted into as per the following reactions that is H C N is reacting with o getting into N C O plus N and there is a another reaction in N C O is reacting with H going to the N H plus C O. Keep in mind that during hydrocarbon reaction, there will be several radicals like O and H and C H will be formed. As a result the N C O is reacting with H going in getting into the product of N H plus C O.

Keep that all these reaction are both forward and backward depending on the temperature and pressure, it will be taking the different path. N H will be reacting H getting into N plus hydrogen and N can be also reacting with o H radical getting into N O plus H; that means, any path it can take particularly when equivalence ratio is less than 1.2. So, in this case what we had seen we are basically seen how this H C N will be converted into N O following this step of reactions.

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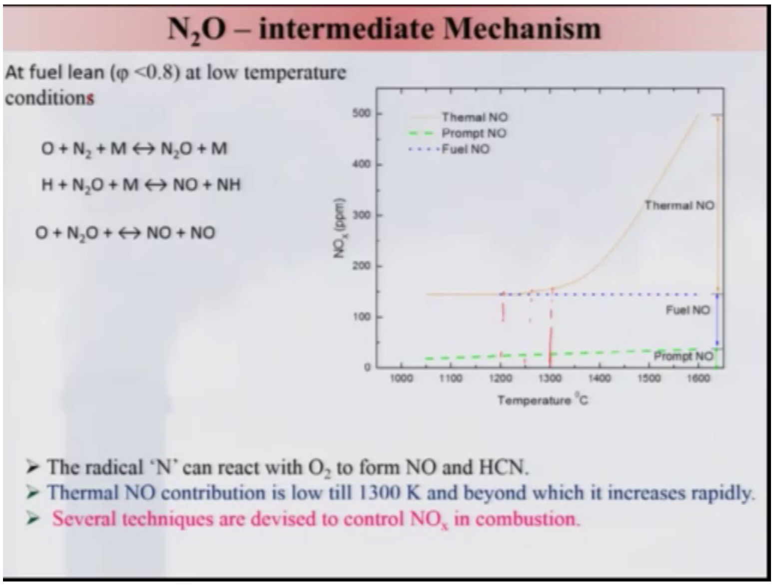

N_2O – intermediate Mechanism

At fuel lean ($\varphi < 0.8$) at low temperature conditions

$$O + N_2 + M \leftrightarrow N_2O + M$$

$$H + N_2O + M \leftrightarrow NO + NH$$

$$O + N_2O + \leftrightarrow NO + NO$$

- The radical 'N' can react with O_2 to form NO and HCN.
- Thermal NO contribution is low till 1300 K and beyond which it increases rapidly.
- Several techniques are devised to control NO_x in combustion.

So, N 2 O in intermediate mechanism, we can see that particularly when the fuel lean condition that phi is less than 0.8 at low temperature condition; O will be reacting, the radical O will be reacting with nitrogen; of course, under third body m is a third body and which will be occurring at little bit high pressure getting into the N 2 O. And then M and this third body can be anything can be a nitrogen can be any others stable species which is not participating in the reaction and H can be reacting with N 2 O; again a third body and getting into N O plus N H.

And O will be reacting with N 2 O and to the N O plus N O. And keep in mind that this will be intermediate species which is; that means, both N 2 O is are formed depending on the situation and also the N O being formed in the passes. So, the intermediate like means N 2 O is the key for the formation of N O in this method. So, if you look at the N

O X emission particularly we are talking about N O now, and with the various temperature you can see that the prompt N O is not changing with respect to temperature and it is having a very low values.

Whereas the fuel N O depending on of course, the condition whether it is a rich condition and also there is a hydrocarbon fuel or not because for hydrocarbon fuel that will be very important one right. And this will be having certain values whereas, the thermal N O remains almost constant till maybe 1250, you can say. And it picks up rather I would say that till 1200 it will remains constant and it picks slowly, but it become faster beyond the 1300. If you look at 1300, it really increases at a faster rate.

So, therefore, the and which is a quite a huge value as compared to other one and the radical N can react with oxygen to form N O and H C N that we had already seen in the Fenimore method. And thermal N O contribution is low till the 1300 and beyond which it increases rapidly several techniques are being devised to control N O x in the combustion and which will be discussing them in a very brief manner rather very few method I will be discussing because of due to the paucity of time.

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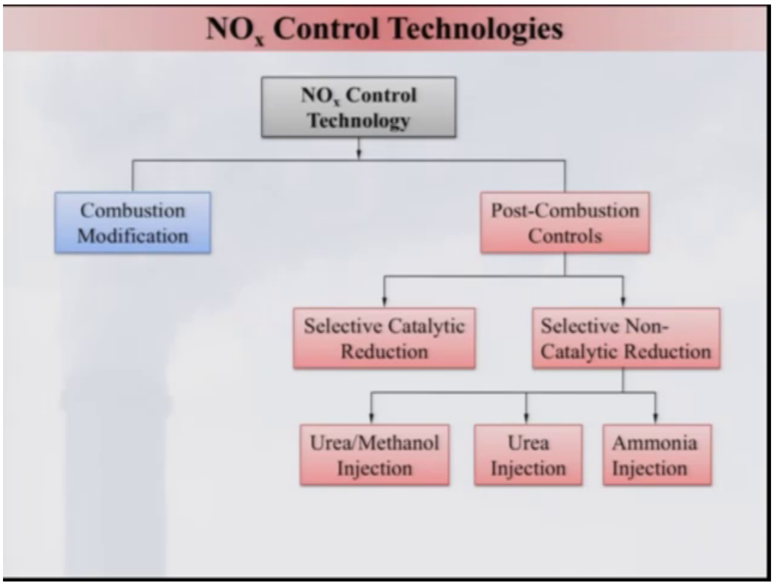

NO_x Control Technologies

NO_x Control Technology

Combustion Modification

Post-Combustion Controls

Selective Catalytic Reduction

Selective Non-Catalytic Reduction

Urea/Methanol Injection

Urea Injection

Ammonia Injection

And N O x control technology if you look at can be broadly divided into 2 categories: one is combustion modification, other is post combustion controls. Post combustion control is a selective catalytic reduction because various catalyst being developed and used such that you can really control the N O X. And there is also selective non catalytic reduction and in which the various chemicals and being used such as urea or methanol can be injected to the product gases such that you can reduce the N O x and. So, also the urea being used to reduce the N O x in the post combustion process and beside this ammonia is also being injected for certain kind of combustion system to reduce the N O x emission before you really let the flue gases to enter into the atmosphere. And this we are not going to discuss the post combustion control methods rather will be discussing combustion modification method; only 2 of them will be discussing combustion modification method.

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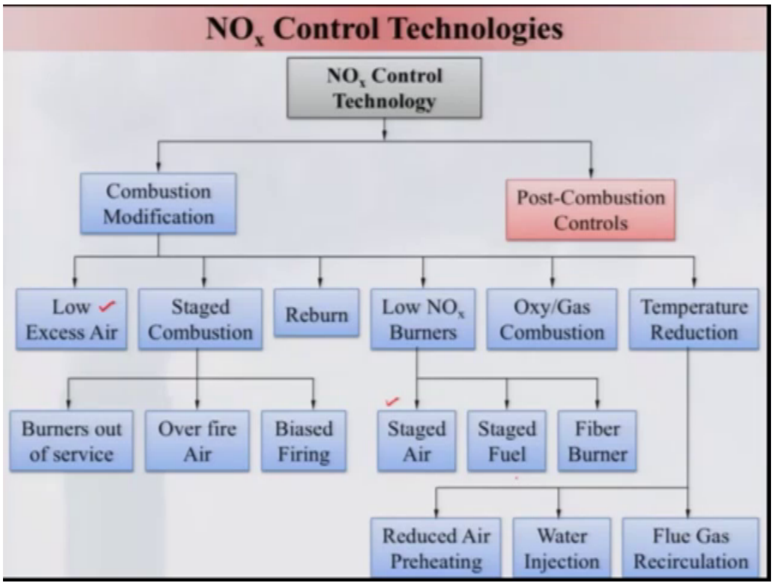

NO_x Control Technologies

NO_x Control Technology

Combustion Modification

Post-Combustion Controls

Low ✓ Excess Air

Staged Combustion

Reburn

Low NO_x Burners

Oxy/Gas Combustion

Temperature Reduction

Burners out of service

Over fire Air

Biased Firing

✓ Staged Air

Staged Fuel

Fiber Burner

Reduced Air Preheating

Water Injection

Flue Gas Recirculation

So, if you look at the combustion application method there are several methods which have been really developed over the years and some or more are also being developed. The if you look at the one method is the low excess air method, one can really use it and which is a very easier to do that and beside this the stage combustion method can be divided into burners out of service. And then because some of the burners you may not use it otherwise over fire the air and other is bias firing and which will be not discussing, but; however, will be discussing about the low excess air method; we will be discussing about this. And there is a reburn method; that means, once you burn it and then again you can basically burn inside that that it will be N O x can be reduce.

And there is another way of that you can design the burner such that the low N O x will be produce and again there we use the similar technique like that is the stage air one can think of. And other is the stage fuel and there is a fiber burner which is coming out that can be operated at a low temperature. And there is also the lot of interest to use the oxygen combustion are such that you can reduce the N O x, one way is that you can enrich the air with the oxygen addition lot of work is going on. Beside this another way is that which is being use for particularly big power plants and then engines also that is temperature reduction. Because that is the coax of the N O form N O x formations that is the thermal N O contributes more amount of N O as compared to the prompt of the fuel N O.

So, one way of is that reduce the air pre heating which is being done basically to enhance the combustion efficiency and also reduce the C O emission level. Another way that water injection which can reduce the temperature drastically and some people also use the also the alcohol injections such that you can add some fuel or the collective value at the same time, you will be using certain amount of energy for vaporization of the alcohol.

And there is another method which is being used nowadays very much and flue gas recirculation circulate the flue gas into the combustion chamber such that will be N O X can be reduce. So, will be basically discussing about the stage air and maybe some of the flue gas recirculation and some other method will be discussing not all the things because of paucity of time.

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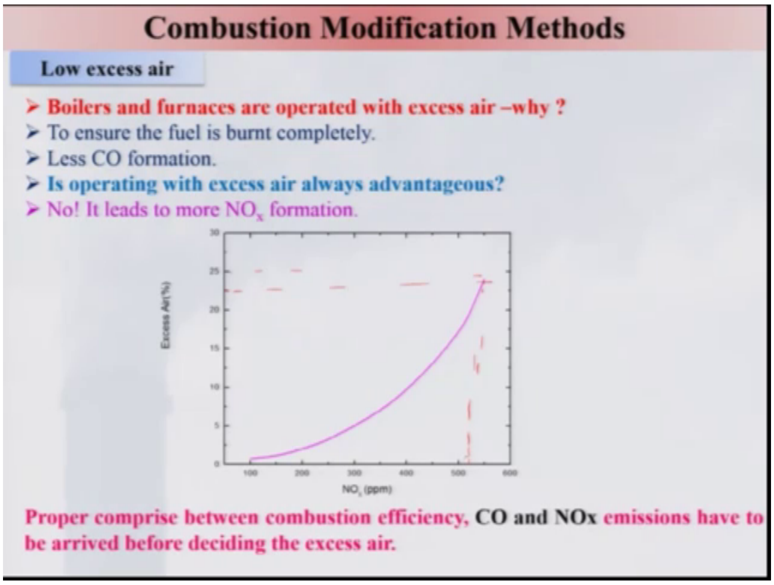

Combustion Modification Methods

Low excess air

- **Boilers and furnaces are operated with excess air –why ?**
- To ensure the fuel is burnt completely.
- Less CO formation.
- **Is operating with excess air always advantageous?**
- No! It leads to more NO_x formation.

Proper comprise between combustion efficiency, CO and NOx emissions have to be arrived before deciding the excess air.

Let us look at low excess air; boiler and furnaces, as I told earlier are operated with excess air because of fact that the fuel has to be burnt completely to have the higher combustion efficiency and low level of carbon monoxide.

And that is why a large amount of excess air, then the stochamate is being used routinely and of course, the advantages is that the combustion is operating with excess air always advantages certainly no, because although the combustion efficiency in an gets enhance. But; however, it leads to a more N O x formation which is a news and so, far air pollution is concerned.

So, let us look at how this N O x formation is getting increase with excess air. So, if it is excess air is very less, so, you can find that basically the around N O x p p m and it, but it as the excess air increases with the maybe from something 1 or 2 percent to 25 percent. There is a 5 times of the N O x formation, the 5 times increase in N O x gases N O x emission. So, therefore, it is a very important to reduce the excess air conjunction, during the combustion. If you will use the less amount of excess air, then naturally what will happen there will be drop in the combustion efficiency and there will be also increase in CO level and; however, N O x formation will be higher.

But what we need that, will have to make a concerted effort to optimise the excess air such that will have a reasonable amount of C O formation and also the reasonable combustion efficiency and with reduction of N O x emission so, that we will have to keep in mind.

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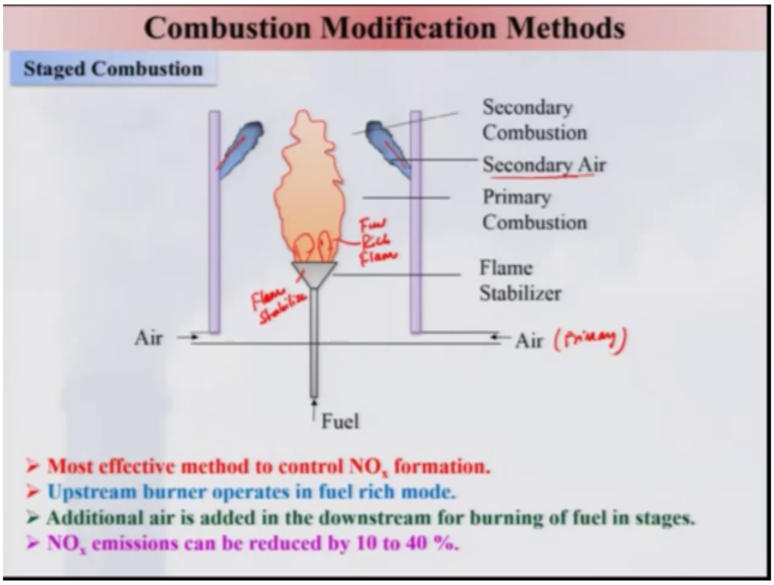

Combustion Modification Methods

Staged Combustion

- Most effective method to control NO_x formation.
- Upstream burner operates in fuel rich mode.
- Additional air is added in the downstream for burning of fuel in stages.
- NO_x emissions can be reduced by 10 to 40 %.

Let us look at staged combustion system and in the stage combustion as I told that in this case the fuel is being use and the this is the air which is coming over in this case and mixing and this is the flame stabilizer which is used to recirculate create a recirculation zone such that it will stabilize the flame. And you can use the excess amount of air, but; however, the air is known as, this is known as primary air.

And there is also another a secondary air which is being injected in such a way that it can cool the flame and some combustion can also take place because generally this can will be rich flame or rich condition fuel rich flame will be there. And there will be some carbon monoxide which will be there which needs to have secondary air. So, that combustion will be taking place. In this case, the carbon dioxide is being reduced at the same time the temperature will be low such that the N O x formation will be also being reduce.

So, this is most effective method to control N O x emission level because as I told earlier the upstream burner operates in the fuel rich mode and the downstream, it operates on the fuel in conditions. And when the additional air is added to the downstream of burning fuel and N O x emission can be reduce by 10 to 40 percentage.

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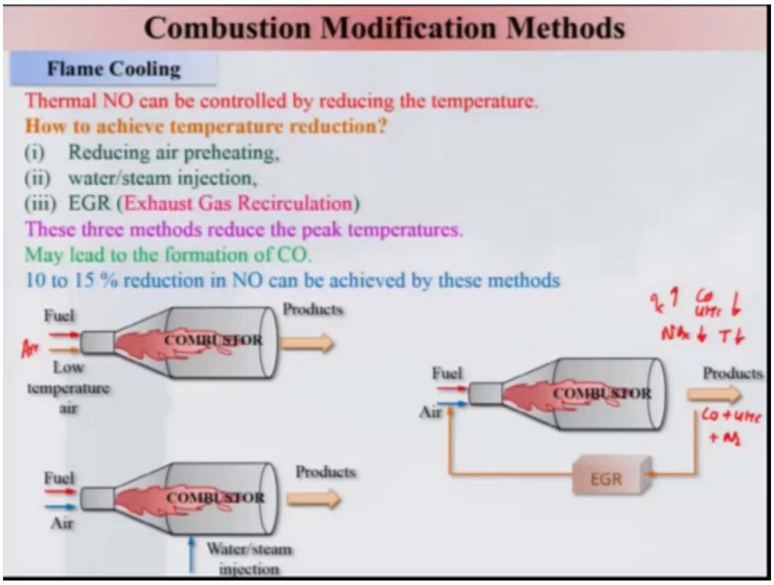

Combustion Modification Methods

Flame Cooling

Thermal NO can be controlled by reducing the temperature.

How to achieve temperature reduction?

(i) Reducing air preheating,

(ii) water/steam injection,

(iii) EGR (Exhaust Gas Recirculation)

These three methods reduce the peak temperatures.

May lead to the formation of CO.

10 to 15 % reduction in NO can be achieved by these methods

And let us now look at the flame cooling and the thermal N O can be controlled by reducing the temperature of the gas which is being produced. How to achieve the temperature reduction is the question. So, this can be by reducing the preheating of air which is entering into the combustion chamber.

The let us look at like a combustion chamber in which the air is coming. This is your air and it can be generally being preheated to reduce the CO emission level and also the enhance the combustion efficiency; however, you can reduce this preheating air temperature. And the another way is the water or the steam being injected out, in this in the combustor you will have to injecting water or the steam such that that water will be evaporated and then that heat will be taken from the combustion products such that the temperature below a down and steam also will be reacting with the CO and will be converting into the basically carbon dioxide.

As a result you can reduce both the CO and the also the N O x emission level. There is another way is a EGR, the Exhaust Gas Recirculation which is the product maybe containing the CO and other unburnt hydrocarbons and which can be recirculated such that when it will be recirculated mixed with air and getting into again burnt and such that the CO will be converted into carbon dioxide. Unburnt hydrocarbon can be converted into carbon dioxide. As a result the combustion efficiency will be increasing and CO U H C will be reducing and N O x is also getting reduce.

Because of when you are adding that lot of some nitrogen gases will be passing through that and it will be lowering the temperature because temperature is being lowered here. And this is a very effective method of reducing the N O x emission, enhancing the combustion efficiency while reducing the CO and U H C. Therefore, it is being used profusely in practical combustion systems and these three methods reduce basically the peak temperature of the combustion products and as a result the N O x being one.

And of course, some of this method may lead to the higher emission level of CO, one has to look at and people have found that 10 to 15 percent reduction in N O can be achieved by these methods. So, therefore, these are being use in particularly the exhaust gas recirculation method is used in practical application.

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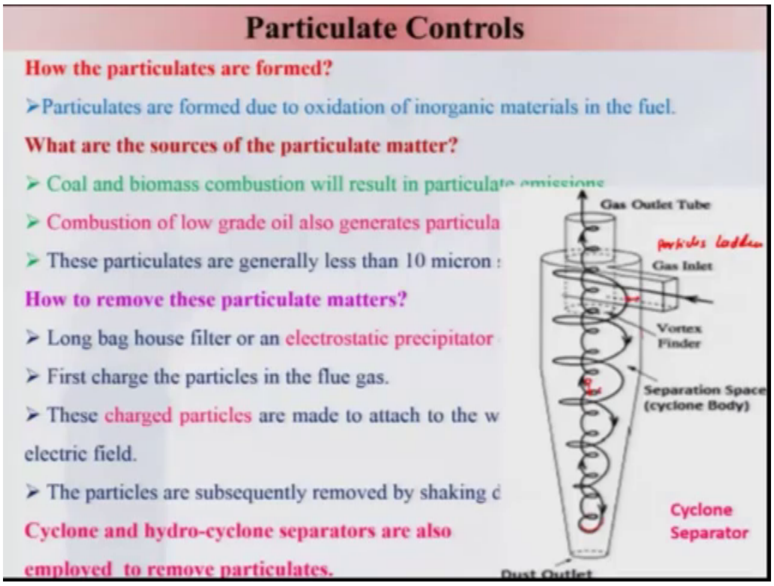

Particulate Controls

How the particulates are formed?

- Particulates are formed due to oxidation of inorganic materials in the fuel.

What are the sources of the particulate matter?

- Coal and biomass combustion will result in particulate emissions
- Combustion of low grade oil also generates particula
- These particulates are generally less than 10 micron

How to remove these particulate matters?

- Long bag house filter or an electrostatic precipitator
- First charge the particles in the flue gas.
- These charged particles are made to attach to the w electric field.
- The particles are subsequently removed by shaking

Cyclone and hydro-cyclone separators are also employed to remove particulates.

So, now let us look at how the particulates are formed in the combustion system. And particulates are basically formed due to oxidation of inorganic material in the fuels beside there is a soot are being formed in the hydrocarbon fuels and also the coal due to the fuel rich condition as we had discussed earlier.

And what are the sources of particulate matter? Basically coal, biomass combustion, result in particulate emissions like ash and the other material in organic materials convert into oxides. And of course, even in gaseous fuel and liquid fuel you can get also the shoot particulates which has to be avoided and combustion of low grade oil also generates particulate matters. And these particulars are generally less than 10 micron size, it can be having certain range and this has to be also removed. But question is how to remove, this particulate in matters long bag house filters and electrostatic precipitator can be use or are being use rather to remove them in particular in power plants.

And in case of electrostatic precipitor the first the charge the particles in the flue gas being undertaken and then these charged particles are made to attached to the wall by passing to strong electric fields. And once it is this particulars are being attach these are subsequently removed by shaking devices such that it can be collected and then one can throw remove that. And where, beside the cyclone and hydrocyclone separators are also being used to remove the particulates. Let us look at a typical cyclone separators here in this gas with the particle or gas.

The particle laden gas are being introduced here in this which is having a tangential component and this moves around with a certain vertical force such that the centrifugal force will be putting and then particle will be moving towards that in the will stick to the to this wall, because of this vertex which is being formed. Beside this once, it will go then it will be coming over here and then again moves with a again smaller vertex and it will pass into that. During the smaller vertex the gravitational force which will be acting here and the particle also will be settled down.

There are 2 ways it can be separated, one is that it will go and stick to the wall of the surface which is basically due to the higher centrifugal force in the vertex and other one is due to gravity. And a once this particle being there, then you can really remove this particulate and the gas which is the particle free gases it can goes out. Their efficiency of this cyclone separator is basically around something 95 to 98 percentage, which is quite good and when the liquid is being use that weight or the hydrocyclone separator is being used.

So, these are the ways by which we can really control the emission from the combustion system. There are several methods which you can also learn and with this I am coming to the end of this courses and I have done lot of things in a brief manner just to expose you such that you can learn it better. And with this I will stop over you might have enjoyed this course and for other things you can go for advanced books and advanced studies such that, you can really develop a good knowledge about the combustion systems. And once you learn the fundamental of combustion well, you can really design and develop the combustion system with the least amount of emission such that we can utilise the energy in efficient manner. And I hope and use that you people will be encourage to learn the subject well and also use in your professional life.

Thank you very much.