Course Name: Combustion of Solid Fuels and Propellants
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Lecture: 25 Combustion of Nitramine Composite Propellants

Hello everyone, welcome to the NPTEL online certification course on Combat Analysis. We have discussed about the combustion of solid fuels and propellants and we were discussing about the combustion of solid propellants. In previous modules we have covered the combustion of different type of solid propellants starting from like double base propellants, then we talked about the composite propellants. Now, since we discussed in previous class that you know since we are talking about the composite propellants I think it is also important to know some of the nitramine composite propellants because they are also going to form the composite propellants like AP composite propellant. For example, like we have already learned about the combustion mechanism of ammonium perchlorate based composite propellants like ammonium perchlorate is used as oxidizer. So, similarly the nitramine propellants can also be composite propellants, nitramine means we are talking about the RDX and HMX as the oxidizer and they can be mixed with different polymeric binders.

For example, like HTPB hydroxyl terminated poly butadiene or even GAP glycidyl azide polymer. So, if we mix with the polymeric binder they can also form the propellant and those type of propellants are called nitramine composite propellants. And then the another category of propellants we have talked about the CMDB propellants like composite modified double base propellants. Basically that is a modified version of double base propellant.

If you recall our discussion during the chemical propellants or we once we talked about this different type of solid propellants there we talked about the composite modified double base. In case of composite modified double base propellant we said that double base propellant is modified its characteristics by adding some amount of you know crystalline oxidizers for example, ammonium perchlorates or even nitramine oxidizers like RDX or HMX. So, we will try to understand the different you know basics of combustion mechanism of nitramine composite propellant as well as composite modified double base propellants. Now, as I said that when HMX and RDX, HMX or RDX particles are mixed with the polymeric binder such as like hydroxyl terminated polybutadiene or even glycydyl azide polymer, nitramine composite propellant is formed. Now, we have to remember that the in case of you know once we add like HMX or RDX we are actually adding some fine crystals, but you have to remember one more thing that unlikely like ammonium perchlorate oxidizer, HMX and RDX molecular kind of stoichiometric.

So, they are kind of you know balanced with fuel and oxidizers. So, upon decomposition and gas phase reactions they generally do not produce any oxidizing species. What we expect from the oxidizer for example, like ammonium perchlorate, ammonium perchlorate will decompose to you know perchloric case ammonia and perchloric acid and later they will further decompose and it is going to produce like oxygen and oxidizing species. But in case of HMX or RDX they are you know having like stoichiometric composition of the molecular actually stoichiometrically saturated. So, it is not going to produce any kind of oxidizer there.

So, if you add the polymeric binder into the you know HMX type of propellant what essentially HTPB or the polymer is going to do is going to produce some carbonaceous you know gaseous substances which will add to increase the specific impulse or the performance. But it is not going to you know that way it is not going to react with the oxidizing species produced from the HMX or RDX. So, before understanding the combustion mechanism of you know HMX or RDX based nitramine composite propellants I think it is important to understand the thermal decomposition of HMX as you have already learned the thermal decomposition of other oxidizers I think let us look at the one of the nitramine oxidizer which is like HMX. So, HMX the name I think you already learned in the discussion of the propellant chapter or propellant module. So, we said that HMX is her majesty explosive or it is you know tetra methylene tetra nitramine cyclo tetra methylene tetra nitramine.

So, if you write down the formula for that one I think all like HMX and RDX can be added to any kind of polymer and they can form the nitramine composite propellant. So, we have already learned earlier that this one is cyclo methylene tetra nitramine or if you write the formula it will be something like you know this we said cyclo tetra methylene. So, I think the formula is something like this not here it is connected here like this. Similarly, for RDX I think we already know that it is cyclo tri instead of tetra it is like cyclo tri methionine tri nitramine. So, as I said we have to remember that the in case of you know nitramine composite propellant we have to remember that these although HMX and RDX are highly high energy materials and they produce like high temperature gaseous products, but we have to remember that they are you know kind of stoichiometrically balance material.

I am talking about HMX and RDX they are stoichiometrically balance materials what does that mean? So, that means that they do not generate excess oxidizer species. So, if you add the you know gaseous fuel fragments through like you know you are adding HTPB or even GAP. So, they will produce fuel species. So, what is essentially is going to do is this is going to increase the volume of the gaseous substances. So, they are is not their role is not to I mean react with the oxidizer species because you know it is not excess oxidizer species are available upon the decomposition of HMX and RDX because they are stoichiometrically balance materials.

So, whatever the binder we are adding the fuel species produced from this you know pyrolysis of the HTPB or even GAP the fuel species will increase the volume of gases and that will you know increase or enhance the specific impulse that is the role is going to play. So, I think we have to remember in the context of nitramine composite propellant once we add polymeric binder with the HMX or RDX this is going to happen. Now, before we proceeding with the you know HMX or RDX based composite propellants flame structure we should actually know that how the thermal decomposition take place for you know for nitramine oxidizer. So, let us say let us look at the HMX case. So, you know if you recall that in general way of you know looking at the thermal decomposition the best way of doing is like doing some you know TGA,DTA measurement thermogravimetric and differential thermal analysis we used to perform.

So, if I just write down if I just show you the general you know thermogram like if you say that exothermic is the upside and endothermic is the downside. So, we may see that the there will be two endothermic peak is shown for HMX. So, generally the endothermic first endothermic peak is corresponding to the. So, this one is corresponding to the phase transformation from beta phase to delta phase and the second. So, and typical temperature of this one is around 463 Kelvin and the second endothermic peak which is corresponding to the you know phase changes.

Phase changes means we are talking about the liquid to solid. So, here this one for phase change from solid to liquid and typical temperature here it takes place around you know 550 Kelvin or so, 550 Kelvin and this one is 463. And so, I have written the exothermic peaks slightly you know away, but it actually right after like 553 Kelvin the exothermic peak is used to form. So, right after this one is going to start. So, this exothermic peak is you know corresponding to the decomposition.

So, or the gas phase reaction. So, if you like want to see the gas phase reaction it is going to produce like a you know high heat release due to the gas phase reaction and typical reaction are something like this like overall decomposition if you see. So, we have like cyclotetramethylene tetra nitramine. So, C4 we can write in this form actually CH2NO2 and that whole 4. This will first you know going to decompose to NO2 + N2O +N2 + some aldehyde.

If you balance it, it will come something like this. Now, since the nitrogen dioxide is an oxidizer is going to react further with the this aldehyde this formaldehyde. So, this formaldehyde is going to react with the oxidizer nitrogen dioxide and they are going to you know produce some gas phase species. So, if you write that equation it is similar to kind of you know if you recall the double base propellant where we have seen this that you know the formaldehyde and acid aldehyde is going to react with the available oxidizer nitrogen dioxide and is going to form the nitric oxide plus CO + H2O. So, you can balance this one.

Now, this is you know probably the dominating reaction initially after the initial decomposition. So, once we say the initial decomposition and this is probably the you know dominating reaction immediately after decomposition, but it is going to form you know some fuel species because we can see that NO_2 is a strong oxidizer and CH_2 is going to work as a fuel component. So, they are going to be like you know very much going to react each other and going to have like exothermic reaction and is also faster and they will form the you know gaseous species. Now, products generated from these reactions can react further and they can even it can react further and like if the species generated from the previous reactions will contain like H_2 as the fuel component CO as the fuel component. So, they will react further and they will produce like you know nitrogen and water.

So, you can balance this one. There are oxidizers like NO and N_2O sorry this NO can react with the fuel component CO also because CO can further be oxidized. So, that can produce like nitrogen plus carbon dioxide and what about this N_2O? N_2O can actually going to form like NO plus N_2. Now, we have to remember that the overall reactions involving this NO and this N_2O they are kind of slow because these are like weak oxidizer. I think we have already discussed this thing in the context of the combustion mechanism of double base propellant and there we have seen that the nitrogen dioxide is kind of a strong oxidizer which is going to take place in the feed zone we have said and in the dark zone you know the reaction is kind of very slow where the nitric oxide is involved and that actually you know considerably slow reactions.

Of course, they are very much pressure pressure dependent. So, we are talking about slow reaction in at low pressure, but this is going to increase rapidly once the pressure go high. So, in at low pressure we can say they are going to react slowly, but as the pressure increases the reaction rate is going to increase at a higher rate. So, I think you know these are the typical decomposition reactions for the HMX and similar way the thermal decomposition of RDX will also take place. So, we can actually see the endothermic and exothermic peaks for the thermal decomposition of HMX and since it is stoichiometrically balanced material as we said that it is not going to produce like excess oxidizer because as you can see that through the reactions also is not producing like extra oxidizer rather it is producing like the combustion products for example, like nitrogen water and carbon dioxide.

Some of the fuel species produced like through these reactions like CO and H_2 which can actually react further with the available oxidizer like NO and is going to form like nitrogen and water. Similarly, like nitric oxide can react with the carbon monoxide which is also a fuel component because that can react further to become CO_2. So, through this reaction they can actually form nitrogen and carbon dioxide. So, that way I think we can understand that you know because of the stoichiometrically balanced materials HMX is not going to produce excess you know oxidizing species. So, even if you add the polymeric fuel into the you know the propellant matrix it is not going to help in a sense of you know combustion through like oxidizer and fuel rather the fuel vapor produced from the HTPB is going to increase the volume of the gas which will in turn you can say that it is going to increase the performance or the specific impulse.

Now, if you look at the flame typical you know flame of HMX now we should remember that these are like fine crystals HMX generally you know crystalline particles they are fine crystalline particles. So, if you want to measure the linear burn rate for HMX is kind of difficult because due to the thermal stress the crystal is going to easily break. So, if you have the you know some if you take bigger crystal and if you use some you know nichrome coil to ignite it. So, let us say we just provide some you know electrical signal and we just use nichromes where to heat up and we want to you know burn this one what is going to happen is due to the thermal stress formed due to the initial burning is going to break into you know small crystals and then individual small crystal is going to burn. So, eventually we will not be able to find out the linear burn rate just by you know burning the individual bigger crystal.

So, if we near really need to measure the linear burn rate of the HMX we have to prepare some pallet by you know pressing through hydraulic press or some pallet maker we can actually make some pallet and then we can actually try to you know measure the burn rate of the HMX. So, you can just start burning from here. So, it will just show the linear regression and it can burn. Now, this photograph shows the typical you know flame pictures at different pressure. So, during the pressure of you know 18 atmosphere or 0.8 MPa we can see the luminous flame cities you know kind of slightly blowing away from the flame from the burning surface. Now, as we increase the as we can see that as the pressure is increased the luminous flame cities rapidly you know approaches to the to the burning surface. However, there are some wavy structures are seen you see this the some waviness structure in the flame sheet we can see here.

So, due to the you know changes in pressure we can see there is a waviness in the flame structure. Now, further increase in the pressure this will become stable and you know it is kind of a one dimensional shape and it is just staying above the you know burning surface.

So, this is the burning surface. So, you can see this is kind of staying near to the burning surface. So, these are the typical flame structures flame photographs of the HMX at three different pressure it has been shown in literature reference has been given here if you wish to look at you can look at more of it. Now, if you just want to look at the typical thermal we can just write it here actually. So, if you just want to try to get a similarity of heat transfer analysis what we did for you know for double base propellant and composite propellant. So, for the nitramine you know oxidizers if you just want to see the typical zones of combustion they are divided into three zones.

First one is the we can say the solid phase zone or crystallized solid phase zone, solid phase zone. Second one we can say it is you know solid and liquid or condensed zone condensed zone. And the third one we can say the gas phase zone where the gas phase reactions will take place. Now, we have already seen this one seen this through the reactions if we just want to write down the you know how the heat transfer is taking place. So, we can actually just use the thermal model what we have used for you know other cases.

So, let us say this is the propellant surface. So, there is a very thin areas where like you know condensed phase reactions will take place. So, this is typically of the order of like 0.1 mm or so. Now, the temperature is going to increase from the initial temperature Ti to some surface temperature Ts and that will finally, go to the you know is going to increase to some flame temperature.

And this is very typical what we have said. So, this is like gas phase. So, this is zone 3, this is zone 2 and this is like the solid zone 1 ok. Now, what essentially is happening that heat transfer from the flame zone is going to the you know condensed zone or the condensed zone or the burning zone. And eventually they it is going to heat up the propellant surface because propellant initial temperature was Ti.

So, the initial temperature will become like the surface temperature Ts. So, we can say that this one like the surface and this typical condensed zone temperature are almost similar just because you know the thickness of this zone is very small about the order of like 0.1 mm. So, we can consider to be average temperature of Ts. So, the temperature is increasing from this Ti to Ts that heat is coming from the you know the heat transfer from the flame zone and the reactions taking place inside the zone 2.

So, whatever the heat transfer is taking place in the zone 2 we can if you just try to write down that that will be like degradation of the you know solid phase degradation. So, some you know m dot into let us say heat of reaction is delta Hc. So, m dot we can write it for unit surface area and we can write this as propellant density into linear regression rate into delta Hc. Whereas, you know the heat transfer from the flame zone is coming as like through the heat transfer kg dT dx, kg is the thermal conductivity of the gas in the gas phase reaction zone. So, these two heat are actually going to use to you know heat up the temperature of the propellant surface.

So, that is going to taken up by the propellant surface which is let us say propellant density into R into some you know specific heat of the propellant and we can write this is this from T s- T i. So, eventually we can write that this heat is taken up or provided by the you know this

$$\rho P \; r \; \Delta Hc + kg \; dT \; dx$$

ok. And one can try to you know get the thermal sorry one can get the boundary conditions and try to get the temperature profile across the you know these zones and one can one can get the. So, we can actually use the linear profile to get the data, but how are the further you know analysis can be performed by knowing some of these parameters. For example, like we can have like density and we can have the density, we can have the specific heat, we can have the thermal conductivity of the gas and we can determine how much you know heat is being produced through the reactions and we can actually get it for different you know pressure as well.

So, several data can be produced by conducting some of the experiments. We can actually try to you know relate this one that how the heat transfer is taking place to increase the temperature of in the solid phase zone and how the reactions are taking place in the condensed zone. So, in a sense the thermal decomposition of the HMX is going to play an important role for the HMX or RDX based composite propellant, what we have just said that they are kind of nitramine propellants ok. Now, if you look at some of the pictures of the typical this is the photograph of this is the photograph of the only the HMX flame. Now, if you look at the typical photograph of AP composite propellants and you know RDX composite propellant, what you can see here that we can see here that AP composite propellant is kind of you know different than the RDX propellant because there is we can see that the luminous flame appearing is appearing almost you know almost near to the flame near to the burning surface.

If you look at carefully it is almost you know appearing here almost closer to the burning surface whereas, the luminous flame you know standing at a certain distance away from the burning surface or certain distance above the burning surface in case of RDX propellant. So, this flame stand of distance is kind of similar to if you compare this as a dark zone for the double base propellant. So, it is almost similar to the you know dark zone for the double base propellant, but you know since we are talking about the RDX composite propellant containing some HTPB binder. So, that will cover with some carbonaceous you know species. So, we can say the gas phase is not homogeneous here rather the gas phase is kind of heterogeneous.

So, the luminous flame is coming due to this you know coming from the carbonaceous you know species as well as from the burning surface. So, what we have seen here it is not exactly the same as the double base propellant rather they are kind of bit heterogeneous because some of the fuel species are also present here which is going to you know create some of these you know luminous light. Now, going further if you know try to see that we can still you know try to put the analogy that the combustion wave structure of RDX you know composite propellant is kind of you know homogeneous compared to the APE composite propellant and it is relatively smoother. Now, of course, the extent of the dark zone is very much depending on the pressure. Now, since they are containing the nitramine composite propellants either it is containing RDX or HMX as the oxidizer and hydrocarbon polymers such as HTPB or GAP they are kind of very much similar to we can say the double base composite propellant what we will discuss in the following lecture that CMDB propellant or composite modified double base propellant.

Now, if we discuss these things further what we have already said due to the decomposition of RDX and HMX that they relatively contain high concentration of nitrogen dioxide or NO2 and the reactions between the NO2 and the other decomposition products for example, like formaldehyde are kind of you know react at a high rate at the burning surface and the exothermic reactions is going to take place. Now, the binder which is let us say HTPB which is kind of a polymeric binder. So, binder is going to diffuse some of the it is you know the gaseous species into the exothermic reaction zone and it is going to you know increase the temperature rapidly. Now, the NO2 will reduce I mean it is going to produce like NO which is also going to produce like luminous flame, but the reactions involving the nitric oxide or NO is kind of slow and of course, it is highly pressure dependent. So, we already said that the reaction involving NO is kind of slow and you know pressure dependent that we have already discussed during the discussion of you know combustion mechanism on double base propellant.

There are there also we have said that you know reactions involving NO is kind of slower whereas, the reactions involving NO2 is kind of faster. Now, because of that you know the luminous flame is somehow stands at a height above the burning surface which we are actually seeing it here. Now, due to this diffusion what we are saying that since they are stoichiometrically balanced material both you know RDX and HMX they are stoichiometrically balanced material. So, what does it mean it is not going to produce like excess oxidizer which is going to react with the fuel species produced from the binder. So, if you look at the picture here these are like typical scanning electron microscope images taken before the combustion.

So, this is just after the forming of the composite propellants involving RDX plus as a this picture is I think taken for polyurethane. So, this is like for RDX plus PU binder polyurethane binder. So, this first one is taken after making the composite propellant involving RDX and PU and this one is after quenching by rapid depressurization. So, the combustion was going on, but after sudden depressurization you can actually turn I mean put it off means you can extinguish it if we just decay the pressure at a faster rate. So, once after quenching by rapid depressurization we can actually look at the you know morphology of the surface again and what we found out that I mean if you look at the picture what literature says that the we can see there are some quench burning surface consisting of finely divided you know RDX particles and binder and melt and diffuse to each other.

If you look at it is quite different than the pre burning structure and the quenching structure. So, this kind of kind of confirm that the since the RDX is kind of stoichiometrically balanced material they are not going to react with the fuel species much because excess oxidizer is not present. So, the fuel species produced from the HTPB or the other binder they are going to diffuse to these RDX I mean gaseous molecule produced from the thermal decomposition of RDX and they are going to produce some kind of fine structures as you can see through this you know ACM micrographs. So, that way you can see it is significantly different you know flame structure of the AP based composite propellant and the nitramine based composite propellants. So, I think these are some you know discussions regarding this for further reading you may follow this book or even some of the literatures I think you can follow in order to understand the you know RDX and HMX based nitramine composite propellants.

The next discussion I think we should do that what about the composite mechanism of double composite modified double base propellant. Let us say if we add ammonium perchlorate in some percentage into the double base propellant what is going to happen? Similarly, if we add some amount of RDX or HMX into the double base propellant. So, then it will not be a homogeneous anymore because we are actually modifying the fuel and oxidizers in the double base propellant because initially double base propellant contains the NC and NG nitrocellulose and nitroglycerin and they are intimately mixed together and they form the homogeneous propellant. But once we are adding the ammonium perchlorate crystals into the propellant matrix then they are forming the you know modified composite modified double base propellant.

So, we in the next lecture we will try to see what are the different you know important parts involved in the combustion of composite modified double base propellant. Thank you.