Environmental Air Pollution

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Lecture No. 12

Internal Combustion Engine and Air Pollution – 2

We will still stay with engines. You all must have heard about knocking and anti-knocking in engines. You also know from general knowledge that earlier, we used to get leaded gasoline and now you get unleaded gasoline or green gasoline. If you go to the petrol pump, you see unleaded gasoline. We are using leaded gasoline for several years. Why did we use leaded gasoline and what are we doing now? We need to understand. It was not the combustion people, not the mechanical engineers or automobile engineers who were in favor of making it unleaded but it was a great revolution by the environmental people... environmental science and environmental toxicology who fought for this and that is how the technology got changed.

The issue of lead was so severe that as we see today, all the countries…. It costs a lot of money. When you are changing your refining process, you are moving from leaded gasoline to unleaded gasoline, it costs a lot of money. You will be surprised to know that all the countries, even very poor countries, have now gone for unleaded gasoline because lead was a serious problem. Maybe when we talk about health effects and air pollution, then I will tell you why lead was such a serious thing. But first of all, let us understand what is knocking. Let us see what the next slide is. Let us start with this.

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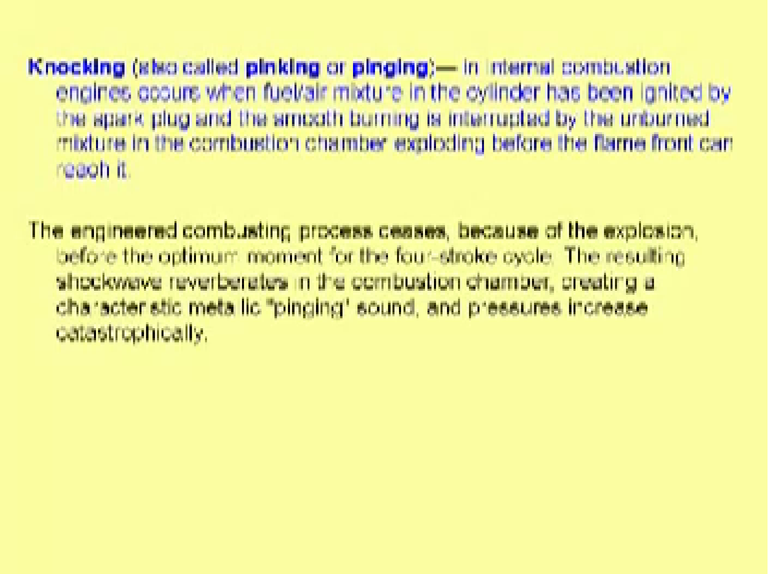

Knocking (also called **pinking** or **pinging**)— in internal combustion engines occurs when fuel/air mixture in the cylinder has been ignited by the spark plug and the smooth burning is interrupted by the unburned mixture in the combustion chamber exploding before the flame front can reach it.

The engineered combusting process ceases, because of the explosion, before the optimum moment for the four-stroke cycle. The resulting shockwave reverberates in the combustion chamber, creating a characteristic metallic "pinging" sound, and pressures increase catastrophically.

We go by the definition and then I will explain to you the figure as to what is happening. If you look at the knocking and try to understand what the knocking business is, in the internal combustion engine, knocking occurs when fuel air mixture in the cylinder has been ignited by the spark plug and this smooth burning is interrupted. You want the burning to proceed. You can imagine that this is my cylinder and the top, there is a little spark ignition engine. It is like this and the flame will propagate. You talk about seconds and milliseconds. It should expand smoothly and it should keep on burning and push the piston down there. That is fine.

Suppose it is interrupted somehow because of some reason – this smooth burning is interrupted by the unburned mixture that is lying on the back (that is still lying on the back – unburned combustion). This mixture is in the combustion chamber only explodes before the flame can reach there. I am trying to reach there with the flame and that has exploded. What will happen?

I am trying to compress something on this side. That has already started explosion and that can compress backwards. Then what happens? A knock. That is what happens in the engine. This process is called knocking. Then, what is happening is this smooth burning is interrupted by the unburned mixture in the combustion chamber exploding before the flame front can reach there. In other words, the engineered combustion process (that you had engineered for the model to work) ceases because of the explosion because you wanted it to go smoothly but we failed because of the explosion before the optimum moment for the four-stroke cycle. The resulting shockwave reverberates back and forth in the combustion chamber, creating a characteristic metallic pinging sound and the pressure increases enormously. Then as a result, your engine knocks, it does not perform and you can even hear the sound – that is what is happening. I want to explain why this happens and how it happens.

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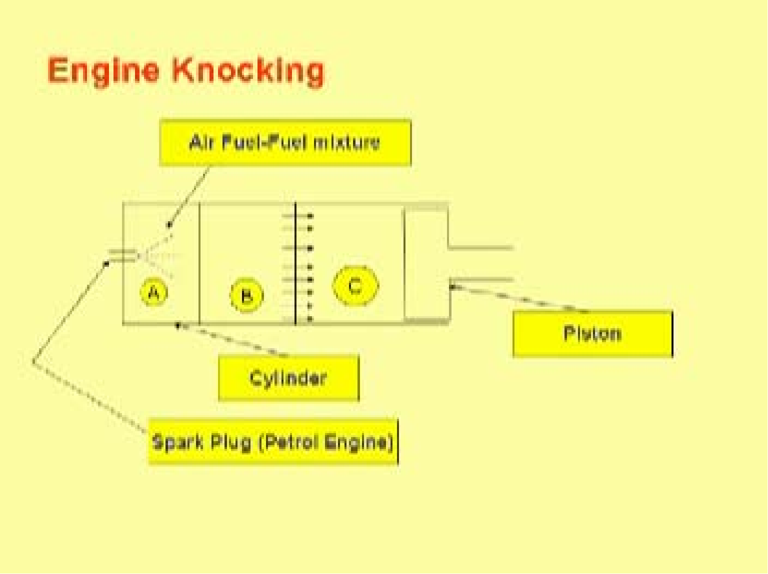

Hypothetically, let us say this is your cylinder and I can divide this into three parts. There is no barrier as such but just imagine there are. Here is the spark plug. The fuel has started burning in this because you put it in this. Then as a result, this is expanding. B is under compression and so is C – under compression. As this photo flame or the flame comes [05:23], B also gets some burn. This is already burned, this also gets burned – it is burning and by that time, the pressure in C becomes enormous because first, this portion burns and this and then by the time…. By that time, the flame reaches C and because of the high pressure, the temperature that goes, this auto-ignites. This was the compression. This also explodes. It pushes this explosion backwards and as a result, you have the knocking in the engine and you do not get proper power. The idea is simple that somehow you should modify your gasoline in such a way that the time for the auto ignition is delayed. If that ignition time is delayed, then by that time, the flame front will reach here and then everything will be all right and you will get the smooth burning. That was the issue.

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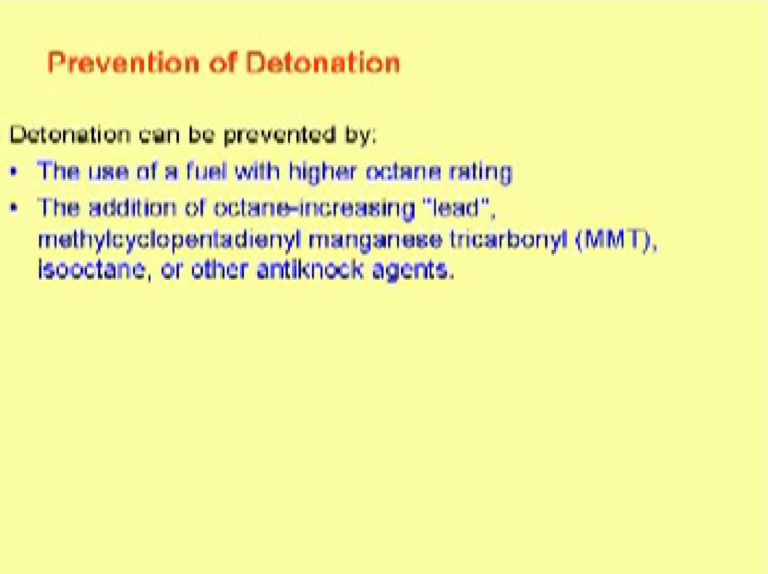

Prevention of Detonation

Detonation can be prevented by:

- The use of a fuel with higher octane rating
- The addition of octane-increasing "lead", methylcyclopentadienyl manganese tricarbonyl (MMT), isooctane, or other antiknock agents.

What and how they could do was…. Detonation can be prevented by the use of a fuel with higher octane rate. I will explain to you what octane rating is. When you go for premium fuel or the octane number is this, you may have some vehicles that will run only with gasoline with octane number so and so because higher the octane number, better will be the performance of the engine – there will be no knocking.

In addition, the addition of octane-increasing lead. The other things that you can use are MMT (in short form) – that is also an anti-knocking agent but lead is one thing that has been found. Lead in the form that I will show you has been found to make this explosion delayed. There is a delay is there and the flame is able to reach. Once it reaches, everything is fine. What does this lead…? We will not get into so much of mechanics here.… Let us define the octane number first because I have used this word.

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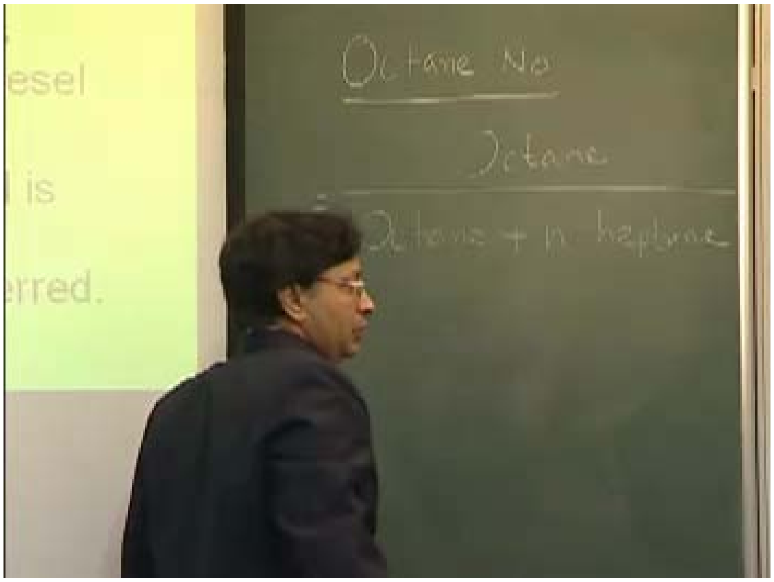

Octane number is ratio of…. This is the ratio of octane you have in your gasoline and the octane plus n-heptane. That is this ratio. This is called octane number. This is the ratio. Does it say so?

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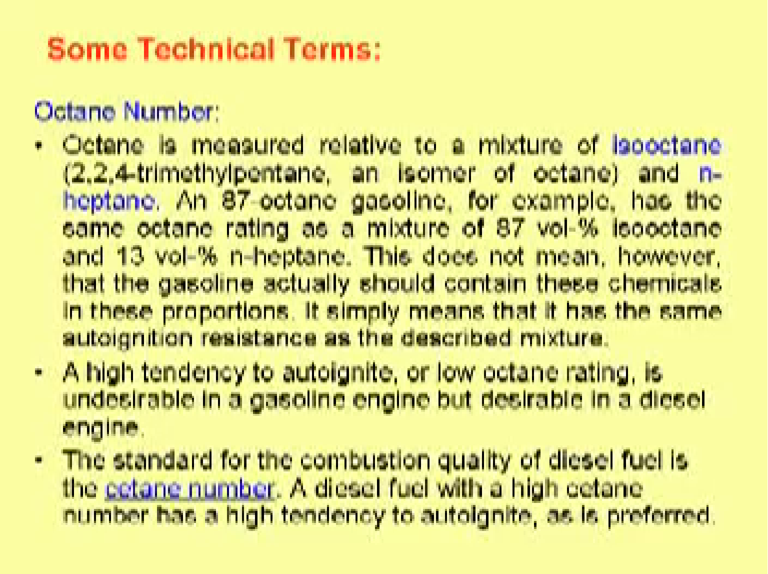

Some Technical Terms:

Octane Number:

- Octane is measured relative to a mixture of isooctane (2,2,4-trimethylpentane, an isomer of octane) and n-heptane. An 87-octane gasoline, for example, has the same octane rating as a mixture of 87 vol-% isooctane and 13 vol-% n-heptane. This does not mean, however, that the gasoline actually should contain these chemicals in these proportions. It simply means that it has the same autoignition resistance as the described mixture.
- A high tendency to autoignite, or low octane rating, is undesirable in a gasoline engine but desirable in a diesel engine.
- The standard for the combustion quality of diesel fuel is the cetane number. A diesel fuel with a high cetane number has a high tendency to autoignite, as is preferred.

Octane is measured relative to a mixture of isooctane (change that to isooctane) and n-heptane. Listen carefully. An 87-octane gasoline, for example, has the same octane rating as a mixture of 87volume percent isooctane and 13 volume percent n-heptane. The interesting thing is that it may not have any octane, it may not have [09:09], gasoline may not even have heptanes. It is the characteristic of your fuel that matches with what kind of behavior that is there. If that is your engine in terms of the knocking and your knocking thing is behaving something similar to the performance because it is a standard performance to see the knocking [09:32] knocking.

If it is comparing something that is similar to this 87 percent, then this fuel may have the… or will be said to have an octane number of 87 and yet, it may not have any octane or heptane for that matter. Is that clear? This does not mean however that the gasoline actually should contain these chemicals in these proportions. It is the characteristic of the fuel which is equivalent to having a fuel that has octane and n-hectane in the order of 87 and 13 percent volume by volume. This is the characteristic.

Sometimes, the octane number can be [10:24] fuel reported higher than 100 also. It is the behavior of this. You have only octane which is like… you will not find any kind of knocking that is…. You have no n-heptane, then octane number is 100 and then everything is all right. When we are enhancing the octane number of the gasoline, then we are not playing with this, this and this. You are putting something else and yet we can say octane number has changed – it appears as if we are changing this but we are not changing this.

A high tendency to auto-ignite or low octane rating is undesirable in the gasoline engine but desirable in the diesel engine. Why? It is because in a diesel engine, we want self-ignition to take place. That number is defined in the diesel engine by the cetane number. We will not get into the detail because we are talking more of air pollution. The standard for the combustion quality of diesel fuel is the cetane number, which is close to around 50.

A diesel fuel with a high cetane number (in diesel, we have cetane number) has a high tendency to auto-ignite as is preferred in the diesel engine. We want it to auto-ignite. You see the difference between octane number and the …. We have given you the meaning. We have given you the definition of octane number and the real sense of octane number also. This is what is the compound of lead that is used or that was used as anti-knocking agent. It is it is mostly by the experiments and science that people developed. It improved the anti-knocking capability of the gasoline.

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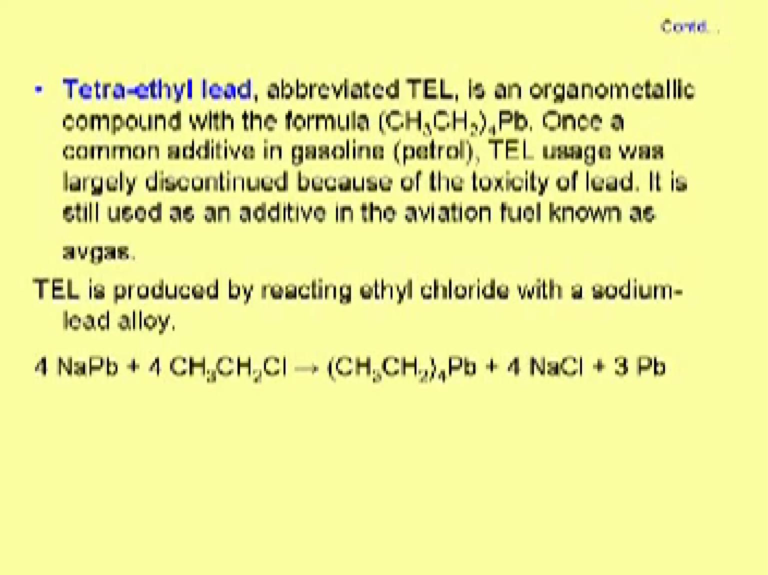

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- **Tetra-ethyl lead**, abbreviated TEL, is an organometallic compound with the formula $(CH_3CH_2)_4Pb$. Once a common additive in gasoline (petrol), TEL usage was largely discontinued because of the toxicity of lead. It is still used as an additive in the aviation fuel known as avgas.

TEL is produced by reacting ethyl chloride with a sodium-lead alloy.

$4\ NaPb + 4\ CH_3CH_2Cl \rightarrow (CH_3CH_2)_4Pb + 4\ NaCl + 3\ Pb$

Tetra-ethyl lead abbreviated as TEL is an organometallic compound with the formula $(CH_3CH_2CH)_4Pb$. It looks like this.

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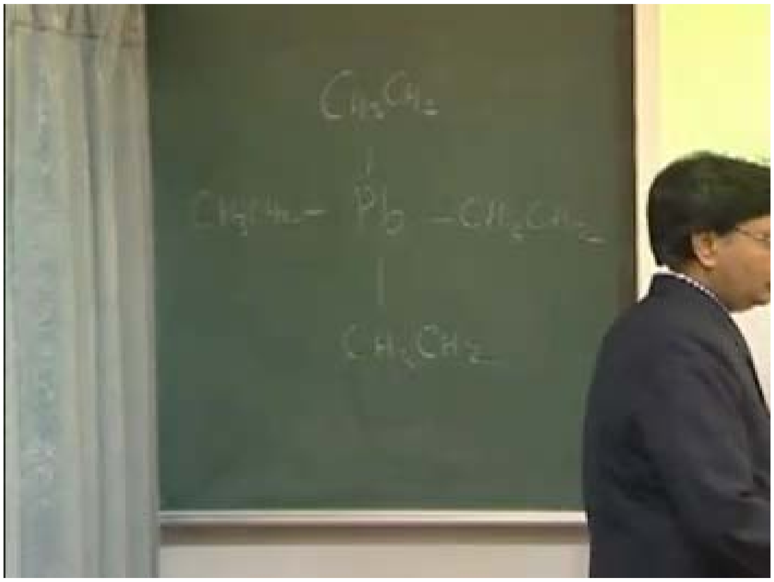

That was the compound that was used. People had done many experiments. How is this produced? TEL usage was largely discontinued because of the toxicity of lead but it is still used as an additive in the aviation fuel known as avgas. I do not know if this is still true. In my opinion, they should stop this but this is all from the literature.

How is it formed? You do not have to know and remember this but this is just to get an idea of how this is formed. You are using ethyl chloride. The chloride reacts with the sodium-lead alloy. You make it react with the alloy under certain conditions and you will get [13:32]. Then of course, some lead is carried back. Things are balanced, I guess. Yes, they are. You produce this and then you mix this. Remember that now we are putting the lead and the lead will not destroy itself.

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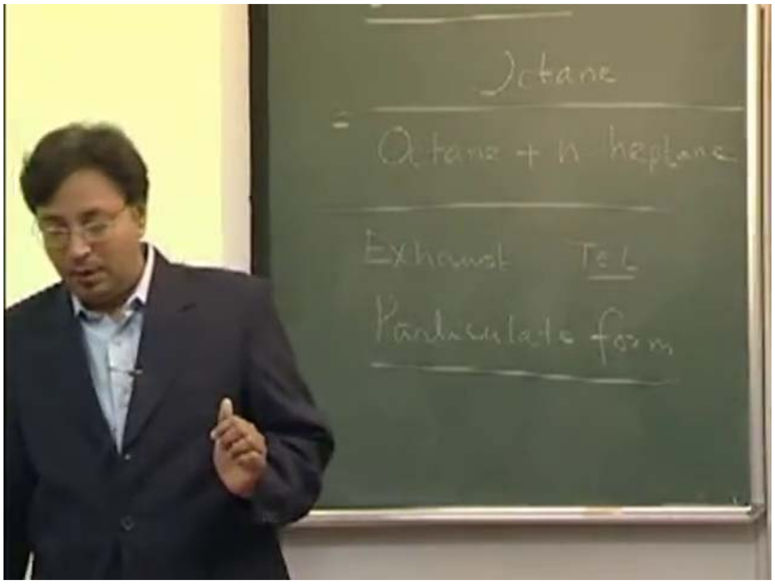

In the exhaust, you will get the TEL (tetra-ethyl lead). Most of it, 90 percent of it is in the particulate form in the exhaust when it comes out. The problem of lead and lead toxicity is…. For the time being, just remember my words – it is very severe. It is a very horrible compound or element. We may have a lot of utility. In the body, we all need some kind of metals in the body including mercury. We need many that you can think of but lead is one metal that the body has no use for. Otherwise, molybdenum. We also need some nickel in the body but people have found that lead has no use. So lead was a serious problem here and then it will come in the particulate form. The other problem that I think we will need to write and specify is…. We will see a little later….

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If you recall or if you know at least from general knowledge, [15:28] in the exhaust, you have CO, hydrocarbon and NO_x. One of the ways to control is to catalytically oxidize this. All the automobiles now have a catalytic converter, especially the gasoline ones. The problem with the catalyst that we were using was that (I will show you in a picture in a moment) lead was a poisoning agent for the catalytic converter.

The life of the catalytic converter will reduce if you are using lead in the gasoline because this will interfere with the catalytic property. As a result, lead was a problem from the health point of view as well as the performance of the catalytic converter, which would go down. People thought that lead must be removed very quickly from the system. Lead was removed historically but we should know why and how it happened.

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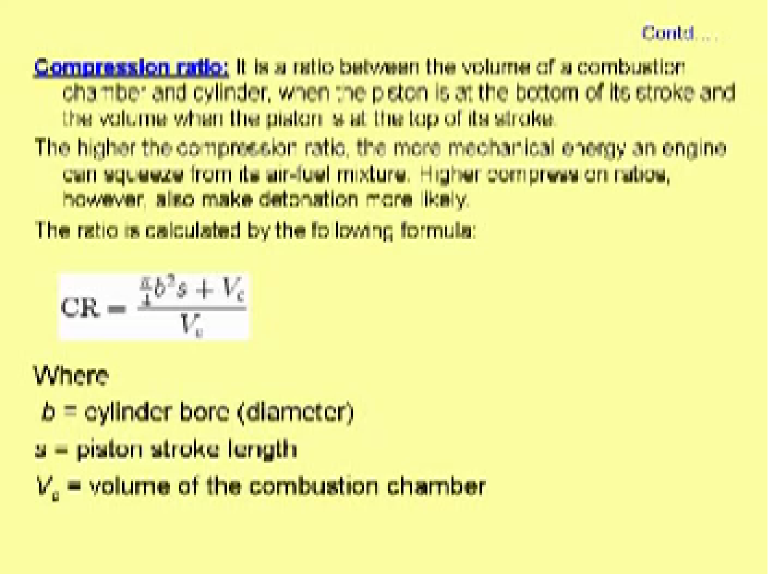

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Compression ratio: It is a ratio between the volume of a combustion chamber and cylinder, when the piston is at the bottom of its stroke and the volume when the piston is at the top of its stroke.

The higher the compression ratio, the more mechanical energy an engine can squeeze from its air-fuel mixture. Higher compression ratios, however, also make detonation more likely.

The ratio is calculated by the following formula:

$$\mathrm{CR} = \frac{\frac{\pi}{4}b^2 s + V_c}{V_c}$$

Where

b = cylinder bore (diameter)

s = piston stroke length

V_c = volume of the combustion chamber

Let us go to something else. We are not discussing a great deal about this but still you should have some idea about the compression ratio. The compression ratio is…. The cylinder bore diameter, the piston stroke length. This is the volume which is when the piston is at the bottom. The chamber…. This is the ratio between the volume of a combustion chamber and the cylinder when the piston is at the bottom of its stroke and the volume when the piston is at the top of its stroke. What you can say if I draw a picture? Will you agree with me? If you do not agree, then ask me the question.

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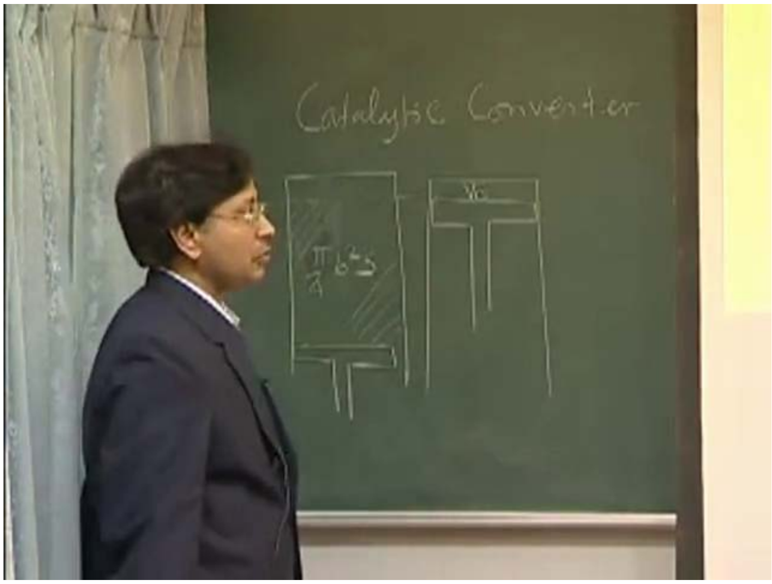

Top position. This is your V_C. This volume will be the diameter times…. Suppose the diameter is being called as b square, this volume will be pi by 4 into b square (diameter is being called as bore diameter) into s (its length) and then you can see what the ratio is.

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Now as I was telling you yesterday, there are other issues with the diesel engine. We are still staying with the diesel engine. With diesel engine, the problem was the No_x that we have described in great detail. We will also talk a little bit about No_x in a moment. But apart from No_x in the diesel engine…. You have No_x plus DPM – diesel particulate matter. That is a very serious problem and that is formed in the diesel engine. Largely expected reaction is…. One of the mechanisms that people have talked about is this, because at some point, even CO can be formed. CO is formed in the diesel engine although it is quickly converted to carbon dioxide and [19:53]. I do not know if this will balance this. Does it? Yes.

This becomes soot. You are not finding the carbon monoxide at the end because this is burned out but CO is formed in the initial stage and that can lead to soot. People try to stop the formation of this CO but that can sometime instantly [20:24] this kind of soot. This is one of the routes. There are other routes people have talked about, but you can see here that the oxidation of carbon monoxide can result in soot or elementary carbon.

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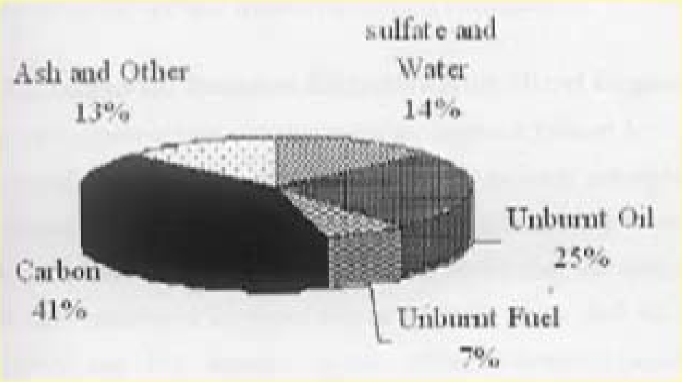

Fig: Typical composition of particulate matter from diesel engine

But apart from that, the general composition of the particles that you see in diesel looks like this: carbon – 41 percent, there will be some ash and other things. Some ash will still be there in the diesel that cannot be burned – very small amount. There will be some metallic components because all the time, metal is hitting with metal and so, there will be a lot of emissions of the metal. Diesel will have some metals and those will come out.

The lubricating oil we will have some metals. The piston and the piston valves have metals and so that will come out. Then, some amount of the unburned fuel oil comes out. Unburned oil is the lubricating oil that will come out. Some of the unburned fuel can come out. Then, you also see a significant amount of water. More than water is the sulfate. In this process, people have found that sulfur there in the diesel that sulfur is somehow….

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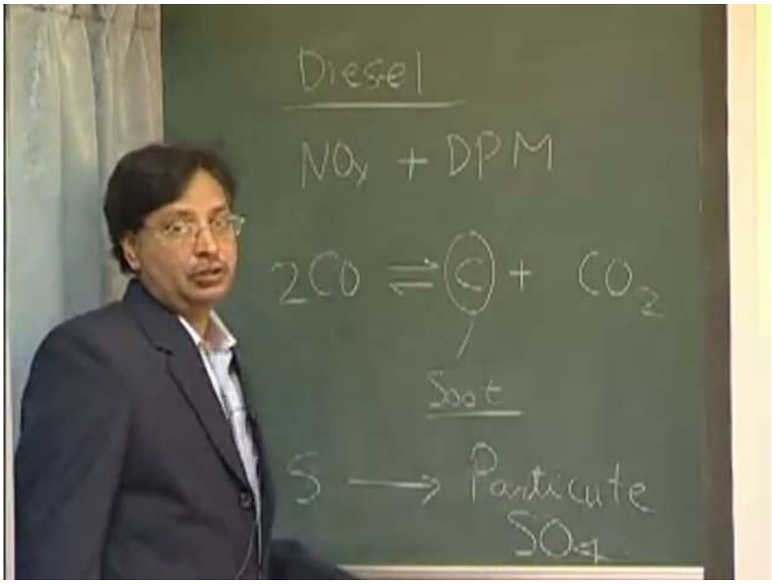

Not the entire but significant amount… particulate sulfate. With my experience, I can tell you that sulfur dioxide has not been the main problem in the country, but still, sulfur has been reduced a great extent in the diesel. To start with, we had something like 1 percent in 1999 and 2000. The sulfur content was about 1 percent in the diesel. SO_2 was not a problem in the ambient air but then, the combustion people could show and they all knew from before and from literature that there a lot of sulfur goes into formation of sulfate. In order to control the particulate emission from diesel, the sulfur was reduced, not because SO_2 was a problem in that [22:46].

People talk about ultra-pure diesel. Right now, in the country, we have something like 0.25 percent sulfur in the diesel. I think in Delhi they have even gone below this thing and finally, they are talking about the sulfur content in diesel of the order about 500 ppm.

How much percentage will 500 ppm be? 0.05, 0.5, is that right? 0.05 percent, yes, correct. We have talked about 1 percent to so much reduction, huge reduction largely because we want to reduce the formation of formation of sulfate particulates not because SO_2 is a problem or SO_2 we are finding as of now is a problem.

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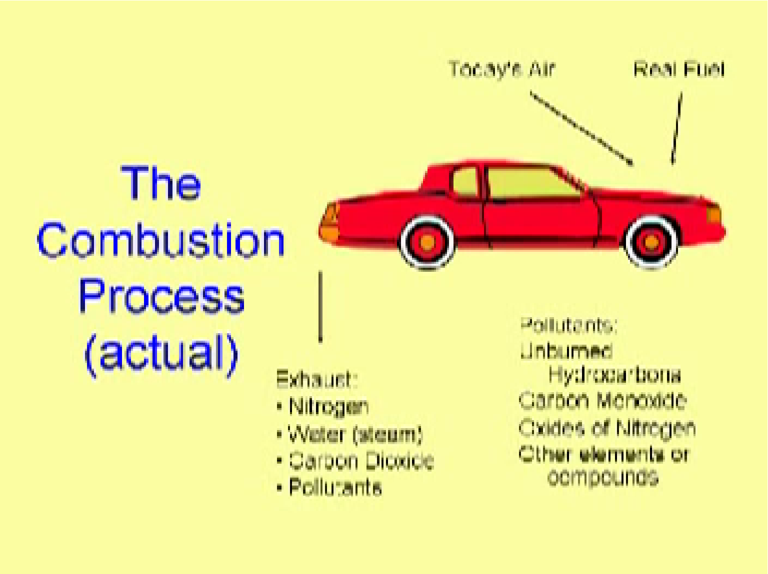

The Combustion Process (actual)

Exhaust:
- Nitrogen
- Water (steam)
- Carbon Dioxide
- Pollutants

Pollutants:
Unburned Hydrocarbons
Carbon Monoxide
Oxides of Nitrogen
Other elements or compounds

We had seen a little bit of this yesterday but let us have quick look at this. In the exhaust, you get the nitrogen, water, carbon dioxide and pollutants. The pollutants you get are unburned hydrocarbons, carbon monoxide, oxides of nitrogen and other elements or compounds. That is what actually happens and then of course you are mixing the things here.

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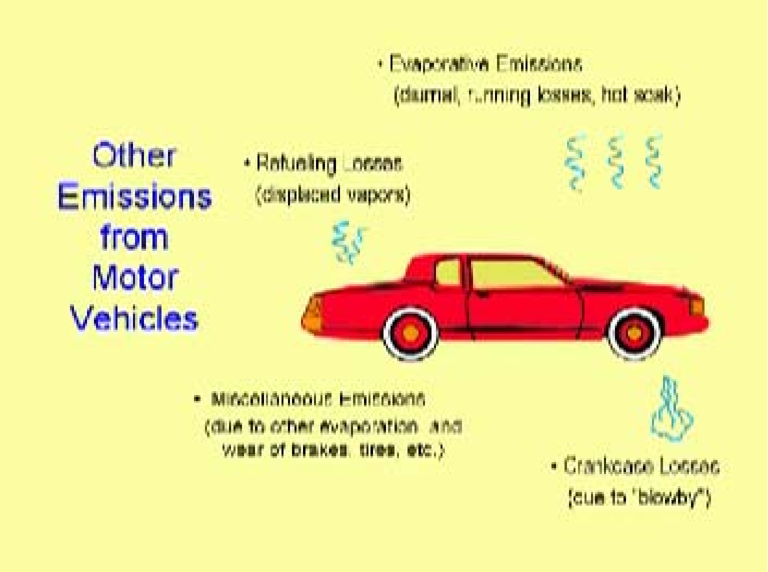

Other Emissions from Motor Vehicles

- Evaporative Emissions (diurnal, running losses, hot soak)
- Refueling Losses (displaced vapors)
- Miscellaneous Emissions (due to other evaporation, and wear of brakes, tires, etc.)
- Crankcase Losses (due to "blowby")

We talked yesterday that evaporative losses are there from the engine. We had discussed last time about blow-by emissions and emissions due to other evaporation. Now, when it comes to research, people are talking about emissions from the… Wear of the brake. The problem is that many times, you can see the brake lining also. They do not have the cover and you can see the brake lining. When the brakes are applied, this lining gets worn and it will be worn out. There is a lot of metals that comes out. Apart from that, the brake lining is always largely made of asbestos. The asbestos particles also come out and that emission will take place the brake lining. The other thing that is non-combustion related but related to automobiles is the tire wear. We will not go so much into the details of this.

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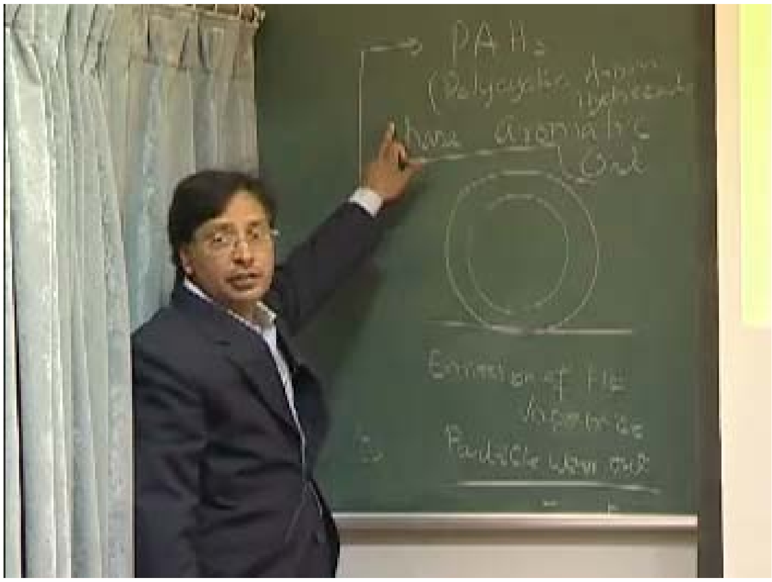

You have the tire and the road surface. One thing is the emission of hydrocarbons, which vaporize because of the temperature. The other thing is just because of the friction, abrasion, there will be particle wear out. Particle wear out is also a very common thing. Especially when they are braking, these emissions become very large. We are really talking about significant emissions here. In addition, all tires have aromatic oil – all will have these. Because of the friction, aromatic oils will give rise to the emissions of what we call as aromatic hydrocarbons. This becomes another serious problem – all cancer-causing compounds.

In fact, our technology for the engine has gone so much that we are reducing huge amount of PAHs. Once you have reduced PAHs, people still did not find reductions in the PAHs around the roadside. They found that this was largely the wear and tear of the tire that was giving rise to the PAHs. One of students is working on this as to how to estimate the PAHs emissions that can come out from this. Do not forget: PAHs emissions and hydrocarbon emissions can also occur not only because of what is in the tire but from the bitumen itself. Bitumen is again organic stuff and the wearing out of the bitumen can also give rise to emissions, which people were not considering earlier, but now, people are becoming serious about it. So, there could be emission from bitumen also.

Apart from that, we should not forget the metals that may be part of the tire (some metals are always there) or on the bitumen or if it is not bitumen, it is a cement road and maybe the cement has some and people are not using fly ash. It is a matter of investigation. I am not saying that from the fly ash, metals will come out so easily but then…. One of the students here who is doing Masters is looking at the metal emission from the non-exhaust emissions but related to vehicles and the roads. These are little things I thought I will mention because of the tire. We talked about blowby emissions.

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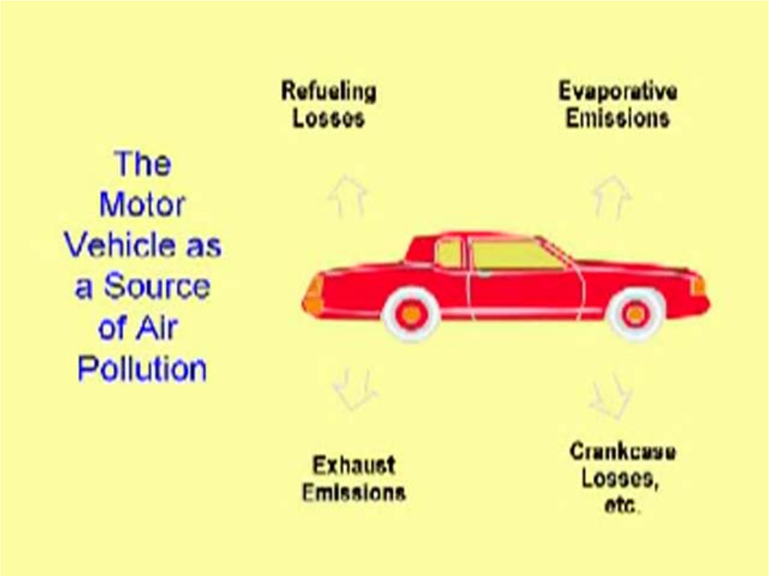

This is largely… this is the burning and the losses: crankcase losses, exhaust emissions, evaporative emissions and refueling losses.

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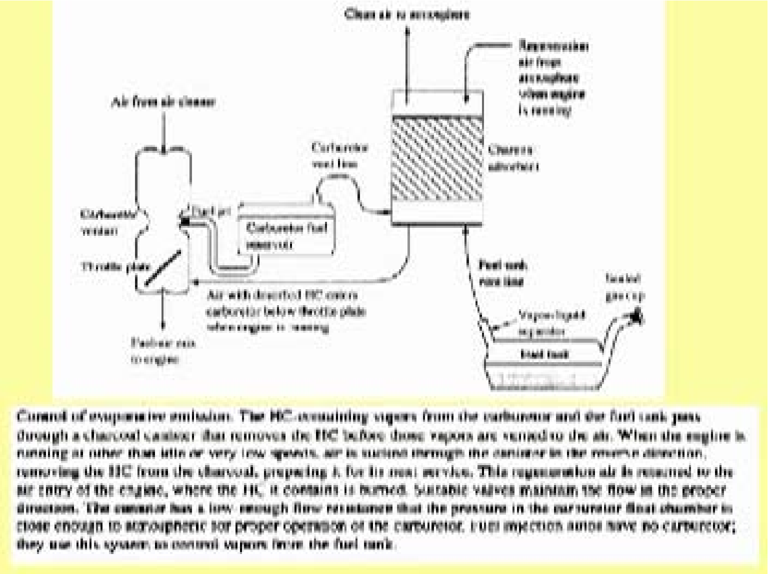

Control of evaporative emission. The HC-containing vapors from the carburetor and the fuel tank pass through a charcoal canister that removes the HC before those vapors are vented to the air. When the engine is running at other than idle or very low speeds, air is sucked through the canister in the reverse direction, removing the HC from the charcoal, preparing it for its next service. This regeneration air is returned to the air entry of the engine, where the HC it contains is burned. Suitable valves maintain the flow in the proper direction. The canister has a low enough flow resistance that the pressure in the carburetor float chamber is close enough to atmospheric for proper operation of the carburetor. Fuel injection autos have no carburetor; they use this system to control vapors from the fuel tank.

I want to talk about evaporative losses. That is what we were trying to discuss last time – about the hydrocarbon emissions from the fuel tank. As you are filling, there will always be vapor pressure; it has to be there. The fuel tank [29:37]. This is not the fuel supply. It is taken… depending on the pressure. There is a little pump that will suck the fumes and there is a charcoal adsorbent that will adsorb the fuel in here. But then, you can also have vaporization in the carburetor reservoir – you see emission there also. That can also be sent to this adsorbent. As the vehicle is moving, what you do is reverse the direction of the flow and then you try to regenerate. From the air, you can drive out these emissions and then put them back in the engine.

Air with dissolved hydrocarbon enters the carburetor [30.35] when the engine is running so that this can be utilized. Otherwise, these are the emissions, which could be out of 15 percent or something. All cars and all engines will have this facility. I also [30:49] from the book what is written here. Control of evaporative emission: the hydrocarbon-continuing vapors from the carburetor and the fuel tank passes through the charcoal canister (your car has a canister now) and removes the hydrocarbon before those vapors are vented to the air. When engine is running at other than ideal or very low speeds, air is sucked through the canister in the reverse direction, removing the hydrocarbon from the charcoal, preparing it for its next service.

This regenerated air is returned to the air entry in the engine where the hydrocarbon it contains is burnt. Suitable valves maintain the flow in the proper direction. The canister has low enough flow resistance that the pressure in the carburetor float chamber is close enough to atmosphere for the proper operation of the carburetor. Fuel injection autos have no carburetor; they use this system to control vapor from the fuel tank. Fuel injection automobiles have no carburetor. They use this system to control the vapor from the fuel tank. We use the same thing if your fuel injection system has no carburetor.

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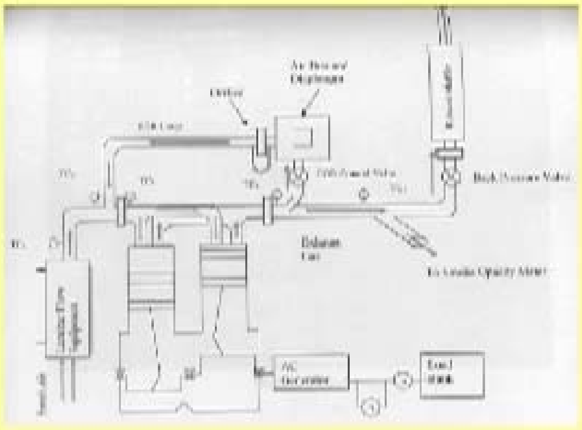

Fig. Schematic diagram of engine set-up using EGR

Now we are talking about the NO_x. We have talked a great deal about the NO_x emission, but there are a few ways in which you control NO_x. One of the methods that has been talked about and some extent used also is exhaust gas recirculation. I will try to show you in this picture. See here the dark arrows, this is exhaust and then, you have something to measure here. A part of the exhaust is taken back and rest is.… You can check if it is smoke and then you can pass it to the smoke meter to see what is the smoke density, to see the particulate emission and the rest of it goes to the exhaust muffler.

Part of it and the diaphragm here and there is an orifice plate. You can manipulate as to how much of the exhaust gas you wants to recirculate. Part of this is recirculated and then it comes here and this is your regular supply of the fuel laminar flow equipment, you have the regular supply here and this is mixed here and now, part of EGR, part of exhaust gas that is recirculated is put into this and people have found that NO_x reduction is there because one thing is the oxygen content is reduced and the second thing is that this gas can absorb some of the temperature because this is not going to burn. This is there to absorb the heat.

Once heat is absorbed… you still get power. There is some reduction in power, yes, but NO_x control takes place because of both: drop in the temperature and you are reducing the availability of the oxygen in the process. But then, the problem here is suppose you do not remove the particles here…. There is a DPM – diesel particulate matter. They can also be recirculated here and then, these particles cause a lot of problem in wear and tear of the engine because these particles will be between the two metallic surfaces and will be surrounding this one. As a result, the wear and tear of the engine is a little bit more, but then people also found because of this, the emission of the particulates increases and as a result, people have to always make a trade–off: want to control NO_x or particulate pollution goes up.

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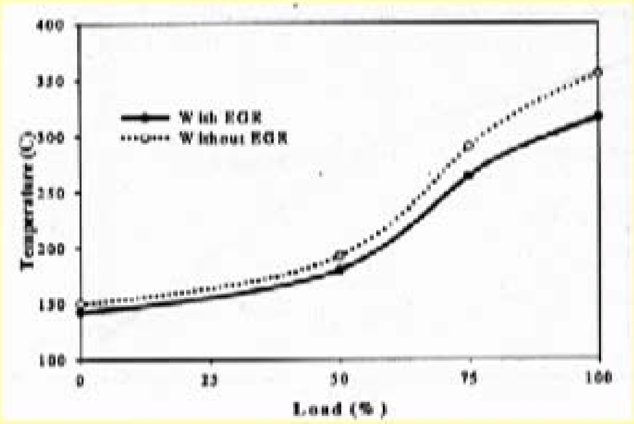

Fig. Exhaust gas temperature with and without EGR

See here. This is what people found. This is the temperature and load. What you see is the reduction in the temperature. Without EGR, temperature was high and this is that of the exhaust. With EGR, temperature is lower even at different loads of the engine. This shows that of course NO_x emission is reduced, NO_x emission is indeed reduced.

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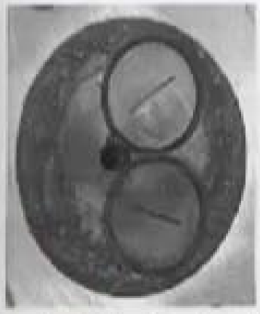

Figure Carbon Deposits on the Cylinder Head of the Engine Using EGR

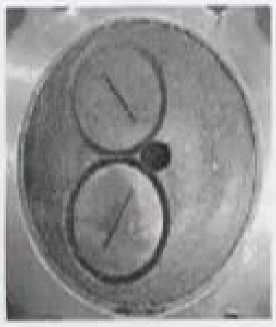

Figure Carbon Deposits on the Cylinder Head of Engine Without EGR

But what the people have found is that with this technique, the soot density increases. Obviously, you are recycling the soot also in the process. So, soot density increases and that causes some problem the wear and tear of the engine and people have also found that….

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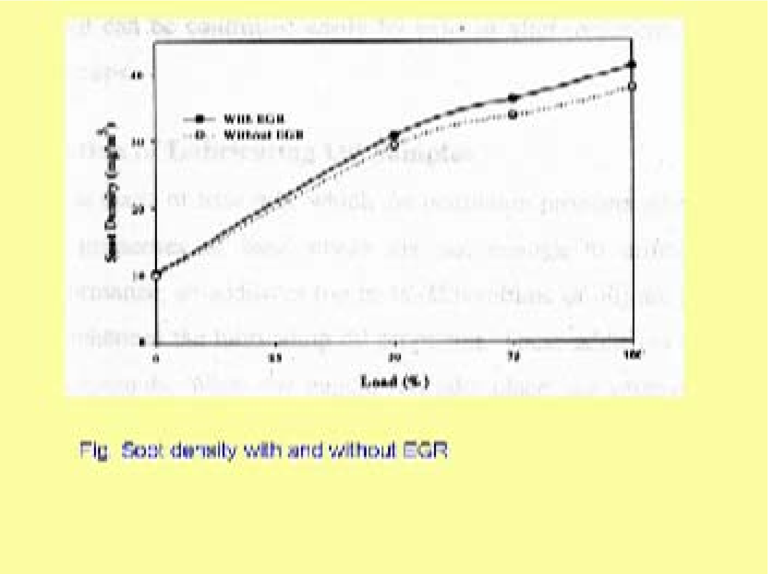

Fig. Soot density with and without EGR

You see here the depositions, carbon deposits on the cylinder head of the engine using EGR and this is the same kind of engine without using EGR. You can see the deposition here are much more as compared to the deposition here. That is again a trade–off between this but whatever ways you can find out to reduce the temperature, that will reduce your NO_x emission. One of the ways is… maybe I should explain that….

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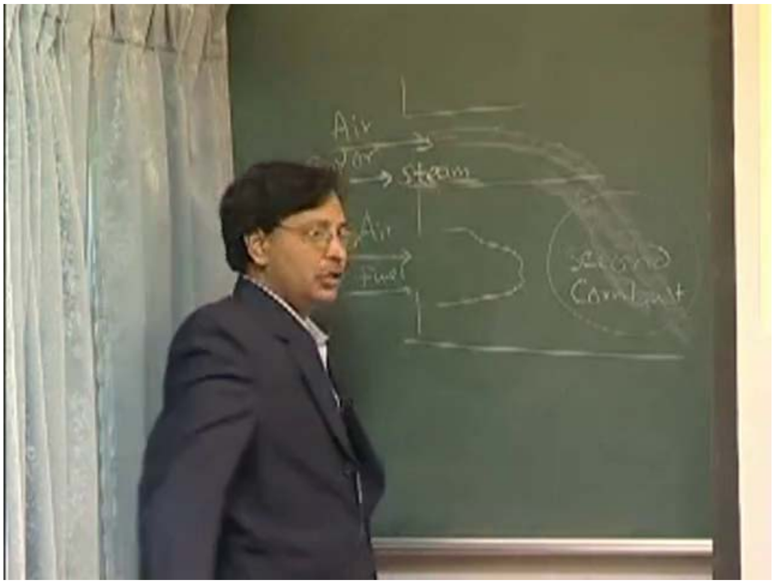

Here is air, here is fuel, this is going in the combustion chamber and then there will be a flame. Do not supply enough air here. Do not supply enough air but supply the deficit here so that you do not have oxygen to react with nitrogen and have this kind of waffle and then supply the secondary air from here which can feed this flame here and then this is a kind of second combustion if you can say, because the whole thing will not burn here and temperature will not be very high. As a result, what you get here is the low NO_x.

But in the process, your size of engine… I will not call it engine but this you can do in the boiler also. The size of the boiler increases. In the boiler, you can certainly do this. The boiler is slightly bigger but in the engine, it become difficult but there are other ways how to handle it. This is air and/or stream or water. Water jets are put. What will water do? It sounds funny – you have combustion and you are also supplying steam. What will the stream do or what will water do?

The specific heat of water is very… it can absorb lot of heat and yet the rise in the temperature is not so much. That is the specialty of water. So it can absorb the heat and as a result, the temperature rise will not be so much. We have some water anyway in the exhaust. If some more water goes in there, what is the problem? People do use this so that in that case, we can reduce the NO_x formation. We have some special kind of burners called low NO_x burners.

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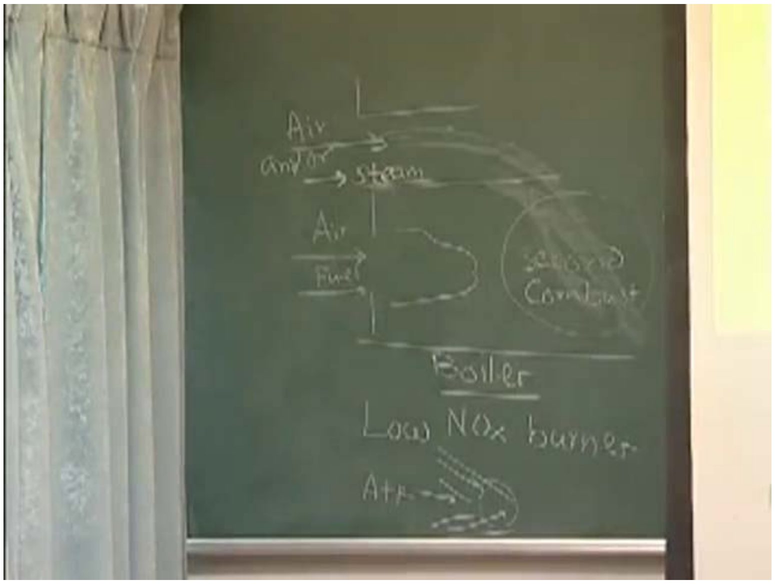

This is something you can do in the boiler. We also have the low NO_x burners. In that case, you have the air and fuel and, the other thing that provides a little bit more air from the other side and then here again, the temperature drops. You burn it. You should remember the amount of the heat is the same. Heat is not changed. It is only the temperature that we are playing with. The heat is always the same. You can almost do everything that you want to do but then, you are reducing simply the temperature because we have seen that higher temperature will favor the formation of NO or we can say it as NO_x.

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Tailpipe Control

- Air pump
  - Adds combustion air to tailpipe
- 2 Way Catalyst (CO/VOC Control)
  - Catalyst design and active metal content
- 3-Way Catalyst (CO/VOC/NO_x Control)
  - Catalyst design and active metal content
- Location of Catalyst near engine
  - Heats catalyst faster to provide emissions control sooner
- Pre capture pollutants during first few minutes of vehicle operation
  - Captures pollutants until catalyst is hot

Combustion to air to tailpipe. Now, we are talking about the catalyst, very briefly, two-way catalyst CO and volatile organic compound are the hydrocarbon vapors. That is called the two-way catalytic converter. Catalyst design and active metal content are there and many of the metals are used as catalysts. Three-way catalyst is the one that can not only handle CO and VOC and NO_x. In this, what you want to do is this will require oxidation to carbon dioxide and water and this will require reduction of NO_x back to N_2 and O_2.

We will see if the details are there. Catalyst design, active metal content. Location of catalyst near the engine (I will show you in the picture): heats catalyst faster to provide emission control sooner because all the reactions will happen quickly if high temperature is there. Precapture pollutants during the first few minutes of the vehicle operation: captures pollutants until catalysts is hot. Then, I can show you here how it works.

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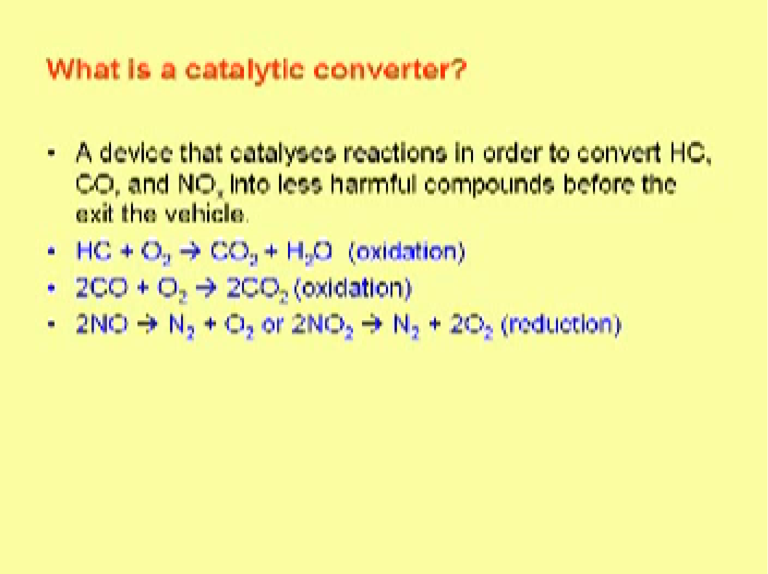

What is a catalytic converter?

- A device that catalyses reactions in order to convert HC, CO, and NO_x into less harmful compounds before the exit the vehicle.
- $HC + O_2 \rightarrow CO_2 + H_2O$ (oxidation)
- $2CO + O_2 \rightarrow 2CO_2$ (oxidation)
- $2NO \rightarrow N_2 + O_2$ or $2NO_2 \rightarrow N_2 + 2O_2$ (reduction)

Basically, you are supplying oxygen is there. [41:32] oxygen you are working on or oxygen can be supplied specially for the catalyst. [41:38] the engine but you can supply this one. CO_2 and water and CO and oxygen again oxidation and this NO is reduced to N_2O_2 or if there is NO_2, that can also reduce. When we are talking about control equipment in the course that comes in the later part of the course, you can see how the NO is reduced to N_2 and O_2.

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Fig. Catalytic converter

This is how it looks. You are lead from here and this is the structure you see and catalytic active metals which are the…?

[Conversation between student and professor - Not Audible (42:21 min)]

Alumina oxide and ceramics are there. We also use platinum. Platinum metal is very useful here. Of course, there are some patents on these.

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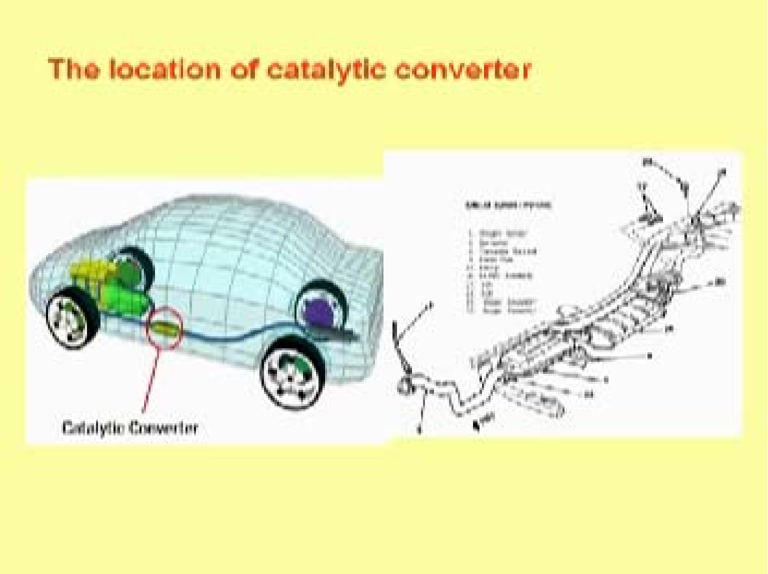

The location of catalytic converter

This is the catalytic converter. This depends on different engines where they like to put in the car. That more or less gives a description of the engine. I want to do something that we should have maybe done in the atmospheric chemistry part. This is something not in books but let us have a look at this.

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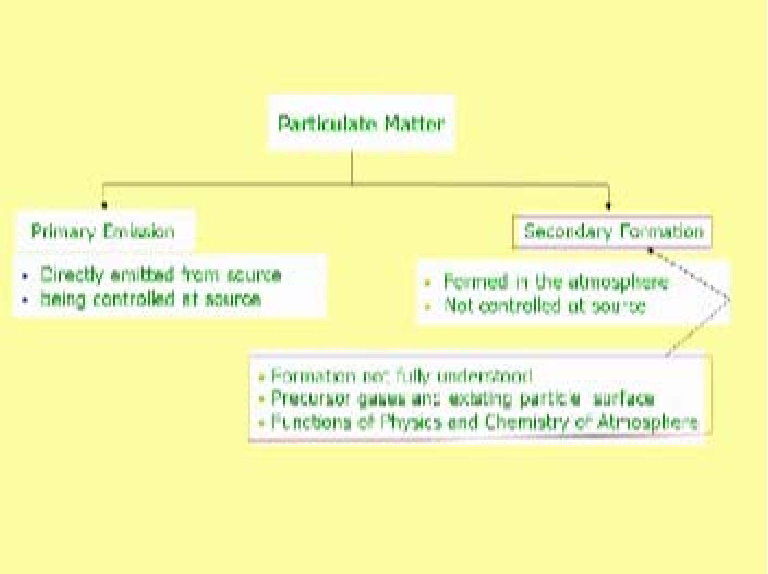

Particulate Matter

Primary Emission

- Directly emitted from source
- Being controlled at source

Secondary Formation

- Formed in the atmosphere
- Not controlled at source

- Formation not fully understood
- Precursor gases and existing particle surface
- Functions of Physics and Chemistry of Atmosphere

What we are looking at is not simply the organics and ozone but we also look at the secondary formation of particles: not controlled at source, formation not fully understood. Now, the gases play a role to produce the particulates or sulfate and nitrates. It depends on the physics and chemistry of the atmosphere.

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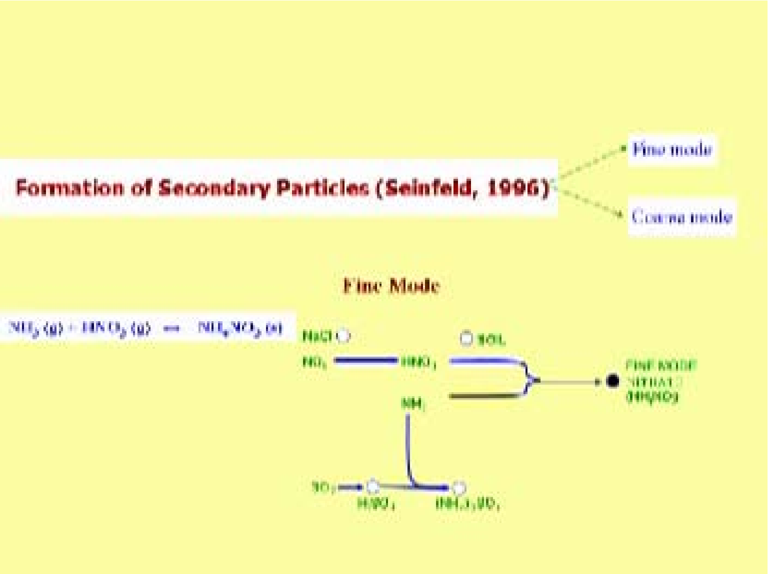

Formation of Secondary Particles (Seinfeld, 1996)

Fine mode

Coarse mode

Fine Mode

$NH_3 (g) + HNO_3 (g) \rightleftharpoons NH_4NO_3 (s)$

I will give you some reactions. One time, I write on the board ammonia, reversible reaction, you can form ammonium nitrate and then, you can also find the ammonium sulfate because of the SO_2 which gets into H_2SO_4 and then ammonia and ammonium sulfate. Here, you can go to HNO_3 and either you can react this with NH_3 this way with HNO_3. [44:14] the fine mode of the ammonium nitrate [44:17] very much on the fine mode. Formation of secondary particles. This is all given in this but you can also form it in the coarse mode. [44:27] the soil it can react and soil particles always much larger because these are formed because of the chemistry but the soil particles will be larger. That also can neutralize HNO_3. Suppose you have calcium in the soil, you can also form probably calcium nitrate but that will be in the coarse mode, larger particles, but otherwise if you are reacting with ammonia, it will be in the [44:49].

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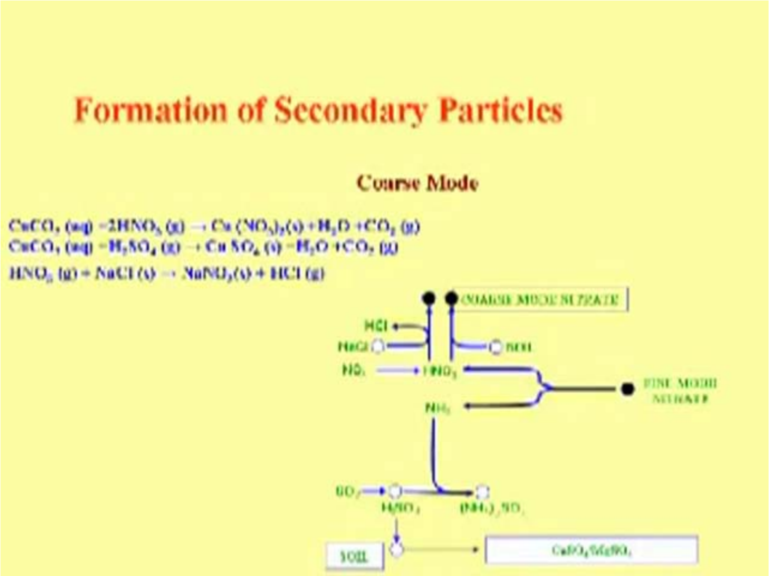

Formation of Secondary Particles

Course Mode

$CaCO_3\ (aq) + 2HNO_3\ (g) \rightarrow Ca(NO_3)_2(s) + H_2O + CO_2\ (g)$
$CaCO_3\ (aq) + H_2SO_4\ (g) \rightarrow Ca\,SO_4\ (s) + H_2O + CO_2\ (g)$
$HNO_3\ (g) + NaCl\ (s) \rightarrow NaNO_3(s) + HCl\ (g)$

Similarly for the secondary particles, the coarse mode. We have the HNO_3 and then you have the soil particles. It can react with this and can find the course mode of the nitrate formation because it can also react with the soil. The tentative reaction is here. When you have a little bit of moisture in the atmosphere, you have calcium from the soil origin that comes in and we just see that it can react with HNO_3 and can produce calcium nitrate. Similarly, [45.22] can produce calcium sulfate and since these particles are large because of the soil, they will be…. Similarly, even NACL. These are what you get in the coarse mode. You should be able to determine with the chemistry whether this is going to be in the coarse mode or fine mode depending on what atmospheric conditions you are dealing with

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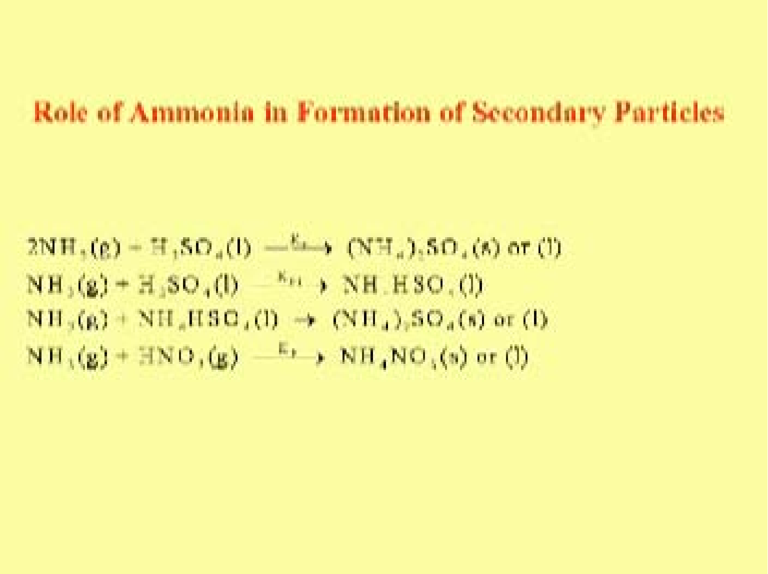

Role of Ammonia in Formation of Secondary Particles

$2NH_3(g) + H_2SO_4(l) \xrightarrow{K_s} (NH_4)_2SO_4(s)$ or (l)

$NH_3(g) + H_2SO_4(l) \xrightarrow{K_{s1}} NH_4HSO_4(l)$

$NH_3(g) + NH_4HSO_4(l) \rightarrow (NH_4)_2SO_4(s)$ or (l)

$NH_3(g) + HNO_3(g) \xrightarrow{K_p} NH_4NO_3(s)$ or (l)

Suppose we are trying the model the fine mode. This will be in the solid form or it could be in the liquid form also. Ammonia and H_2SO_4 can make ammonium bisulfate. Ammonium bisulfate can again [46:12] ammonia sulfate and it can form ammonium nitrate. What we really need to see are these constants. We have to very carefully write the equations for this and then we can solve the equations for what will be the source of ammonia, the sulfur dioxide in the power plant and you will be able to say, provided we are able to model it, that although there was no emission from the power plant in terms of particles (because you are cleaning everything and the stacks look clean) but still in the downstream, you can find a lot of particles. Somehow, we strongly believe here that it is a major source of particulate contribution and investigations are still going on.

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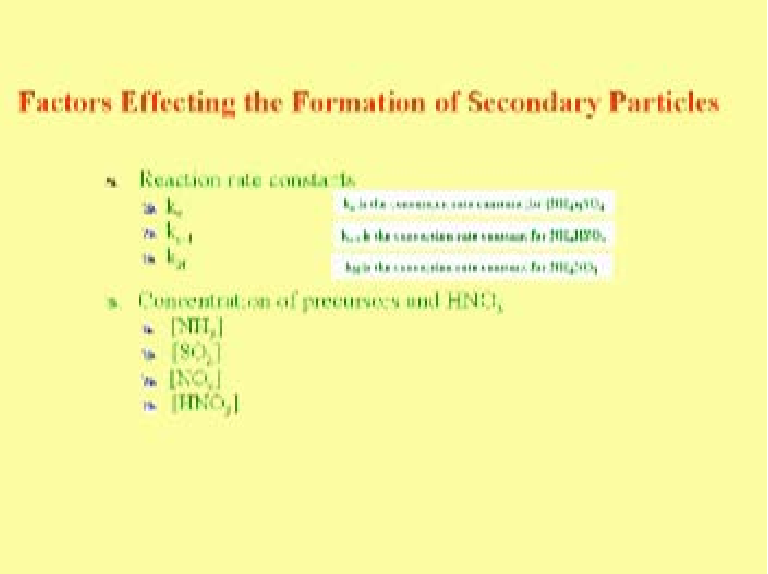

Factors Effecting the Formation of Secondary Particles

- Reaction rate constants
  - k_s
  - k_{s-1}
  - k_N
- Concentration of precursors and HNO_3
  - $[NH_3]$
  - $[SO_2]$
  - $[NO_x]$
  - $[HNO_3]$

Once we study these k_s k_{s-1}, k_n and ammonium nitrate, ammonium sulfate and then how they are formed and what is their concentration and the quantity that we have, then we will be able to see…. I can also tell you one thing very quickly. This is very volatile. If you do not measure it, capture it properly…. We will not be able to capture on filter paper if the temperature is high. These are the rate constants that we have seen. I will pass on the slides to you. Concentration of the precursor gases depends on ammonia, SO_2 and you should model the formation of HNO_3 and then formation of sulfates and nitrates with this thing.

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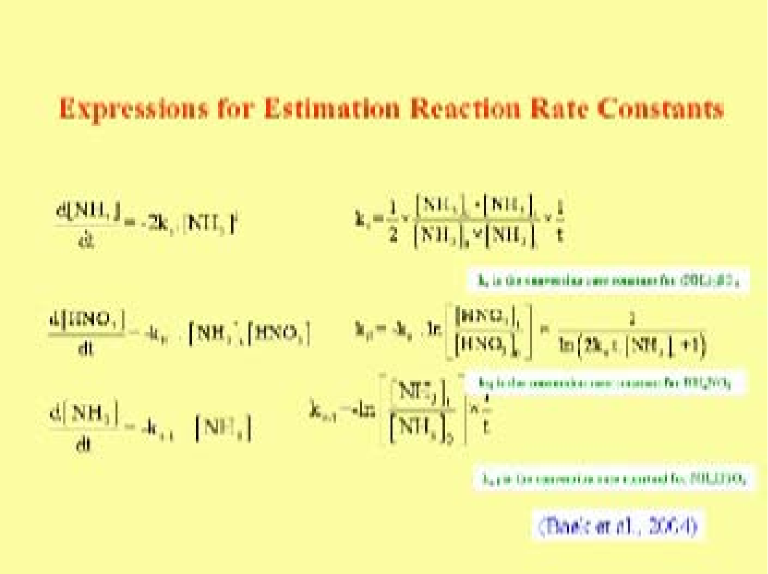

Expressions for Estimation Reaction Rate Constants

$$\frac{d[NH_3]}{dt} = -2k_1 [NH_3]^2$$

$$\frac{d[HNO_3]}{dt} = -k_{II} [NH_3]_t [HNO_3]$$

$$\frac{d[NH_3]}{dt} = -k_{III} [NH_3]$$

(Baek et al., 2004)

Try these out. I will try to send you this reference. If I do not, then just let me know. It is the very same concept that we learnt about the pseudo-steady state. You can write the equations of both ammonia, HNO_3 under different conditions whether this is the route or that is the route. Then, you can estimate the rate constraints. It has been found that this k depends not only on the temperature but also humidity (humidity plays a significant role) and it also depends on the amount of energy in terms of Watts per meter square that we are getting. It also depends on the temperature.

Once we are understand these things we can model the plume [48:39], at what distance you will find the ammonium sulfate and ammonium nitrate and you will find the impact. I will send you this. If I do not, please remind me. Try to understand everything because we have covered the theory as to how we write these equations because eventually, we want to predict the concentration of ammonia, ammonium sulfate and ammonium nitrate. This should be the last slide, I guess.

Maybe if time permits in the next class, I will show you some of the calculations that have been done to show that yes, ammonia sulfate will be formed and ammonia nitrate will be formed. We will stop here but do not forget that from the atmospheric route, we can get significant amount of the particulate matter because of the precursor gases emitted at the source. We are controlling the particulate matter at the source but you also need to control the gases if you really want to improve our air quality in terms of the dust because our conditions are very dusty and this particular contribution can be very significant. We will stop there.