Course Name: Combustion of Solid Fuels and Propellants
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Lecture: 23 Effect of Transients, Vehicle Acceleration, Binder, Catalysts on Burning Rate of CP

Hello everyone. So, we were discussing about the various effects on the burn rate of composite propellant. We have already discussed the effect of pressure, effect of particle size ammonium perchlorate particle size on the burn rate of composite propellant. We also talked about the effect of initial temperature of the propellant, because initial temperature of the propellant has an influence in effect, because the propellant gets heated by getting the heat from the flame. Once the flame hits of the propellant surface, the heat is going to transfer through conduction and the initial temperature of the propellant is going to change. And we have seen that the Ti is going to change to surface temperature Ts.

Now what about the influencing factor of this variation of Ti and that we have discussed through a temperature sensitivity coefficient. And we have also said that the for double base propellant the temperature sensitivity coefficient is comparatively higher than the temperature sensitivity coefficient of composite propellant. Then we have said that there are various you know influencing parameters which we need to consider in order to understand the these effect on the burn rate of composite propellant and in solid propellant in general. So, we have also said that other than pressure and initial temperature there are effects for effects of transients for example, like the effect of you know starts and stop or the variation in chamber pressure that is going to influence the burn rate.

The vehicle accelerations and spinning like the motor is accelerating with sudden acceleration due to which the burn rate of the propellant may also change. We have also said the composition of the propellant has you know major role on the burn rate of the propellant. So, composition means not only the size of the ammonium perchlorate, what about the effect of the binders? If we use different type of binders will they play a role on the burn rate of the propellant? What about the catalyst? Catalyst means the burn rate modifiers. If you recall during the discussion of the solid propellants we have said that although burn rate modifiers are used in a small quantity they have some significant role in you know modulating the burn rate. For example, like there are certain burn rate modifiers or catalyst which can enhance the burn rate whereas, there are certain category of modifiers which can actually inhibits the burn rate or decrease the burn rate.

So, the modifiers which can increase the burn rate they are like positive catalyst, the modifiers which are going to decrease the burn rate they are called the negative catalyst. So, we will discuss the you know how they are influencing on the decomposition of the ammonium perchlorate or the overall burn rate of the propellants in this lecture. So, let us quickly look at the effect of transients what we have just said that the you know during the operation of rocket engine the pressure may not remain steady. So, you know during we have to you know remember that the pressure what we said if you recall the pressure time curve we also plot there it may change and then it remain equilibrium and is going to tail off. So, during the ignition phase you know pressure is going to increase the chamber pressure going to increase port volume once the flame is going to spread port volume is going to filled up and then it reaches to equilibrium pressure.

So, during the these transients events also your burn rate is not exactly the same as the burn rate we consider for the you know equilibrium pressure. So, if you consider the transients events like starts and stop generally if you look at the ideal rocket assumptions there we have said that the change of the mass flow rate during the you know starts and stops or the transients processes we generally neglect it for the ideal you know rocket assumptions. But what about the chamber pressure variations because there may be some you know fluctuations in chamber pressure it may not be very high, but still it is not fully steady there may be some change in chamber pressure. So, what about that influence? So, we must need to consider the effect of transients you know due to the you know change in chamber pressure. So, there may be some time varying functions we have to consider about the burn rate like this may change with time.

So, you have to you know expand this series and if you just simplify this. So, the readers are requested to look more about this through the literature and they can find out how these you know transients effect are effects are model like there are some you know simplifications have been done. So, authors are requested to follow this one there must be some you know simplified models to you know model the transient effect. So, they can get the influence, but the main objective of bringing this one is to just to know that what are the influencing factors on the burn rate of composite propellant or you know solid propellant in general. Now, there is another effect is the effect of vehicle accelerations.

Now, you can see once the rocket is moving up and up the whole vehicle is you know subjected to acceleration. So, it is a continuous accelerating vehicle. So, is there any influence of the vehicle accelerations on the burn rate of the propellant. Now it has been reported in literature that if the you know acceleration vector is oriented with the you know port geometry with a 60 to you know 90 degree angle with the you know acceleration vector, then it has you know major or significant influence on the burn rate. But if it is you know not making you know larger angle with the acceleration vector angle means we are talking about the propellant surface.

So, if it is making an angle with the acceleration vector larger angle, then there is a high chance that it is going to influence the burn rate. The value of acceleration is also very important. Smaller you know acceleration is not have that much influence on the burn rate.

Generally if the acceleration is like more than 10 times g, then it has been said that it has you know major influence on the you know change in the burn rate or you know increase in the burn rate. There are some you know literature review one can look at that how the you know burn rate of the propellant is changing due to the effect of acceleration.

Now we must need to remember that the there may be some threshold value due to which the tangible effect will be observed, but we must also need to remember that the effect of acceleration is dependent on you know chamber pressure and the composition of the propellant. Of course, although we are saying so that the vehicle acceleration is going to influence the burn rate of the propellant, but in a sense this is also going to be dependent on the chamber pressure and you know the composition of the propellant. So, generally the slow burning rate propellant is more affected by the acceleration compared to the high burning rate propellant. So, slow burning rate propellant will you know will be more affected by the vehicle acceleration compared to the you know high burning rate propellant. So, these are like less impacted due to the acceleration of the vehicle.

Now it has been also observed that the pressure index n is also has an effect you know due to the acceleration of the vehicle. So, in general it has been seen that the value of n is you know going to be enhanced due to the acceleration of the vehicle. So, these are you know some literatures may be referred to due to referred for this understanding that how for different propellants what we say that slow burning propellant will get affected more due to the effect of the accelerations whereas, high burning rate propellant will less impacted and as the acceleration is going to be higher the influence on the pressure index n will be higher or the pressure index is going to increase. So, can we really go and look at what are the certain type of propellants and what exact values or what percentage it is changing for that I think some detail literature may be consulted. Now you know there may be a chance that the propellant surface may you know have some crack due to.

So, if you look at the inside part of there may be some crack due to you know rapid accelerations of the vehicle or you know due to certain you know sharp ingredients sharp pressure gradients certain change of the pressure. This may also going to you know improve the burn rate because you see this is creating some surface area separately which is going to you know increase the burn rate, but we of course, do not know that in which direction this is forming and how this is going to change the burn rate. So, there is no satisfactory theory behind it. However, since it is producing separate you know burning surface area this will enhance the burn rate, but we need to really be careful that whether this crack will lead to sudden you know you know sudden increase of pressure chamber pressure which will in turn is going to increase the burn rate which may not which should not lead to the failure of the motor. So, of course, it is enhancing or augmenting the burn rate, but this would be you know considered in light of the safety or the stable operation of the rocket.

So, different experimental data should be consulted for the design purposes and in general it has been also done to understand the influence of the you know vehicle acceleration on the burn rate. Now, we have also said that not only the ammonium perchlorate crystals has the influencing role on the burn rate of the propellant, but there are you know there is a major you know factors played by the effect of binders. So, binders may be like you know different type of binders have been tried and of course, they are having varying you know physio chemical properties as we have already seen during the discussion of the solid propellants that binder is the kind of a structural glue which is going to hold the solid crystals like ammonium perchlorate or if we have like aluminum particles in the ingredients. So, it the binder is going to provide the you know glue for holding the solid particles within the propellant matrix. So, there are different type of binders have been tried for you know preparing the composite solid propellant.

For example, like hydroxyl terminated poly butylene which is like a very common you know binder used. The other binders may be like hydroxyl terminated poly ether, polyol, hydroxyl terminated poly acetylene, hydroxyl terminated polyester. So, there are different type of binders have been tried and along with that they are different you know type of physio chemical properties are also involved. Now, we have seen that specific impulse is also dependent on the type of binder and mass fraction of the binder and once they are mixed with the epi particles they their performance is going to change. Now, if we look at the first one plot where this poly butadiene, poly urethane and poly acetylenes have been compared with a different you know percentage of the binder content starting from like 7.5 to 25 or more. Now, here we can see that the burning rate of epi composite propellants appear to be like dependent on these thermochemical properties. We can see that you know specific impulse is kind of higher and it is maintained in the region for the higher mass fractions of poly urethane. If you see for the poly urethane you see this triangle legend which is like it is maintaining the higher ISP in the region of higher mass fraction of poly urethane. So, higher mass fraction of poly urethane means we are talking about like 15, 20 or more.

So, it is maintained. However, for other cases like poly butadiene which is the circle one, poly butadiene the poly acetylene they are actually dropping they are dropping for you know higher mass fraction of the binder. So, this is the binder content. So, if you see after like 15 percent or so, they are actually showing the dropping in nature, but it is not drop that sharp. So, poly urethane has some you know positive effect because the poly urethane is containing some oxygen in the you know molecule present in the poly urethane that is probably going to you know increase the burn rate and eventually that is going to provide the higher specific impulse value. Now the we have also seen that the adiabatic flame temperature is going to increase if we decrease the binder content because the then the oxidizer to fuel ratio will be you know far towards I mean close towards the you know higher temperature.

So, lower the binder content is going to improve the you know temperature of the combustion products. Now, if you look at the burn rate versus pressure for various you know polymeric binder shows a different type of burning profile. So, they are in general they are following the linear train where you can see that the burning rate is going to increase with chamber pressure. So, they are plot you know logarithmic they are plotted in logarithmic scale. So, burning rate is going to linearly going to increase with the pressure and you can see for different type of binders the burning rate is actually changing and they are actually maintaining a same you know initial temperature with 293.15 Kelvin. So, here we are just seeing the effect of binder on the burn rate of epi composite propellant with various binder. So, HTPB, HTPE, HTPO, HTPA and polystyrene we can see that HTPB binder is somewhere over here whereas, for other binder they are actually showing even better you know burning rate once it is increased with chamber pressure. Now, coming to the higher burn the higher pressure region. So, we have seen this is in the lower pressure region. So, you look at the chamber pressure value it is only up to like 0.2. So, which is like 2 atmosphere to about like around you know 8 atmosphere on 7 atmosphere. So, there we have seen that the binders is clearly showing that it is linearly following and even it is increasing with increasing pressure. Now, if you look at this plot where we can see that for the case of HTPA and for the case of HTPO, hydroxyl terminated polyacetylene we can see that after a certain pressure. So, you see this one and this one and also it is with other also as it is not increasing at that rate compared to the lower pressure. Now, with the higher pressure if you see the slope is not very high you see compared to the HTPB, HTPB is kind of increasing here whereas, they are not increasing at that rate.

So, if you compare the burning rate versus pressure in the high pressure region for the binder like HTPA hydroxyl terminated polyacetylene or HTPO they are actually showing some dropping nature after certain you know pressure. So, around 6 or 7 MPa they are not going to increase further. So, burn rate is not going to increase further with the you know with the increase in pressure. So, this is very important consideration that the this is going to show some kind of a mesa burning trend like once we raise go beyond like 3 MPa we can see this it is going to be a show some kind of a decrease in burn rate. If you recall that we talked about the mesa burning, the normal burning, mesa burning and plateau burning.

Plateau burning is like a remaining constant where n equal to 0 and the mesa burning shows like the decrease in burn rate. So, the further effect further increase in pressure has a negative effect on the burn rate and we can see the mesa burning after the pressure somewhere around 8 or so. So, therefore, we can see that the burning is kind of you know interrupted above this pressure. So, for particularly for HTPE and HTPO this type of burning profile has been seen. So, we can in general what we can say is that the binder not only you know influences the burn rate, but also the pressure index or the pressure component pressure exponent of the burn rate in the high pressure zone.

So, here if you try to find out the value of you know r equal to f to the power n, if you try to find out the value of n we can say that the pressure index n or pressure exponent n is not the similar compared to like different binders. You see for case of like HTPO and HTPA they are actually going to become negative after certain pressure. So, although in case of low pressure regimes we have seen that they are following you know linear trend and continuously increasing. However, in the high pressure regime they are not following the similar trend. For example, like HTPE is clearly showing the linear I mean clearly showing the increasing trend whereas, the HTPO and HTPA they are actually showing decreasing trend or mesa burning profile after certain pressure.

So, that way they are going to change the pressure exponent. So, it is not only is going to change the burn rate, but also is going to influence the pressure exponent. So, we should you know remember these things that binder has very much influencing role on the burn rate as well as the you know pressure exponent. Now coming to the other you know influencing parameter which is the catalyst. Now catalyst as I said catalyst may be like two types one is the positive catalyst which can you know increase the burn rate and the other catalyst which can the decrease the burn rate which is called the negative catalyst.

So, or catalyst means we can say that they are burn rate modifiers. There are certain oxides of iron iron you can see it is going to influence the burn rate as we increase the pressure. For example, like Fe_2O_3 other way oxides of iron are like Fe_3O_4 they are used as burn rate modifiers and since they are going to increase the burn rate with respect to pressure they are termed as the positive catalyst. So, you can see we have to remember that how they are influencing the burn rate they may actually help in decomposition of ammonium per plate or they may actually increase the reaction rate in the gas phase. Because once the oxidizing species and the polymeric fuel vapour or the vapour species form due to pyrolysis of the polymeric binder they are going to mix in the gas phase.

So, if it is influenced by the catalyst the gas phase reaction is going to improve and that way it is going to influence the burn rate. So, in a sense we can say the positive catalyst can improve the decomposition process as well as the gas phase reactions. Now, what we should remember that the diffusional mixing between the gaseous decomposition products and the epi particles this is going to depend I mean this is going to you know determines the heat flux feedback coming from the gas phase to the condensed phase. Because if you recall the you know flame typical flame structure of the composite propellants. So, we have said that the three flames are remaining at a same plane we have we have considered and this is called the stand-off distance stand-off distance.

So, the heat feedback coming from the you know gas phase to the condensed phase is going to influence the burn rate of the propellant. So, at the burning surface how the heat feedback is coming that is going to very very important. So, if you put some kind of catalyst. So, this catalyst may is going to improve by changing the you know the reaction rate in the gas or we can say the reaction rate in the gas phase is going to be in is going to be enhanced by addition of catalyst. Now, this catalyst will act on the decomposition of the reaction of the condensed phase or in the reactions of the gas phase of the you know gaseous decomposition products.

So, as I said there are two types of catalyst positive catalyst that can increase the burn rate whereas, the negative catalyst that will decrease the burn rate. You know organic oxides for example, like you know organic iron oxides normal like iron oxides can act as positive catalyst. There are other you know compound which can act as catalyst like calcium carbonate CaCO3, strontium carbonate SrCO3 they can also act as you know burn rate modifier or burn rate enhancer. They are also going to act as positive catalyst. You know strontium carbonate can be available in mineral as strontinite.

So, this can also influence the burning rate of the propellant. Now, if you look at the different type of iron oxides have been used different time in the sense like different size of the iron oxides are used. Now, what we should remember this thing is that they are going to improve the surface reactions in the catalyst in the burning zone. So, if you look at the you know burning zone here. So, if the catalyst are there, their surface area is very important because the surface reaction is going to be enhanced by the catalyst.

So, therefore, the particle size reduction is very influential or the per you know per unit surface area per unit of the mass of the particles are is going to very important or the specific surface area that is going to play a role in enhancing the reaction in the surface. There are other catalyst like the Nb12 ferrocene, di Nb12 ferrocene and iron acetate. So, the other catalyst are also tried is like you know hydrated ferric oxide, Nb12 ferrocene, there are di Nb12 ferrocene these are also tried as burn rate modifiers or positive catalyst rather. If you look at this one, this one is another type of catalyst like carborane, n-hexyl carborane they are also tried as burn rate modifiers or positive catalyst. We can see here that this n-hexyl carborane are basically going to provide some you know boron atoms in the surfaces in the propellant surfaces.

So, that will is going to serve as fuel component in the combustion web and the thermal decomposition of n-hexyl carbon n-hexyl carborane is going to generate boron atoms. So, this is going to generate boron atoms and if you recall we had said in the introduction part that boron is also going to act as fuel because it has a very high you know heating very high energetic content or in terms of you know gravimetric and volumetric heating value boron has very high energetic content. So, this will act as fuel as well which in turn is going to you know provide heat at the burning surface. So, this you know enhance heat flux going to decompose the AP particles further and the binder on the burning surface which in turn is going to improve the burn rate of the propellant. So, if you look at the non-catalyzed composite propellant versus the catalyzed composite propellant which is containing like 13 percent n-hexyl hydrocarbon n-hexyl carborane.

So, that is the reason that it is going to improve the burn rate of the composite propellant because on decomposition of this n-hexyl carborane is going to produce some amount of boron atoms which will act as fuel in the burning surface and that will provide the heat flux to the propellant surface which will further you know help to decompose the ammonium perchlorate and the polymeric fuel binder which will in turn is going to increase the you know oxidizer species and the fuel species which will going to eventually going to burn in the gas phase and that will eventually going to increase the burn rate ok. So, that is why they are called like the positive burn rate modifier or they will act as like positive catalyst. Similarly the opposite you know role is played by some different catalyst which are called like negative catalyst which will inhibit the burn rate or which will reduce the burn rate. So, I think we will talk about the negative you know burn rate modifier in the next class. Thank you.