Fundamentals of Combustion

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Lecture – 59

Combustion of carbon particle – Part 1

Coal combustion

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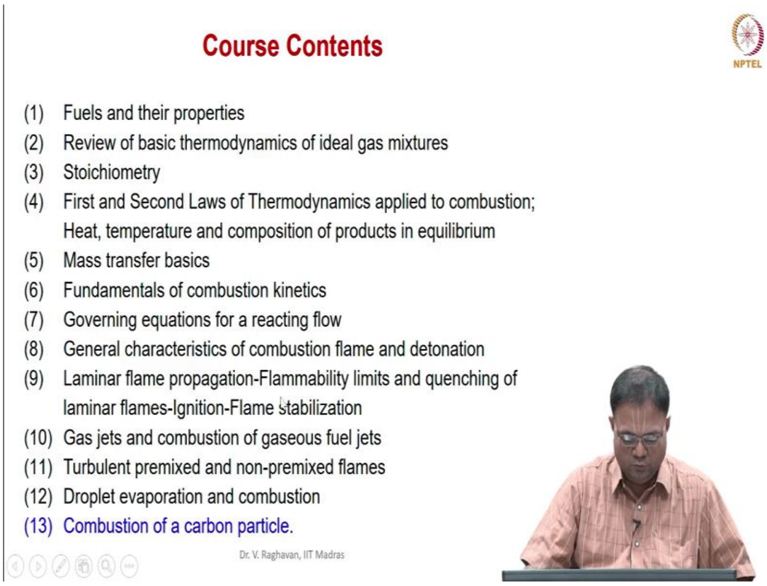

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So, the topic today is the last topic Combustion of a carbon particle.

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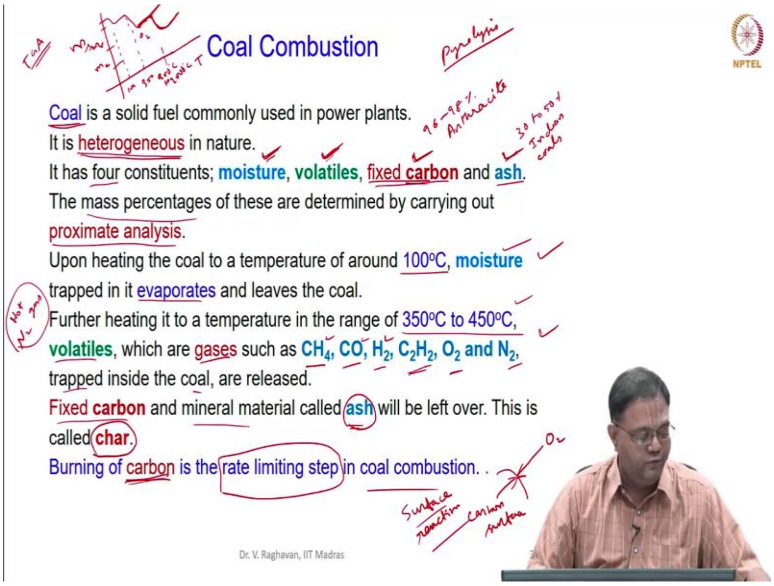

Coal Combustion

Coal is a solid fuel commonly used in power plants.
It is heterogeneous in nature.
It has four constituents; **moisture**, **volatiles**, fixed **carbon** and **ash**.
The mass percentages of these are determined by carrying out proximate analysis.
Upon heating the coal to a temperature of around 100°C, **moisture** trapped in it evaporates and leaves the coal.
Further heating it to a temperature in the range of 350°C to 450°C, **volatiles**, which are gases such as CH_4, CO, H_2, C_2H_2, O_2 and N_2, trapped inside the coal, are released.
Fixed **carbon** and mineral material called ash will be left over. This is called **char**.
Burning of carbon is the rate limiting step in coal combustion.

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So, in a coal combustion, it also applies to any other solid fuel such as biomass, wood etcetera. So, here you can see that a solid fuel generally coal or biomass they are called as charring solid fuel, and they are heterogeneous in nature. Let us take coal. Coal is commonly used in several power plants. Basically, in India lot of power plants use coal as the fuel. And coal is a heterogeneous fuel.

For example, if we take liquid fuel it exists in liquid phase, gaseous fuel exists in gaseous phase. But if there are more than one phase in a particular fuel itself then such a fuel is heterogeneous in nature. So, why coal is heterogeneous? It is because of the 4 constituents it has. See you can see that it has moisture. Coal basically is formed underground. The plant and animal waste, they are buried under the earth for long time and they are subjected to high pressures and temperatures of the earth.

So, eventually they form the fuel called coal. When the coal is evolved basically a lot of water content is trapped inside it. So, liquid water, some moisture is trapped inside it, then lot of gaseous substances are trapped inside they are called volatiles. How much time the vegetation remains underground that will basically fix the amount of carbon it has, the fixed carbon graphite.

So, that is the fixed carbon content what it has. Then, it will also have lot of inert minerals which is called ash. So, these are the 4 constituents of coal. What is there? So, in any charring fuel like coal or biomass, you will have these 4 contents, but they will vary. The best quality coal will have about say 96 to 98 percent of fixed carbon.

So, when the carbon content is very high that will actually give the higher rank to the coal. The pure carbon is the best, the graphite fuel, what we have solid fuel. But we do not have pure carbon, the amount of time the vegetation spends inside the earth and subjected to high temperature and pressure, based upon this the rank of coal will vary. It is actually based upon the location of the earth also.

Anthracite for example, will have very high amount of fixed carbon. But if you take say bituminous, then lignites etcetera, so there are several varieties of coals they are ranked basically upon the carbon content and when the carbon content decreases you will see that there will be increase in volatiles. Based upon the region where it is obtained, there can be good amount of moisture content also inside it.

Basically, if you take Indian coals, Indian coals have very high amount of ash say about 30 to 50 percent ash in Indian coals. So, this is also one of the important characteristics, so high ash coals, Indian coals are high ash coals.

You can see the heterogeneous nature of the coal. It has a moisture content, gaseous things trapped inside it, then fixed carbon which is pure graphite, and then ash. Based upon the rank of the coal where it is available etcetera, you will get these components, to find the mass percentages of this component we do what is called proximate analysis.

When I do a proximate analysis, we will determine the mass weight or weightage of these components. So, for example, I will say 5% moisture by mass, then volatiles say 20% and fixed carbon 60% and so on. So, basically if you see this, proximity analyzer works on a simple principle. First, you take some samples of coal and heat it to around 1000^oC uniformly. So, what happens is after this when the temperature is slightly more than 100^oC you can see that the moisture will evaporate. So, there will be a slight mass loss.

So, normally you also record the mass of the sample versus say temperature. Initially, the mass will be 100% and after some time there will be a slight reduction in mass. So, if you see what is the mass loss that will be the mass corresponding to that of the moisture. Then you heat it more, when the temperature range is about say 350^oC – 450^oC, so after that there will be no mass change. When the temperature increases to 350^oC to 400^oC.

So, this will be the 100^oC point and when the temperature reaches say 350^oC something like that, there will be another mass loss which will indicate the release of the gaseous fuels which is trapped inside the coal.

So, those fuels for example, you can see the variety of fuels methane, carbon monoxide, hydrogen, some hydrocarbons like C_2H_2, then some oxygen also will be there, nitrogen also will be present inside. So, these gases are trapped inside the coal and they will be released when the coal is heated to this. So, you can see there will be another mass loss and then the mass will remain constant.

So, with these two process basically when you want to release moisture or when you want to release volatiles, you may heat it in an inert medium like nitrogen, hot nitrogen gas. You may heat it in an inert medium, just it will be. So, it is only thermal process. Releasing of moisture, releasing of volatile will be only a thermal process which is generally called pyrolysis.

Heating up the cold sample will result in the release of moisture at a certain temperature range say 100^oC – 110^oC. The gaseous components trapped inside the solid fuel which are called volatiles are released at a higher temperature range say 350^oC to 450^oC. By doing so you will get the amount of volatiles. So, you know the initial mass and you know the masses when the volatiles released etcetera.

Now, the remaining will be the fixed carbon plus ash. So, this fixed carbon and the mineral material which is called ash, they are together called char in general they are together called char. This char will not convert at all. If you just use inert gas hot inert gas whatever will be the temperature, only if you use inert gas it will not convert at all, so it will just show as a straight line after that, if you use inert.

But if you start supplying oxygen, then what happens is the carbon will now burn with oxygen to form carbon dioxide, carbon monoxide etcetera. So, then if you use after a particular temperature. Say this is around say 900^{o}C to 1000^{o}C, you will get a mass loss again. So, this is in oxidizer medium or air medium. For example, there will be mass loss, then this mass will correspond to the mass of the carbon. So, this will be mass of volatiles and so on.

Now, after that what would be the rise in temperature? You heat it further what would be rise in temperature? The mineral material ash is inert, so it will not convert at all. So, that will remain as the residue.

So, this is the way you do. This is also called thermo gravimetric analysis. So, by doing this thermo gravimetric analysis or proximal analysis, you will be able to know what is the moisture content, volatile content that is the trapped gases and the fixed carbon content as well as the mineral content in the heterogeneous solid fuel, it may be coal or biomass.

So, if you see it is a very complex fuel when compared to what we have dealt with gaseous fuels and liquid fuel so far, you can see that this is very complicated. You can see that this is a thermal process called pyrolysis which has to be done to release the moisture, to release the volatiles etcetera.

The volatiles once they are released, they should now mix with the ambient air and form reaction zones homogeneous reaction zones or what we call gas phase reaction zones, and that will further heat up the solid which is the left over fixed carbon and ash.

And they will now heat up to a particular temperature say around 900^{o}C to 1000^{o}C, then they will start converting and the conversion of carbon is not a simple gaseous reaction. So, what happens there is a carbon surface. So, this I call carbon surface and oxygen from the ambient diffuses towards the carbon surface and a surface reaction takes place.

So, you can see that the burning of carbon itself is not a straightforward, it is very tough to really understand how the carbon burnt, especially, when ash is present. And once you have a solid fuel like coal, once this trapped moisture, trapped volatiles etcetera are released you can see that there will be pores which are formed. Now, what happens is there is a porous diffusion of the ambient gases into the solids and so on. So, it is a very complicated process, burning process here. So, we have to really make lot of assumptions to understand and analyze the results.

So, in summary you will see that coal is a complicated fuel which is heterogeneous in nature because of the fact that there are liquid components like moisture, gaseous components like volatiles and graphite, pure graphite will be present in fixed carbon plus there will be inert minerals which are called ash. Now, by doing proper characterization using a TGA or proximate analysis we will know the mass fractions of these components.

Now, if you see, the moisture does not participate in any reaction its only water vapor which is coming out, but the volatiles which are coming out they are constituted like say by methane, carbon monoxide, hydrogen, C_2H_2, O_2 etcetera. Now, we can see that these will react in the gas phase and they will form homogeneous reaction zones a gas phase reaction zones which will be further helpful in heating the solid fuel itself. So, we know how the mixture of gases will burn in the gas phase. We have already seen how the fuel will burn.

Homogeneous reactions are easy to really analyze, so we know how to do this. And especially when there is a carbon bed, and the volatiles are released, and oxygen comes from the ambient diffuses into these, mixes with the volatiles and burn in a diffusion mode or non-premix mode, it is easy to really analyze the homogeneous reaction zones. However, the carbon itself, fixed carbon itself will burn in a surface reaction mode and for this we need to understand certain other things also which we will see now.

Now, the burning of carbon is the slowest process. So, that will be the rate limiting step in the coal combustion. So, we have to understand the burning of carbon thoroughly. So, that will be the topic which we will cover now. So, this is not going to be applicable only for coal, please understand that it may be biomass. Biomass also will have some amount of carbon. For example, biomass will not have much higher amount of carbon like that of coal etcetera.

However, if you see it may have say, 20% to 30% of fixed carbon and so on. Based upon what is the type of biomass what we deal with and so on. Again, there also the carbon combustion is the rate limiting. So, we have to understand the burning of carbon.

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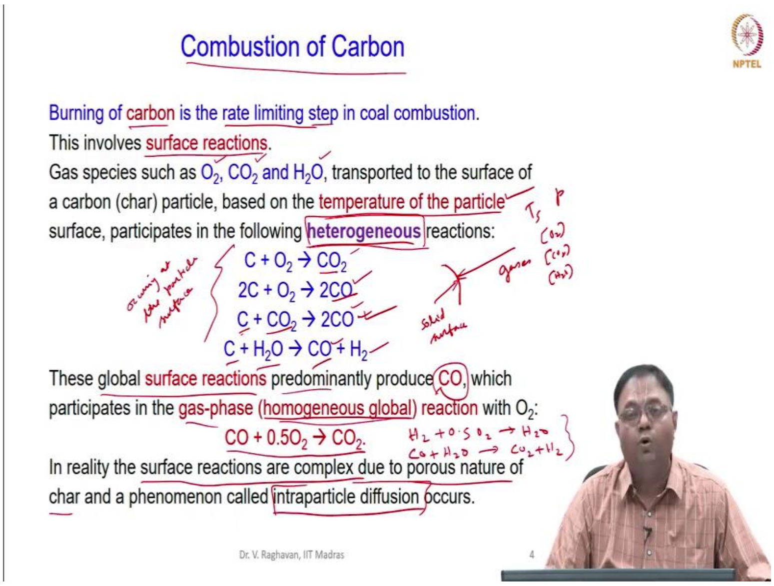

Combustion of Carbon

Burning of carbon is the rate limiting step in coal combustion.

This involves surface reactions.

Gas species such as O_2, CO_2 and H_2O, transported to the surface of a carbon (char) particle, based on the temperature of the particle surface, participates in the following heterogeneous reactions:

$$C + O_2 \rightarrow CO_2$$
$$2C + O_2 \rightarrow 2CO$$
$$C + CO_2 \rightarrow 2CO$$
$$C + H_2O \rightarrow CO + H_2$$

These global surface reactions predominantly produce CO, which participates in the gas-phase (homogeneous global) reaction with O_2:

$$CO + 0.5O_2 \rightarrow CO_2.$$

In reality the surface reactions are complex due to porous nature of char and a phenomenon called intraparticle diffusion occurs.

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So, combustion of carbon. So, the combustion of carbon is the rate limiting step in any bio solid fuel combustion, not only any solid fuel combustion.

As I told you this will involve surface reactions. So, if you take gases like O_2 CO_2 and H_2O they will diffuse through the surface of the carbon. And if we see that the carbon will be heated to a temperature where this surface reaction can take place. So, for example, if it is heated to say 900^{o}C plus, say 900^{o}C or 1000^{o}C something like that then based upon temperature of this carbon particle, what happens is the surface reactions are going to be triggered.

Please understand that these reactions, surface reactions are heterogeneous in nature, because there is a solid surface and these gases diffuse towards the surface and penetrate into the surface basically and the surface reaction takes place based upon the temperature of the particle at the surface. So, obviously, you can see these are all, wherever I put C here they are all graphite on the surface.

Now, O_2 diffusing to the surface will react with C and produce CO_2, so that means, CO_2 will be formed at the surface. Similarly, there are locations where CO also can be formed at the surface, predominantly CO will be formed. Then, CO will go to the gas phase and react with oxygen to form CO_2, the CO_2 diffuse towards the surface or the CO_2 formed at the surface also can again diffuse further and they will react with the carbon to form CO.

Similarly, water vapor which is either released from the coal or which is formed due to the combustion of the volatiles can diffuse towards the surface and C + H_2O reaction can trigger to give CO + H_2. Again, H_2 will go to the gas phase react with oxygen to form H_2O, H_2O penetrates within this. So, these are all reactions occurring at particle surface.

So, surface reactions are heterogeneous in nature because we have a solid and the gas which is coming in.

$$C + O_2 \rightarrow CO_2$$

$$2C + O_2 \rightarrow 2CO$$

$$C + CO_2 \rightarrow 2CO$$

$$C + H_2O \rightarrow CO + H_2$$

So, these reactions will not take place again. It is complicated, these are global reactions basically. Again, there will be some steps to involve and these are all primarily classified as first order reactions, and if you see this the amount of the gases which are going to be penetrated into the surface plus the surface temperature, pressure etcetera will dictate the reaction rates.

So, the surface temperature say T_s, then the pressure and the concentration of the gases say O_2, CO_2 or H_2O, these will affect the reaction rates.

Now, when I say heterogeneous reaction, I mean that there should be something called absorption of gases to the surface, then the reaction takes place, then the desorption; that means, the product which is formed that should be released away from the surface.

So, the absorption of the reactant gas into the surface, then occurring of the surface reaction, then the desorption where the products which are formed on the surface are released to the gas phase.

So, these are the steps involved in the heterogeneous reactions. Now, if you see this predominantly you can see CO is formed. So, the global surface reactions which are given above predominantly produce CO. So, this CO which is produced here will again go to the gas phase to react with O_2 to form CO_2, you can see this is a gas phase homogeneous reaction. Other reactions are also there. Similarly, H_2 which is formed here can go to the gas phase to form H_2O.

Similarly, CO + H_2O in the gas phase can react to form CO_2 + H_2. Then methane etcetera. So, again volatiles, these are all the products which are formed within the surface they are going to the gas phase and reacting. Volatiles such has CO, CH_4, C_2H_2 etcetera that also will have a gas phase reaction. So, that is known.

So, these are the reactions homogeneous in nature, because these are gaseous products which are going out. If they have a fuel component that will react with the oxygen available in the atmosphere, that will also produce the gas phase reactions. It is a combination of homogeneous plus heterogeneous reactions that we have to understand, but the main focus should be on how the heterogeneous reactions take place here.

So, that is the main thing. So, as I told you surface reactions are very complex especially due to the porous nature of the char or the carbon particle itself. It has the trapped moisture, trapped volatiles are released, they will come out and they will create some pores, already the coal itself can be porous.

Further, due to the release of these components, volatile and moisture components, you can see there will be a porosity involved and due to which a phenomenon called intra-particle diffusion, within the particle there will be diffusion, which can take place. So, this is very complex and modelling cannot be done or even any theoretical or numerical modelling is very complicated to do it including the intra particular diffusion.

But we need not even do this, we can understand the overall way to analyze by using the species and energy balances that is what we are going to concentrate on. However, the point we have to stress here is we need to understand first of all how the reaction takes place, what is formed in the surface. So, there are several models which are involved to analyze this. We will just quickly see what are they.

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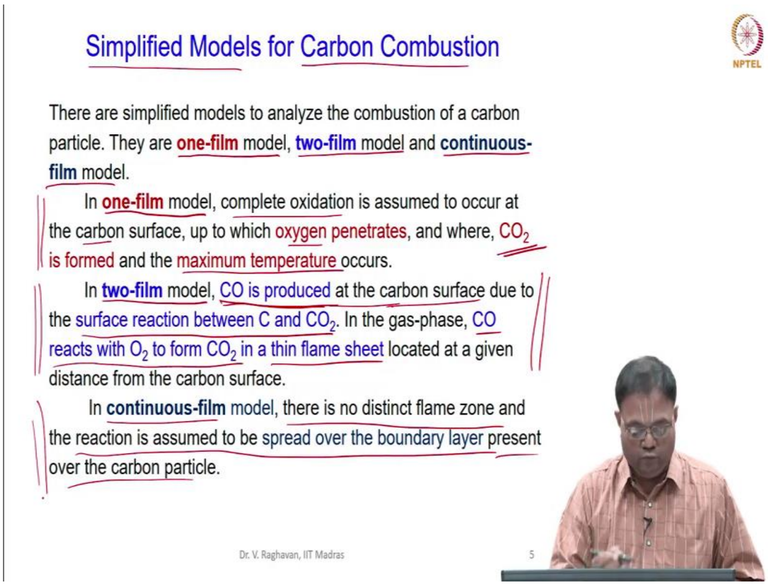

Simplified Models for Carbon Combustion

There are simplified models to analyze the combustion of a carbon particle. They are **one-film** model, **two-film** model and **continuous-film** model.

In **one-film** model, complete oxidation is assumed to occur at the carbon surface, up to which oxygen penetrates, and where, CO_2 is formed and the maximum temperature occurs.

In **two-film** model, CO is produced at the carbon surface due to the surface reaction between C and CO_2. In the gas-phase, CO reacts with O_2 to form CO_2 in a thin flame sheet located at a given distance from the carbon surface.

In **continuous-film** model, there is no distinct flame zone and the reaction is assumed to be spread over the boundary layer present over the carbon particle.

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So, simplified models for understanding carbon combustion are mainly 3. First one is called one-film model, and the second one is called two-film model, and the another one third one is called continuous-film model. It is a simplified model. So, we will just use the species and energy balances etcetera and try to do this.

So, again we will see lot of assumptions are involved in all these models. Let us take one by one. We will see in detail the one-film model and some features of the two-film model in this particular lecture. So, one-film model assumes that complete oxidation of carbon occurs at the surface where oxygen penetrates into it.

So that means, C + O_2 will occur to form CO_2 at the surface itself that is all. So, that is only at one go. There is a hot carbon surface, oxygen penetrates into this and CO_2 is formed, finished that is all, no other reactions are considered in this.

So, I will read it, complete oxidation is assumed to occur at the carbon surface up to which the oxygen is going to penetrate. Then, CO_2 is formed there; obviously, due to the heat release maximum temperatures is seen at the surface. So, temperature will decrease from the max value towards the ambient value. So, this is the one-film model, the simplest model.

However, when measurements are taken very close to the char surface, the carbon surface, etcetera, you can see that people have seen very less CO_2. CO_2 should be maximum correct, but they have seen very less CO_2 and they have seen less oxygen also; that means when the oxygen penetration or CO_2 formation could not have occurred very near to the surface.

So, keeping that in mind people have postulated what is called two-film model in which first CO_2 is produced at the surface. So, that is what the reactions also indicate. You can see, 3 out of 4 reaction forms CO, this indicates the CO formation at a surface. So, this is more realistic model. But again, when you try to increase the complexity the analysis also become complex.

So, here what happens is CO is produced at a surface, but this is due to the reaction between C + CO_2. This third reaction $C + CO_2 \rightarrow 2CO$, that reaction triggers at the surface. So, surface reaction between the hot carbon surface and the CO_2 which is penetrated from the gas phase to inside the surface that will take place to produce CO.

Now, the CO will diffuse towards the ambient and react with O_2 to form CO_2, this is called two-film. So, the first is the formation of CO due to the penetration of CO_2 from the ambient which is formed at the ambient and it penetrate into the surface hot surface where CO is formed. Then, the CO goes to the surface and forms CO_2. These are the two-films here.

So, there are two regions. One is surface and the flame where CO is oxidized to CO_2 that is the thin flame sheet. So, that and the surface that will be one region, then from the thin flame to the ambient will be second region. So, two-film what we call. First film or the inner region, second film is the outer region. So, this basically is the two-film model.

Then, continuous-film model, there is no distinct flame zone. So, what it assumes is there is a carbon surface and there is a boundary layer, within the boundary layer everything is over, the reactions are over then ambient comes. So, within the boundary layer what happens is the formation, all the 4 reaction take place here in the boundary layer and the combustion is complete. So, that is the continuous-film model. There is no distinct flame zone and the reaction is assumed to be spread over a boundary layer present over the carbon particle.

So, these are the 3 models which are available. We will go into detail of one-film model because we can see some insights of the controlling parameters etcetera then we will also see some basics of two-film model in this course.

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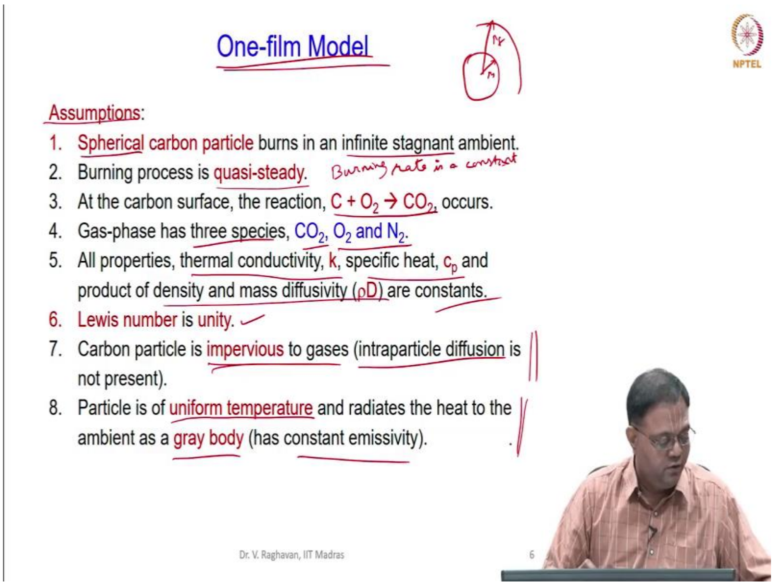

One-film Model

Assumptions:

1. Spherical carbon particle burns in an infinite stagnant ambient.
2. Burning process is quasi-steady. Burning rate is a constant
3. At the carbon surface, the reaction, $C + O_2 \rightarrow CO_2$, occurs.
4. Gas-phase has three species, CO_2, O_2 and N_2.
5. All properties, thermal conductivity, k, specific heat, c_p and product of density and mass diffusivity (ρD) are constants.
6. Lewis number is unity.
7. Carbon particle is impervious to gases (intraparticle diffusion is not present).
8. Particle is of uniform temperature and radiates the heat to the ambient as a gray body (has constant emissivity).

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Now, one-film model, again any theoretical model we have to make several assumptions, many of them you know now because we have done already the diffusion flames and droplet combustion etcetera.

So, based upon this similar type of options will be there. Here the carbon particle is assumed to be spherical because I want to use a spherical coordinate here. So, the carbon particle is spherically symmetric. So, when there is a flame formed it is also spherical in nature. So, this will be say r_s, surface radius and this will be r_f. So, exactly what we saw in the droplet combustion similar thing we will assume here. There will be a radius for the carbon particle and there will be a radius for the flame.

So, spherically symmetric, only one coordinate is radius here. So, that will be the assumption, first assumption made. And there is no convection, so stagnant ambient. Burning is quasi steady, the burning rate is constant. So, this is what quasi steady means. Then, in the one-film model as I told you only one-shot carbon and oxygen reacts to form CO_2. So, oxygen comes to the hot carbon surface and converts into CO_2. And heat release happens, maximum temperature will prevail there.

So, in the gas phase obviously, air and CO_2 will be present. So, air is O_2 + N_2 and CO_2. So, these are the 3 species which we will consider here. Then, usual assumptions, thermal conductivity, specific heat and the ρD product of density and mass diffusivity are constants. Apart from that Lewis number also is taken as one. Then, the tough part for the surface reactions etcetera only till the surface the oxygen can penetrate and it should consume that.

Please understand unlike for the gases penetrating into a liquid droplet they should dissolve, but we have assumed it is not going to dissolve, so there is no net mass flux for the gases, other gases correct which will come to the surface of the droplet. But here oxygen penetrates to the surface and reacts there, so that difference you have to keep in mind.

But anyway, it is not going to again go into the pores and an intra particle diffusion etcetera are not considered. It is very complex and not required also. So, impervious to the gases including O_2. So, this is very important assumption which should be made to make the problem simpler.

Now, another assumption is the particle is heated up. The particles are small in nature, small in size, so that when the particle is heated up the surface temperature is everywhere inside the particle. So, there is no heat transfer required to be solved within the particle, so particles of uniform temperature.

Now, another assumption please understand that when the carbon particle burns it will be red hot. So, there will be radiation from the particle surface. So, please understand these are all reduction reactions here basically. So, even though this is CO + C, C + O_2 is oxidation, then C + CO_2, C + H_2O they are all reduction reactions. So, what happens is the particle should be at very high temperature.

When the carbon particle is at a very high temperature, when it is incandescent, the hotness will be reflected by the bright red color. So, the radiation has to be taken into account. Now, when radiation has to be taken into account we have to make some assumption about the body. It is not a black body, so it should be taken as a gray body where the emissivity is taken as constant.

So, it will not depend on wavelengths and so on. So, gray body assumption is made and the carbon particle radiates the heat to the ambient as a gray body, so that assumption is made. So, when you solve for heat balances radiative heat transfer also is accounted here. These are the assumptions made to simplify the other way complex problem, and I will talk about the profiles, typical profiles.

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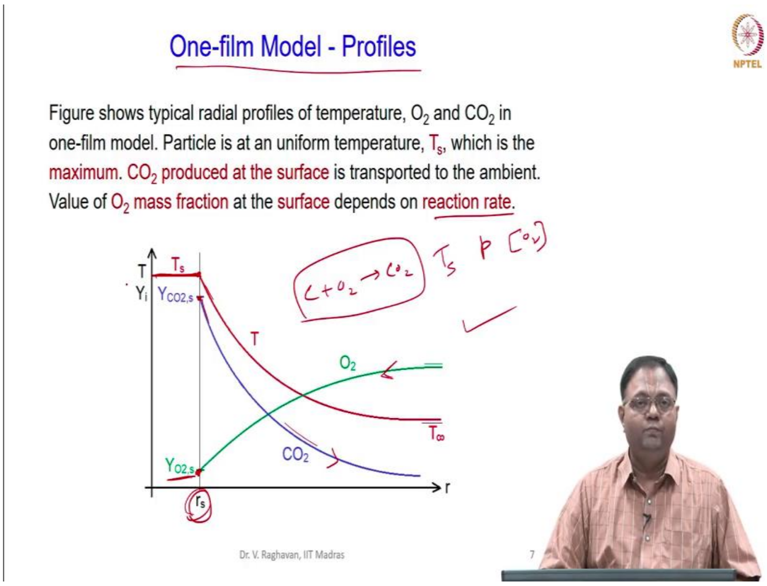

One-film Model - Profiles

Figure shows typical radial profiles of temperature, O_2 and CO_2 in one-film model. Particle is at an uniform temperature, T_s, which is the maximum. CO_2 produced at the surface is transported to the ambient. Value of O_2 mass fraction at the surface depends on reaction rate.

$C + O_2 \rightarrow CO_2$

T_s P [O_2]

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As I told you, this is the surface, r_s is the radius of the carbon particle where all the reactions are going to be over that is the only one reaction that will be over here. Inside this the temperature is uniform you can see there is no variation in temperature. And surface temperature is T_s here. And from the surface the temperature reaches the maximum temperature because there reaction is going to occur. And I can see the temperature drops to the ambient temperature in a non-linear manner.

Similarly, oxygen from the ambient diffuses into the surface and it is consumed there. But please understand it is not completely consumed. So, based upon the reaction rate, which is dependent on T_s, again the oxygen concentration and pressure, and concentration of O_2 the reaction rate will be specified. So, based upon the reaction rate there will be some value of mass fraction of oxygen at the surface. It cannot be 0. When the temperature reaches higher and higher then it will tend to 0, Y_{O2} at s will tend to 0.

Now, carbon dioxide is produced at the surface. So, it is maximum there and when it is desorbed then it is again going to be transported to the gas phase, both convection and this diffusion.

So, here also you can see that since O_2 comes to surface and get consumed here, this O_2 also is transported by both convection and diffusion. So, unlike the oxidizer actually penetrating towards the flame or in the evaporation case when the droplet is evaporating then the ambient gas penetrates to the surface, but it will not be consumed there, so net flux is 0.

So, only by diffusion the gas comes to the surface when the droplet evaporates. In this case, oxygen comes to the surface, since it reacts there will be a net flux for that also. So, this is the important thing we should understand, the structure of the one-film model. So, a very simplified model where we have only one plane where the reaction is complete that is at the surface.

And the surface reaction is $C + O_2 \rightarrow CO_2$, and you can see that maximum temperature and the product will be maximum at the surface and they are transported away. So, diffusion, conduction plus radiation also will be there in this. This profile will be got including both conduction as well as radiation. We will come to that.

But the internal conduction within solid particle is neglected because we assume that the entire solid will be at the same temperature as that of the surface.