Course Name: Combustion of Solid Fuels and Propellants
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Lecture: 24 Effect of Catalysts on Burning Rate of CP (contd...)

Hello everyone, we were continuing our discussion on combustion of solid propellants. In this lecture we discussed the effect of various you know influencing parameters on the burning rate of composite propellants. And we have discussed so far the effect of the pressure, effect of ammonium perchlorate crystal size, the other parameters such as the like the gas velocity inside the port, the transients effect like the pressure fluctuations can also influence, the vehicle accelerations can also influence the burn rate.

However, we need to remember that in the high pressure the mixing process between the gaseous fuel produced due to pyrolysis of the polymeric binder and the oxidizing species produced due to decomposition of ammonium perchlorate is a vital one. Because in the high pressure although the reaction rate is very fast the diffusion rate is not improved that way. So, in a sense in the high pressure range the epi composite propellant is dominant by the diffusion process or mixing process between the fuel vapour and the oxidizing species. Whereas in the low pressure ammonium perchlorate premixed flame dominates.

So, this part I think we have discussed thoroughly earlier and we have seen the effect of ammonium perchlorate crystal size as the crystal size becomes smaller the standard distance becomes smaller and the heat feedback coming from the gaseous reactions is also going to increase which will in turn helps in improving the burn rate or enhancing the burn rate. And we should appreciate that the burning rate or the burn rate or the regression rate of solid propellant is very important parameter for the design of you know rocket motor. So, the influencing parameters we need to understand that what are the major influencing parameters for burning rate of composite propellants. And of course, this diffusional process is very important that is why the major parameters influencing the burn rate are the pressure and the ammonium perchlorate crystal size. However, there are other parameters which can also influence the burning rate of composite propellants.

Now in today's lecture we will talk about the effect of catalyst on burning rate of composite propellant. I think we have already started our discussion in the previous lecture that there are certain catalyst or burn rate modifiers which can you know increase the burn rate of composite propellants. Those are termed as the positive catalyst and there are certain burn rate modifiers which are going to influence the burning rate in such a way that the burn rate is going to decrease those are called negative catalyst. So, in this lecture I think we will talk about both the positive catalyst as well as negative catalyst and their role on the burning rate of composite propellants. Now let us quickly look at what we are talking about here that if we look at the burning surface here this one you know composed of various size of crystals which are like ammonium perchlorate crystals.

And we said that there are three you know flame let us say they are appearing at a certain plane from a distance x* from the propellant surface. So, this is our you know flame. So, the heat feedback is coming from the flame to the propellant surface. So, we can say the heat flux feedback from the gas phase to the condensed phase at the burning surface is taking place. So, the catalyst can act in both ways like either it can act on the decomposition of the ammonium perchlorate.

So, it can improve the decomposition reactions in the condensed phase or it can act on the reaction in the gas phase of the gaseous decomposition products. So, whatever the reactions is taking place of the gaseous decomposition product the catalyst can act on that. So, these ways these way it can either increase the burn rate of the propellant or it can decrease the burn rate of the propellant. So, if they are going to increase the burn rate of the propellant increase the burn rate. So, we can say the catalyst that increase the burn rate of the propellant we call them as positive catalyst.

For example, we have already seen that some iron oxides like Fe2O3 some organic iron compounds can act as positive catalyst. Whereas, there are certain catalyst that decreases or reduces reduce the burn rate of propellant are called negative catalyst. Some examples are like lithium fluoride, calcium carbonate, strontium carbonate, SRCO3. So, they act on the act on you know reducing the either the decomposition of the ammonium perchlorate or in the gas phase reactions which in turn influence the burn rate by reducing the burn rate of the propellant. So, there are certain you know ingredients which may be used in a small amount, but they are having influencing effect in terms of you know changing the burn rate.

Now, let us look at the positive catalyst and then we look at the negative catalyst. So, I think we have already looked at a plot where it shows the change of burn rate versus pressure for various you know particle size of iron oxide catalyst. So, you can see the non-catalyzed one is shown by the black squared legend. So, this is the non-catalyzed case this one. Whereas, for the catalyst case we can see that the burn rate is going to increase as we you know adding the catalyst, but there is a change we can see here once we reduce the size of the catalyst because you see this 0.16 is this one, this one is 0.01, 0.16 micrometer catalyst size, this one is 0.3 micron whereas, this one is 0.2 micron.

So, various size of catalyst have been tried and we have see we are we are seeing here that as the catalyst size is reducing the effect on the burn rate is actually improving because you know the total surface area of the catalyst particle at a fixed concentration is going to be an important factor like the surface area of the catalyst. Because that will in turn is going to influence the reaction is going to influence the reaction rate. Now, the surface area of the catalyst is going to play an important factor for you know attaining the high catalyst efficiency and which in turn is going to influence the reaction rate and eventually that will you know increase the burn rate of the propellant. Now, if we use a very finely you know divided iron oxide particles for example, like 0.2 micron, 0.2 micron means 200 nanometer, 160 nanometer, 300 nanometer and it can be observed from this plot that compared to the non-catalyzed case for the catalyzed case the burn rate is going to increase and as we have smaller size particles for catalyst we can see the burn rate is actually even higher for small size catalyst compared to the bigger size catalyst. There are other you know iron or organic iron compounds which are more effective in terms of increasing the burn rate because you know they may form like district discrete iron oxide particles during their decompositions.

So, certain you know organic iron compounds for example, like n-butyl ferrocene there are other also n-butyl di n-butyl ferrocene, iron acetate, hydrated ferric oxides. So, there are certain iron compounds which can be more I mean which was founded to be more effective because you know upon decomposition of these catalyst is going to produce very fine iron oxide which in turn is going to help in you know improving the reaction rate of the propellant and which in turn is going to increase the burn rate of the propellant. Now they are is going to you know bonded with the polymers like the HTPB polymer or even polyester polymers which are used as binder.

So, basically the catalyst are bonded to the polymers which are used as binders in the propellant. Now there are other catalyst which have been tried for example, like if you look at this plot we can see there are other catalyst which is showing almost like 10 folds of increasing burn rate. If we see here that almost for all pressure cases for non-catalyzed versus catalyzed if you look at this one, this one is like n-hexyl carburet. There are other of course, carboranes are used n-butyl carburet, there are iso-butyl carburet IBC and then n-hexyl carburet or NHC. Now why they are very important in terms of catalyst just because the carbon contains carbon, hydrogen and boron atoms.

Now once they decompose so once the carburet goes into thermal decomposition it produces boron atoms which is highly energetic. If you recall our discussion on the solid propellants during that time I think we talked about the different type of metallic fuels. If you recall that we talked about the metallic fuels, we talked about the different polymeric binder, we talked about the different oxidizers. In terms of fuel we have said that there are different metallic fuel which are tried as the fuel part of the propellant. In that sense we have said that boron is one of the important fuel because it has high gravimetric and volumetric heating values.

And in case of this catalyst, carbon type of catalyst they are going to once decompose they are going to form like boron atoms which are highly energetic and it is going to be oxidized by the oxidizing fragments formed from the AP decomposition and that is going to react with that oxidizing fragments or oxidizing species. So, that will eventually is going to produce you know high heat at the burning surface and that in turns is going to enhance the decomposition of the AP particles and of the binder present in the burning surface. So, what we are just saying here that the catalyst are present, ammonium perchlorates are also present so ammonium perchlorates present and these are bonded in the HTPB binder.

So, if you recall the normal you know reaction mechanism or the burning mechanism of composite propellant what we said that ammonium perchlorate is going to produce some you know APPF or ammonium perchlorate premixed flame your fuel is going to produce some fuel vapour which is going to mix and they are going to produce some primary diffusion flame and later on they are going to form some you know secondary diffusion flame or final diffusion flame. So, once we add this carborane type of catalyst what is happening upon decomposition of the carborane they are going to form some boron atoms you know they will form some boron atoms and these boron atoms is going to oxidize by the presence of the oxidizing species produced due to the decomposition of the ammonium perchlorate.

So, once the boron particles react with oxidizing species they are going to produce high heat. So, which in turn is going to increase the temperature of the gaseous species and is going to improve the heat feedback coming from the gas phase reactions. So, the boron particles burn in the in this zone and is going to provide the heat feedback to the propellant surface or the burning surface of the propellant which in turn is going to improve the you know decomposition of ammonium perchlorate as well as the pyrolysis of the HTPB or the polymeric binder which in turn is going to increase the regression rate of the propellant or the burn rate of the propellant.

So, the positive catalyst play a role either by you know improving the decomposition of the ammonium perchlorate or the polymeric binder pyrolysis of polymeric binder or it can eventually going to improve the gas phase reactions you know happening in the flame zone. So, in a sense the catalyst ultimately is going to increase the burn rate of the propellant and that is why they are called positive catalyst.

Now, interestingly we have to look at one more thing here that if you look at the for any you know percentage of catalyst such as iron oxide catalyst the burning rate increases with you know decreasing D0 of the catalyst here Fe2O3 catalyst. Now, otherwise if you look at the addition of particle for example, like let us say if we just consider any particular pressure let us say 2 MPa or maybe some 5 MPa. Here you can see once you add the catalyst the burning rate is increasing from about you know it was somewhere over here for somewhere over here for non catalyst case which is going to increase to here for catalyst case if you decrease the particle size it may go even higher.

Now, the surface area of each of these Fe2O3 particles plays very crucial role in you know its catalytic effect. Now, since the pressure component exponent remains almost unchanged upon the addition of the Fe_2O_3 catalyst the we can say the catalyst is considered to be the more effective in increasing the rate of gas phase reaction rather than you know having effect on the reaction in the condensed phase.

So, in experiment it has been observed that the pressure exponent you know does not change much for the Fe_2O_3 catalyzed propellant. Therefore, we can say that it is more effective in increasing the you know reaction rate of the gas phase reactions rather than you know playing an effect or playing in positive effect in the condensed phase reactions because the pressure exponent is not changing that much. But there are certain catalyst which can you know improve the condensed phase reactions or sometime like it can improve the decomposition of ammonium perchlorate for example, like certain oxides which can play a role in improving the decomposition of ammonium perchlorate or it can change the thermal decomposition of ammonium perchlorate by you know reducing its temperature or some you know high temperature decomposition and low temperature decompositions those processes can be modified by presence of some oxide catalyst.

There are other catalyst for example, like copper chromate $CuCrO_4$ copper chromate, but you know it can improve the bond rate of the composite propellant, but it may compromise with the thermal stability of the propellant. Generally once we add copper chromate with the ammonium perchlorate based composite propellant the thermal stability of the propellant is kind of lowered and sometime it is lead to some spontaneous ignition.

So, that way it is not very thermally stable and in that sense copper chromate cannot be you know considered to be a good catalyst because it is actually leading to some you know degrading quality of the composite propellant. However, you know carburan are carburan are kind of effective catalyst in you know improving the bond rate because you can see it can increase the bond rate in terms of like values almost like 10 times for various pressure ranges. And the major reason for this one is that you know the thermal decomposition of carbon is going to produce boron atoms which is highly energetic and that is going to react with the oxidizing species formed due to the decomposition of ammonium perchlorate which in turn is going to increase the heat release in the reaction and that will improve the heat feedback coming from the gaseous reaction zone to the condense zone at the burning surface and which in turn is going to increase the bond rate.

So, these are like positive catalyst which is going to increase the bond rate of the propellant, but there are certain catalyst which can you know decrease the bond rate of the propellant. For example, like lithium fluoride we have already said that there are certain catalyst which can you know negatively impact the bond rate of the propellant those are called negative catalyst.

So, one such catalyst is lithium fluoride and you can compare the you know thermal decomposition data of lithium fluoride compared to like ammonium perchlorate. So, if you look at the top figure here this was actually we have seen earlier that this is the typical ammonium perchlorate decomposition. So, this is typical like TGA,DTA curve we have seen it is like the mass loss this one is the mass curve this one whereas, this one is the DTA one which tells us like the exothermic and endothermic peaks. So, this part we have already seen because this is non-catalyzed case. So, we can see there are you know exothermic peak here and endothermic peak here because of the decomposition and melting and here exothermic reaction is taking place or because of the decomposition this one is like around 560 TO 525 or so.

Now, once we add like 10 percent lithium fluoride the thermal decomposition process is actually modified. Now, instead of having single exothermic peak it is showing two exothermic peak one is here second one is at beyond like 750 Kelvin whereas, the first one is kind of modified to a slightly lower temperature what we have seen there. So, we can see also the endothermic peak is you know observe at around you know 5 16 Kelvin 5 16 Kelvin. The exothermic peak originally was at 7 25 now appears at you know 6 35 Kelvin and the endothermic reaction occurs between like 520 to 532 Kelvin this you know this endothermic reactions. Now, we are seeing an additional exothermic peak here which is you know temperature region beyond you know 720 or 750 to 790 Kelvin.

So, two exothermic peaks we can see here. Now, we should also look at what is exactly happening here because if you look at the decomposition reactions primary endothermic reactions are like NH4ClO4 plus. So, it is like one NH4ClO4 which is the balanced one is like something like this. So, sorry this is LiF which is going to form like 0.497 NH4 unreacted one plus 0.503 ammonium fluoride plus lithium perchlorate LiClO4. LiClO4 is lithium perchlorate. Now, this is going to you know decompose further and it is going to form the lithium chloride and oxygen. So, this is going to decompose further and it is going to produce oxygen plus lithium fluoride lithium chloride. So, we can say that the first stage decomposition reaction will be first stage decomposition will be like going to produce ammonia because ammonium perchlorate is going to produce ammonia plus perchloric acid plus that lithium perchlorate.

And in the second stage reaction second stage decomposition we can say that this ammonium perchlorate is going to decompose further and is going to form oxygen plus lithium chloride. So, we can say that upon addition of 10 percent of lithium fluoride the decomposition process of ammonium perchlorate is going to be modified and the decomposition reaction will be changed to this. Because earlier we have seen that ammonium perchlorate decomposition will form like perchloric acid ammonia and then will further you know going to produce oxygen and HCl. However, once you add 10 percent of lithium fluoride this will going to change the decomposition reaction and it will produce the this type of species. Of course, oxidizing species are present there, but it is going to change.

So, what we can say that the decomposition process of ammonium perchlorate is going to be altered by the addition of 10 percent lithium fluoride. Of course, this is for a particular fixed amount, but there may be a different amount can be tried. So, due to the rapid you know decomposition and gasification beyond certain temperature like 630 Kelvin or even higher the liquidified residue is going to remains. Now, that residue can be you know stay up to certain temperature like 720 or 750 and that will is going to decompose further and is going to finally, is going to produce the residue as lithium chloride. Because that is after the second stage decomposition.

So, lithium chloride is going to produce. Now, if you look at the burning characteristics of the lithium fluoride loaded ammonium perchlorate based composite propellant, what you can see is the burning rate of the lithium fluoride based lithium fluoride loaded solid propellant we can see this is like without lithium fluoride catalyst. Now, once we add some percentage of lithium fluoride like 0.5, 1 percent, 2 percent we can see the burning rate is going to decrease as you can see this is decreasing in nature. You will compare any just take any of the pressure data we can see here the burn rate is going to decrease it is decreasing for any case like if you consider 2 MPa pressure also you see the burning rate is going to decrease. Interestingly it is not only decrease, but there are certain point where is going to flame is going to extings also is going to extinguish.

You see there are certain cases where not only decrease the burn rate, but also inhibits the steady state combustion below a certain pressure. So, that will lead to some self extinction it is mentioned here. So, lithium fluoride is not going to only decrease the burn rate of the propellant, but also at certain pressure it may lead to extinction of the flame. So, this is going to cause the putting of the flame. Now, if you look at this left hand side figure here it is like discussed about lithium fluoride with 0.5 percent concentration and compared with the non-catalyzed case.

The burn rate reduction of the lithium fluoride is due to you know modification of the condensed phase reactions we have already said earlier because that is modifying the condensed phase reactions of AP, but when the you know particles are decomposed the finally, the burning surface will lead to certain you know condensed phase product like lithium fluoride particles that will remain on the quench burning surface. What we have just said in the reaction that this lithium fluoride will be remain in the burning surface and that has been shown through some you know this reactions sorry through the micrographs of the quenched ammonium composite propellant burning surface. Without you know lithium fluoride case and with lithium fluoride case.

So, for A this is with without lithium fluoride that is non-catalyzed case whereas, the 0.5 percent lithium fluoride case this is showing the quenched you know product which is going to stay there as the lithium fluoride. Whereas, in case of ammonium perchlorate composite case no ammonium perchlorate particles were present in the case of non-catalyzed case. So, eventually we can say that this is going to you know decrease or reduce the burn rate of the composite propellant if we add lithium fluoride. So, there are certain you know oxidizers which can improve the burn rate or increase the burn rate of the propellant whereas, there are certain catalyst which can actually play a role in you know decreasing the burn rate by modifying the condensed phase reactions or by modifying the gas phase reactions. As we have seen that ammonium in case of ammonium perchlorate based solid propellants once we add iron oxide Fe2O3 as catalyst they can you know increase the burn rate by modifying the gas phase reactions.

Whereas, they do not participate in the modifying the condensed phase or decomposition of ammonium perchlorate whereas, in case of negative catalyst for example, like lithium fluoride it can change the decomposition processes of ammonium perchlorate and thereby reducing the burn rate. Now, with that I think we close our discussion on the you know burn rate mechanism of ammonium perchlorate based composite propellants. But there are other categories of propellants if we recall that we discussed about classification of composite classification of solid propellants in terms of like homogeneous propellant or double based propellant then we said composite propellant or heterogeneous propellant.

We also said like nitramine propellants and we have said that composite modified double base. So, I think we should spend some time on discussing about the you know burning mechanism of nitramine propellants or first we talk about the thermal decomposition of the nitramine like HMX or an RDX and then we will briefly talk about the burning mechanisms of the nitramine propellants.

And then I think we should spend some time on discussing the AP CMDB or AP loaded composite modified double based propellant and the nitramine loaded composite modified double based propellant. Because we have seen earlier in the discussion that the double based propellant can be modified by adding some ammonium perchlorate as additional oxidizer or HMX or RDX as additional oxidizer and then the propellant will be changed to composite modified double based. So, I think we should also discuss about the burning mechanism of those and then I think we can close the you know module on the burning mechanisms alright. So, we will talk in the next lecture. Thank you.