Course Name: Combustion of Solid Fuels and Propellants
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Lecture: 19 Combustion of Composite Propellants-Introduction

Hello everyone. So, we are continuing our discussion of combustion of solid propellants. In the previous lectures, I think we completed our discussion on the combustion of double base propellant or the homogeneous propellant. The features of the double base propellant we have seen that since it is homogeneous propellant because the constituents which are measured like nitrocellulose and nitroglycerin, they are mixed intimately and they form a homogeneous mixture. And because of that the burning features are kind of you know gas phase reactions is going to take place and this kind of like a premixed combustion and we can say the homogeneous combustion took place. And we discussed about the various zones of combustion like solid phase degradation zone, then we have talked about the fizz zone, we talked about the dark zone and then we talked about the secondary luminous zone or flame zone.

In case of composite propellant, the constituents are fairly different compared to the double base propellant. Here the crystalline solid oxidizers are present in the propellant matrix and many occasions the metal metallic fuels are also added into the propellant formulation. So, if you recall what we discussed earlier during the discussion of the typical ingredients of composite solid propellants, we had discussed about the various you know crystalline oxidizers whereas, you know perchlorate based oxidizers such as ammonium perchlorate is the common one for composite solid propellant. And it is majorly you know used in the booster stage for satellite launch vehicle.

The other solid oxidizers can be ammonium nitrate, potassium perchlorate, potassium nitrate. The fuel binder which acts as the structural glue for holding the solid crystals such as ammonium perchlorate or aluminum particles within the propellant matrix, the polymeric binders act that you know binding characteristic or rather it provides the structural glue to hold the solid crystals within the matrix. Now, there are several you know fuel binders have been tried HTPB, CTPB, PVC. Then we also talked about the different metallic fuels for example, like aluminum, boron, beryllium, zirconium, iron. The major idea behind using the metal fuel is that the volumetric heating value and of course, the gravimetric heating values of metal fuels are supposed to be higher than the polymeric fuel which is the binder.

So, if you compare the heating value of the HTPB and compare that with the metallic fuel it is so, it is observed that the metal fuel has the higher volumetric heating value compared to the hydrocarbon fuel. So, that is why the metallic fuel can be added in order to enhance the energetic potential of the propellant and in such it can release energy once the metal particles burn in the gaseous state or rather I would say like inside the propellant once it is burn it is going to release energy and that will increase the combustion chamber temperature or product temperature which will eventually lead to higher performance. Because if you recall the Isp is proportional to the square root of chamber temperature. So, if somehow if we increase the chamber temperature by adding some energetic materials which can burn along with the hydrocarbon fuel or the binder that will increase the temperature in inside the combustion chamber which will eventually increase the Isp and that is why it is required to increase the performance. There are other ingredients which are used at a small quantity, but they can play a big role there for example, like curing agent.

Curing agent can be used as a small percentage, but that can you know make the pre-polymer to form like a longer chain polymer and that can eventually become solid. So, if we talk about HTPB, HTPB can be solidified by using the different curing agent and this will actually hold the ammonium perchlorate crystals or even aluminum fuels inside it and the solid grain can be made. It may take some time it may take about 5-6 days depending on the curing environment and the curing agent you are using. So finally, we make this slurry mixtures, we put the this mixture into a mold and mandrel and then we want it to be like a solid grain. So, this is the solid grain.

So, the curing agent is going to play a role in the solidification process. So, it will make this solid grain. There are some other ingredients like plasticizers which may be used in a smaller quantity. They are not used in a bigger quantity, but the main role of plasticizer is to increase the fluidity because you can see this is a slurry mixture. So, we need to have some fluidity of the slurry mixture so that we can transfer into the casting.

So, for the processing purpose we need to increase the fluidity lowering the viscosity that is generally done by this plasticizer. I think I do not need to go into more detail about this because we have already talked this thing in the discussion during the discussion of solid propellants and there are different ingredients. Similarly, burn rate modifiers are also there which can act as you know increasing burn rate or decreasing burn rate. So, that can be like positive catalyst or negative catalyst. It can work both ways.

So, they are also used in you know various propellant formulations based on the requirements. Now, we have talked about the different type of oxidizers nitrate based and perchlorate based. So, this table is giving us a comparison of various crystalline oxidizers like ammonium perchlorate, potassium perchlorate, sodium perchlorate, ammonium nitrate. So, you can see they are chemical symbol, molecular weight, density and the oxygen continuing the molecule is also given. So, most common oxidizer as I told that the major applications will find the ammonium perchlorate as the oxidizer in the composite propellant formulation.

It has like low end, low cost, readily available and performance is higher. So, that is the prime choice for you know composite propellant. So, you know in booster rocket this is the common ingredient used is the HTPB plus AP as the oxidizer plus you know some cases aluminum particles are also used to enhance the energy. However, AP is kind of workhorse oxidizer for the booster stage because of its high performance and you know stable characteristics. Other perchlorate based oxidizer are there, but their burning rate is low, performance is medium.

For example, like potassium perchlorate, sodium perchlorate is also there, but the problem is sodium perchlorate is hygroscopic. So, this is higher, but hygroscopic is a major problem. Ammonium nitrate on the other hand it is a smokeless propellant because you see it does not contain any chlorinated compound inside its molecule. So, it does not have any chlorine compound. So, it does not give any chlorine compound upon decomposition or after the combustion products it does not contain any chlorine compound.

So, it is that way environmentally benign and smokeless. Performance is actually medium. The major problem with the nitrate based oxidizer or rather ammonium nitrate they are hygroscopic in nature. So, that gives it is a major setback for using in the propellant application. The other issue with ammonium nitrate is the phase transformation.

So, it changes its phase at certain temperature generally at the temperature even as low as 32 degree centigrade which actually gives change in volume in the crystal structure that actually not accepted just because this may create some void in the grain which is eventually lead to you know issue with the performance. So, although ammonium nitrate is smokeless oxidizers it can you know it does not give any adverse products coming out of the exhaust, but major issue with the ammonium nitrate oxidizer is the hygroscopic in nature and this is the another problem the phase transformation. I think we have already discussed this one as well we have mentioned while talking about the ingredients for solid propellant. So, keeping in mind one thing we can understand that the by nature the composite solid propellant is different than the double base propellant. So, by nature it is a it is heterogeneous in structure compared to the double base propellant.

So, if you look at the cross sectional view of a composite propellant what you can see that the ammonium perchlorate crystals or if others crystalline oxidizers are present in the propellant matrix. So, that gives us you know typically a heterogeneous structures that the oxidizer particles are dispersed into it. If you look at the photograph of the solid propellant containing like 65 percent of ammonium perchlorate content there also you can see the large and small crystals are actually dispersed along the surface of the propellant grain. So, if you look at the propellant surface closely you can see this type of features if you look at this surface, but if you cut at different height of the grain as well and if you just look at the cross sectional view we can actually find out this type of morphology that the smaller and large ammonium perchlorate crystals are dispersed all along the surface. If we add aluminum particles into the combinations then we can see some aluminum particles are also present in the propellant matrix.

So, eventually adding of solid particles or solid crystals into the propellant matrix makes its you know heterogeneous propellant. So, the composite propellant by nature it is a heterogeneous propellant. So, the burning characteristics is going to be different than what we have seen the burning mechanism in case of double base propellant. So, it is also mentioned that unlike double base propellant a composite propellant is heterogeneous in nature. So, we are expecting that the burning characteristic will be very much different than the double base propellant.

So, if you look at closely how we are trying to understand the burning mechanism in case of double base propellant we had considered the propellant surface and we had said that there will be some solid phase degradation going to take place somewhere at the propellant surface. Then you know there will be some fizz zone, there will be some dark zone and there will be luminous zone. So, temperature essentially is going to increase from some initial temperature to surface temperature that will you know in the fizz zone is going to further increase in the dark zone it may fairly remain constant and the flame zone again is going to increase to flame temperature. So, this is let us say Td this is surface temperature Ts and this is let us say initial temperature Ti. So, this type of temperature profile we have seen and they are actually you know fuel and oxidizing species are forming you know gases they will mix here and they are going to have the flame.

So, we have also seen the flame that they are located at a distance from the propellant surface it is distended from the propellant surface. So, flame is located something here because the decomposition of the I mean the gas phase of the fuel vapour and the oxidizer vapour will mix here and they will form the mixture. So, basically they are going to have some premixed type of mixture and they will form the flame which is distended from the propellant surface. But eventually this type of combustion is kind of homogeneous combustion because the nature of the double base propellant is homogeneous because NC plus NG mix together intimately and they form a homogeneous propellant. Now if you look at the case for the composite propellant what you can see the composite propellant let us say if you comparing the composite propellant only let us say containing HTPB plus AP.

So, HTPB this is the binder which may act as fuel also because this is a hydrocarbon. So, it can act as fuel as well because this is a hydrocarbon and AP this is the oxidizer. So, the oxidizer particles are dispersed all along the propellant surface if you cut it again in the next layer also you can see the particles are there. So, they are very much different than the ammonium sorry than the double base propellant. So, this is the double base propellant.

Now, we can expect that the ammonium perchlorate decomposition is going to play a role here in the burning process of the composite propellant. So, this is the case of composite propellant. So, in order to understand the burning mechanism of composite propellant we also need to understand how the ammonium perchlorate particles are decomposing because they are going to decompose and going to provide the oxidizing species which will eventually react with the fuel species coming from the HTPB. So, this is the HTPB which is the polymer. So, HTPB is going to provide the fuel species and ammonium perchlorate is going to provide the oxidizing species and eventually they will react and they will have exothermic reaction and they are going to form the flame.

So, this is the fuel species. So, before proceeding further I think we will try to see the decomposition of ammonium perchlorate. So, I think the decomposition of ammonium perchlorate can be well understood by considering the thermogravimetric analysis. It is termed as the TGA or it is a combination of differential thermal analysis DTA which basically tells us that how a material or a sample is going to behave or what are the different thermal event is going to take place if we heat up the sample. So, this machine actually takes care of the thermal event at a different temperature of the material. So, it is a control heating of a sample and that actually compare with a reference sample.

So, generally it is done with some with a microbalance. So, one crucible the sample is given and another crucible the reference is given. In many occasion reference material is taken as the alumina or aluminum oxide which is fairly inert or refractory type of material so, fairly inert and they are actually heated. So, this whole chamber is actually under heating. So, once we heat up the sample because of the nature of the sample there will be some you know changes is going to happen.

You know sample may melt, sample may change its crystal phase like alpha rhombohedral to other phases, sample may go into like glass transition temperature, glass transition temperature it may have some recrystallization. So, many things can happen. So, this thermogravimetric analysis is going to tell us about the thermal event as we increase the temperature. Of course, at a different heating rate this there may be shift in the event. So, let us say at a lower heating rate some events are happening at a certain temperature, but if you change the heating rate to a higher heating rate the there may be some shift in these events, but overall nature of the events are almost going to follow the same.

However, due to you know higher heating rate some scenario may change depending on the materials. Now, coming back to the thermal decomposition of AP what we can say is that if we look at the figure here you know the DTA curve is going to give us some qualitative representation of various thermal event ok, it is going to give us various thermal events. For example, like if you look at this curve. So, as we increase the temperature it is so, that it is going to initially it is remaining fairly constant and then it the mass is dropping.

So, this is a mass fraction. So, mass is dropping as you increase the temperature whereas, the DTA curve is going to tell us whether some event is you know exothermic means it is going to release energy or it is going to take energy. So, for example, like if we are going to heat up some material and if it is melting so, that means, it is taking heat from the environment or the ambient conditions whatever set there or the heat we are providing to the sample. So, it is going to take off heat that means, it is endothermic whereas, in few samples exothermic reaction may take place due to the decomposition. So, that will actually going to give us you know exothermic or endothermic features. So, basically the DTA curve is going to tell us this type of events sometime it can give us the event of melting also.

So, it is not going to give us the quantitative information about the how much heat flow is going to you know go there during this exothermic or endothermic event rather it can give us some qualitative representation. If you want the quantitative information about the you know amount of or change in enthalpy then we have to go for DSC analysis or differential scanning calorimetry that type of analysis we have to use is a different instrument sometime it may come with a combination of TGA also. But if you want the qualitative analysis then you have to go for sorry not qualitative, quantitative the amount of it quantitative analysis if you want then we have to go for differential scanning calorimetry. However, the DTA is going to give us at least the information about whether it is happening the exothermic reaction or endothermic reactions. For example, if you look at the decomposition of I mean sorry the thermogram of ammonium perchlorate what you can see an endothermic peak can be seen around you know 520 Kelvin which corresponds to some you know change in crystal phase.

So, basically this is a change in crystal phase and as per the literature it has been identified that at this temperature the AP change its crystal phase from orthorhombic to cubic that is crystal. So, basically this endothermic peak represents the change in crystal phases due to which we are seeing the endothermic peak. Now once we go for you know high temperature we can see the exothermic peak happening a temperature you know between 607 to 720 Kelvin and of course, there is a mass loss happening here if you look at here there is a corresponding you know mass loss is also happening. So, this exothermic reactions are actually happening due to the decomposition of ammonium perchlorate and the typical decomposition the typical decomposition reactions are something like you know NH_4ClO_4 that will initially decompose to ammonia plus perchloric acid $HClO_4$ and that will further $HClO_4$ further decompose to form you know HCl plus O_2. So, basically this exothermic reactions happens through these reactions and they produce excess oxygen as oxidizer.

So, that oxygen is going to work as oxidizer while burning this in the oxidizer fuel combination. Now of course, as I said the exothermic peak may shift in the higher side if the heating rate changes because this is done in a smaller heating rate for a higher heating rate there will be some shift in the exothermic peak, but however, general trend is not going to change much it is almost the similar, but these are the major you know reactions for the decomposition which is happening for ammonium perchlorate. So, this tells us you know some idea about how the decomposition of ammonium perchlorate is happening because that is very important in the burning mechanism of the composite propellant because initially once the AP decomposes is going to form some you know initial flame which later we know that this is going to have like ammonium perchlorate premixed flame ok. So, because of the due to the decomposition of ammonium perchlorate it is going to form some ammonium perchlorate premixed flame and later on it is going to react with the fuel species formed from the pyrolysis of HTPB and it is going to form some diffusion flame. So, I think we will talk that part little later.

This is just give you some introduction about the you know background of that part that how the combustion of AP based composite propellant is going to take place. So, now coming to some you know typical flame of AP HTPB case, what you can see here? You see this is a combination of AP and HTPB where AP is 86 percent, HTPB is taken as 14 percent. What you can see here is that it is mentioned as coarse and fine AP c means coarse AP f means fine. So, once the packing is done for ammonium perchlorate how it is going to happen? If you look at the particles are added into the propellant matrix, if you look at if you just add only the coarse particle there may be some you know gap between the coarse particles remain. So, if you make a combination of coarse and fine particles the packing density or the sorry rather the packing efficiency will be improved because that is going to take up by the smaller particles.

So, in many occasions this bimodal type of combinations like coarse versus fine particles are used. So, coarse and fine. So, it is not always necessary that they are having like a 50 to 50 percent 50 percent combinations, but they may be mixture of like 80, 20 or 70, 30 depending on the requirement and the size of the ammonium perchlorate crystals. Now, in this case in the literature it is in the study it is shown that once you have like 86 percent of AP and 14 percent of HTPB you can see some bluish flame is shown here.

You see this is a bluish flame seen here. As we have you know increase in to increase the HTPB percentage the flame colour and flame structure is going to change because now you are changing the fuel here. You are keeping the oxidizer percentage 84 percent now you are increasing the fuel. So, it is actually changing the flame, but in these two picture we are not able to see the difference, but if the fuel percentage is actually increased further we can see the flame bluish flame is now turning out to be the yellowish flame. So, not sufficient amount of you know oxidizer is available to burn all the fuel species and because of that some you know yellowish colour is actually showing here. So, as you can see this is becoming slightly in the fuel rich side because it is not burning properly.

So, and accordingly the flame temperature also you can see it is actually decreasing for this case it was 2680 for 84 once you increase the fuel it is not burning properly. So, because of that you can see the temperature is also decreasing. Now if you look at the effect of the pressure we can see that once you increase the pressure we can actually see for the same combination of AP and HTPB like 86 percent AP 14 percent HTPB here also 86 percent AP 14 percent HTPB we can see the as you increase the pressure the burning rate is actually increasing. So, what we have seen earlier that the burn rate is going to a function of pressure for the double base propellant similar thing can happen for this one also that as you increase the pressure the burn rate is going to increase. And one can actually do the similar experiment in a Crawford burner it is a constant pressure burner like you can maintain a pressure by filling up nitrogen and we are letting some propellant strand to burn and if we have set some specified length we put some two fuse wire and that fuse wire will be connected with some timer unit that will count the time between this two fuse wire.

So, once you start burning from the top and letting the circumferential part inhibited by some coating. So, the burning will take place only from the top surface and it will regress further. So, if you measure the time taken for this length to burn we can easily find out the regression rate for this particular pressure let us say P 1 we can get the value of R 1. That I think we can do it for other propellants also wherever there is a combination of oxidizer and fuel we can do that, but this thing can be done for the composite propellant and we can find out the value of R 1. So, if you do it for other pressure we can actually find out how much time it will take maybe different it is T 1 it may be T 2.

So, experiment shows that as you increase the pressure it is actually increasing. So, very much we can say that it is also a pressure dependent, but I think you we can actually look at the decomposition and the fuel species how the diffusion flame is forming and we can look at how the effect of you know this one we said that how the ammonium perchlorate decomposition is going to affect the burning processes. How they are going to interact to each other the fuel species the oxidizer species coming out from the ammonium perchlorate decomposition they are going to react with these fuel species they may form some you know initial diffusion flame and later on the fuel vapor and the oxidizer vapor from the premixed flame can actually mix together and form a final diffusion flame. So, one thing we can see the difference between the double based propellant and the composite propellant is that the double based propellant can be considered to be kind of a premixed flame whereas, the composite propellant containing the premixed flame and the diffusion flame. I think in the in the next lecture we will just discuss this part in detail that how ammonium perchlorate premixed flame is going to form and then how the you know interaction between the oxidizer species formed from the premixed flame is going to react with the fuel species formed from the pyrolysis of HTPB and how they are forming the diffusion flame.

And, we can see that the flame is actually standing from a distance from the propellant surface and we can consider this to be a standoff distance and from there actually we can start doing the analysis that how the heat transfer from the flame is coming to the propellant surface. And, eventually we can actually try to get some you know analysis and try to put the regression rate equation and we will try to understand again for a composite propellant how the burning rate is very much dependent on the pressure. So, what we had we had done for the double based propellant we will try to do the similar exercise and we will try to understand how this you know burn rate law is very much valid for the composite propellant ok. So, I think this R equal to a to the power n.

So, it is equally valid for this one. So, how we are actually getting this one, how we are relating that pressure is you know very much influential for the burning rate of composite propellant as well and what a is doing for the composite propellant. So, that I think we will talk in detail in the next lecture. Thank you.