Course Name: Combustion of Solid Fuels and Propellants

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Lecture: 10 Solid Propellants-Selection Criteria (Continued)

Welcome back. So, we will continue our lectures on solid propellants. Today, we will continue our discussion on the propellant ingredients. If you recall what we discussed in the previous lecture, we started with the discussion on fuel. As you know, the common propellant ingredients are fuel, oxidizer, binder, plasticizer, curing agent, burn rate modifiers, etc. There may be more than 200 ingredients, depending on the functionality of each ingredient they have been tried.

As I said earlier, fuel and oxidizer are the principal ingredients because without fuel or without oxidizer, the rocket propellant ingredient will not be complete without fuel or without oxidizer. Only fuel and oxidizer are not going to burn. So, it needs to have at least fuel and oxidizer. Other than that, it needs to have some binder because we have to bind the solid particles.

So, these are mostly solid crystals. So, we need to have some binder, which is kind of a, you know, glue type of glue that can bind the solid particles together or form the fuel matrix. So, we started our discussion on the fuels. Various fuels have been considered or thought of as solid propellants. The common one is the aluminum particles.

So, these are basically spherical aluminum particles. They may range from 5 to 60 microns and typically burn inside the solid rocket motor and form aluminum oxide. Since we said that metal particles generally have higher energetic values, they provide heat to the overall combustion and heat release from the combustion reactions, and the aluminum will become aluminum oxides. As it proceeds towards the nozzle side, the aluminum oxides may become liquid as the temperature drops, or if the temperature is low enough, the aluminum oxide particles may form into solids. Aluminum, I mean liquid oxide particles, may become solid.

That may be a disadvantage in the form, like some of the, you know, oxide particles may deposit on the inner liner of the chamber or even in the nozzle portion. So, that may you know the overall change of the rocket's mass ratio. Now, we also said that boron is also considered to be one of the promising ingredients as fuel, but you know the difficulty in burning boron in an efficient way within the reasonable combustor length or within the given residence time of the combustor. It does not really have, you know, commercial applications. However, boron has been used extensively to see whether it can actually release heat in the combustion chamber. The other ingredients can be like beryllium, which is also thought to be a promising fuel or metal particle, but the oxides of berylliums are very toxic.

So, generally, it is not considered, although the heating values are higher for beryllium as well. Now, we are looking at comparing heating values of various fuels. Now, if you look at the comparison of heating values of aluminum, beryllium, boron, carbon, and other materials in comparison with HTPB. So, HTPB is like a rubbery substance. It is a polymer that is mainly used as a binder, but since it is a polymer, it can be used as fuel. Similarly, paraffin wax is another fuel ingredient that can used as a binder as well.

So, if we compare the commercial polymeric fuel with the metallic fuels, you can see that beryllium has the highest thermometric heating values compared to all others. Whereas, boron has the highest volumetric heating values compared to all other ingredients. So, in a sense, boron stands out to be the promising candidate in terms of volumetric heating values because the aerospace vehicle, we said that it is a volume-limited system. So, a volumetric heating value means it can give us, like you know, with a lower space, we can actually pack more. I mean the sorry with the minimum amount of volume, it can produce higher energy density. So, it is like per centimeter cube or per meter cube.

In that sense boron stands out to be the promising candidate, but as I said the efficient boron combustion is difficult due to its native oxide layer present on the particle surface it inhibits its ignition and hence the combustion as well. So, energy utilization is difficult. So, if you look at the stages of boron ignition combustion, it primarily covers the boron oxide cell. Now, that liquid layer on that solid core boron exists once the temperature is beyond 722 Kelvin because the melting point of boron oxide is around 450 degrees centigrade or 722 Kelvin. So, the molten oxide layer will inhibit the oxygen reactions with the core boron particles.

So, that is one of the drawbacks for boron particles, you know, ignition and combustion, which actually inhibits its full energy utilization. Once the oxide layer evaporates, the boron core boron will be used with the available oxidizer. So, these are the several stages of boron ignition combustion, and due to this, some additional time is required to complete the combustion. So, for the given resistance time, sometimes it is not, you know, sufficient to complete the combustion of boron, and the full energy utilization is somewhat not possible. So, I think we will talk about metal particle combustion later in this course because there is a separate module on metal particle combustion.

So, we will talk about that later on. This is just to give you some ideas about the what are different types of metal particles that are considered fuels for solid propane ingredients. So, in a nutshell, we can say that aluminum is a more common one, whereas other ingredients such as boron are also considered, but the utilization of boron energy is still not harnessed, just because of the difficulty in burning efficiently within the given residence time or the reasonable combustor length. Whereas, beryllium is discarded just because of the toxic nature of its oxide. On the other hand, you can look at the density of various metal particles like aluminum, beryllium, boron, carbon, and iron.

If you compare the density with the hydrocarbon fuels or the binder, let us say polymeric binder or HTPB, you can see the density is almost 3 times. If we see, the aluminum density is almost 3 times of HTPB. So, that way, we can actually compact more amount of fuel within the given volume. On the other hand, these metals' volumetric heating values are higher than the available polymeric fuel. So, in a sense, the metal particles can be utilized if we can somehow bind them within the given, you know, binder, and that can actually give us high performance in terms of like the Isp as well as the volumetric, I mean, sorry as well as in terms of the density Isp.

Because the density here is quite high compared to the available polymeric fuel such as HTPB, alright. Now, as I said, the primary ingredients of the solid propellant are the fuel and the oxidizers. Now, there are different types of oxidizers that are considered, such as solid propellants, inorganic oxidizers, and some organic oxidizers or explosives. So, inorganic oxidizers are mostly solid crystals, for example, ammonium perchlorate, which is considered as the common oxidizer for composite solid propellant.

So, we will talk about the different types of inorganic oxidizers and the different types of organic oxidizers used for solid propellants. So, let us look one by one. So, as I said, the most common oxidizer is ammonium perchlorate, which is NH4ClO4. These are basically crystalline oxidizers. So, they are basically crystals, and they are, of course, inorganic oxidizers. Now, the ammonium perchlorate oxidizer has a high oxidizing potential, and it is the preferred oxidizer due to its performance.

Although we know that it contains chlorine atom within the molecule of the ammonium perchlorate, so, upon reaction, it is going to produce HCl. Although we know that it is hazardous for the environment and the personnel working nearby, this is still kind of a workhorse oxidizer for composite propellants used for solid rockets. So, it has been a preferred oxidizer for a long time because of its good performance, and we can maintain the quality, the uniformity of the particles, and, of course, the availability. So, based on that the, ammonium perchlorate is considered the most common or most widely used crystalline oxidizer. So, these are like a perchlorate-based oxidizer.

Other oxidizers can be nitrate-based oxidizers, such as ammonium nitrate. The other perchlorate oxidizer can be potassium perchlorate or sodium perchlorate like we can show here. There are various other perchlorate oxidizers like ammonium perchlorate, potassium perchlorate, and sodium perchlorate, and the respective molecular masses are given here.

This is like 117.49; here it is 138.55; here it is 122.44. Density is also, of course, higher than the available polymeric fuel; it is always higher than the normal hydrocarbon density, which is of the order of 900 to 920 kg per meter cube. So, generally, they are denser than the polymeric fuel. Now, the oxygen content available in the molecule is already given here for ammonium perchlorate is 54.5; potassium perchlorate is 46.2, and sodium perchlorate is 52.3.

So, you know, depending on the availability, the performance generally the ammonium perchlorate is the preferred oxidizer. The other oxidizers can be like ammonium nitrate. As you can see, the oxidizing potential is also kind of very high here, but there are some issues with the ammonium nitrate oxidizer or overall, like where the performance penalty takes place because this is kind of hygroscopic in nature.

And because of the hygroscopic nature of the ammonium nitrate, it absorbs moisture, and it is changing its phases in the crystal. Sometimes, it may, you know, make it to some volumetric changes in the crystal as well. So, the hygroscopicity and the temperature deformation, like if we change the temperature of the environment due to some means or if there is a change in the storage temperature, the ammonium nitrates actually change its phases and due to which there will be some void may be created within the crystal itself which may lead to problem in the performance later on. So, although ammonium nitrate-based oxidizer has other known positive attributes, for example, it does not contain any chlorine atom within the molecule. So, it is not going to produce any kind of reactive or hazardous products like HCl because it only contains hydrogen, nitrogen, and oxygen.

So, it is in that sense it is environmentally benign, and the oxygen continuing in the molecule is also higher, but due to the other issues like hygroscopicity and the phase transformation due to the effect of temperature, this oxidizer is not you know commonly used for high performing rocket, but for some medium performance and smokeless propellants where we can find application of ammonium nitrate. Of course, some modifications have dried in order to improve the performance of ammonium nitrate oxidizers like PSAN or phase-stabilized ammonium nitrate. Some amount of nickel oxide is added in order to reduce the change of phases within the oxidizer. So, the oxidizers are mostly the particles or crystals of various sizes as I said here, the ammonium percolate they are used in various sizes. It could be like 600 microns, which is generally considered to be coarser, or it can have like a smaller size as like 80 microns as well. But if the size is less than 40 microns, it is considered to be hazardous because it can easily decompose or it can easily ignite in the storage location or even in the air itself because this is kind of, you know, very hazardous. It can sometimes it can lead to detonation as well.

So, this is handled with care, but generally, the mixture of, you know, two different sizes are used in order to improve the volumetric loading because if you see, there are some bigger crystals packed together, there will be some inter particular spacing present, you know. So, to improve the packing, some small crystals are mixed with this to improve the loading densities like this. So, in most of the occasions, the bimodal oxidizers are preferred like it is a mixture of two different sizes. One may be the coarser, and another may be the finer one or the medium size. So, this is the common one. As I said, for the ammonium nitrate, the phase transformation takes place. The ammonium nitrate it has some issues with phase transformation. You know, the phase transformation at 32 degrees centigrade can cause about, you know, 3.4 percent change in volume, which is kind of significant because if it creates some kind of a void within the propellant grain, that may lead to, as you know, big failure later on.

So, this can actually change you know, this will lead to change in the physical and the ballistic property of the grain. So, this will very much influence or impact the physical and ballistic properties of the grain. So, we must have to use this ammonium nitrate oxidizer very carefully by stabilizing using some nickel oxide or potassium nitrate that will somehow lead to, you know, reduce the phase transformation, and that is why it is called PSAN or phase-stabilized ammonium nitrate. So, even if it is using even if it is used, it is used with some phase stabilization also, the moisture absorption is going to degrade the performance.

So, that is another issue with ammonium nitrate. So therefore, for high-performing rockets, ammonium nitrate is not preferred; rather, ammonium percolate is the preferred oxidizer still now. So, these are all about the inorganic oxidizers, but there are some organic oxidizers that have been used as well. So, what are the organic oxidizers? So, they are organic compounds with radical or other, you know, oxidizing fractions in the. So, these are, like, you can say, organic compounds with NO_2 radicals. Very quick examples if we want to know are like the nitramines. They are the very common, you know, organic oxidizers.

So, nitramines mean we are talking about the HMX and RDX. They are considered to be like explosives. So, HMX is the name is Her Majesty Explosive which is, you know, the chemical name is cyclotetramethylene tetranitramine. So, you can write down the formula accordingly, and it will be like $C_4H_8N_4(NO_2)_4$. So, that is, the HMX is one of the organic oxidizers another organic oxidizer or it is used as an explosive also which is

RDX which is commonly known terminology this is known as R&D explosive. So, instead of tetra, it contains tri.

So, its chemical name is cyclotrimethylene trinitramine. Sometimes what happens is that if we add the RDX or HMX they may you know they have the potential to react themselves. So, they are generally kind of we need to add some, you know, amount of fuel or oxidizers in order to balance the materials; otherwise, you know, it is going to reduce the temperature or the or the Isp. So, when binders are added to HMX and or HMX or RDX crystals, it is necessary to add another oxidizer like AP or AN because you know this material can react and burn itself when initiated with enough you know activating energy. Of course, at certain conditions, they may detonate to it may detonate under certain conditions, but we have to remember that both HMX and RDX are stoichiometrically balanced.

So, these are kind of stoichiometrically balanced. So, in order to improve the performance or if you need to know the impact of the temperature and the Isp, we have to add some amount of, you know, oxidizers or fuel to change the mixture ratio. So, whenever there is, you know, some binder fuels are added to hold the HMX or RDX in the matrix, it is necessary that some amount of AP or AN is also added. So, you know this type of oxidizer has applications in a separate category of propellants called nitramine propellant. In fact, there is, you know, a modified version of the double base propellant where these types of oxidizers are used, and they are called composite modified double base propellants.

So, once we talk about the category of propylenes or the category of solid propellants, we will talk about HMX and RDX again. So, these are various oxidizers we have already discussed. Now, we must remember that the fuels and oxidizers are solid particles. So, we need to have some kind of glue or some kind of binding material to bind them together because only solid particles, if we put it, are not going to form a solid propellant grain if you recall what we had earlier.

So, the binder has already been written here. So, if you recall, in our previous discussion, inside the rocket, we put one solid-shaped mass, and by now, we know the name it is called the propellant grain. So, this is propellant grain, and as you said, propellant grain means it consists of fuel and oxidizers. So, let us say we have metallic fuel. So, metallic fuels are kind of some aluminum particles, let us say, and we have some, let us say, bigger size, you know, AP crystals or mixture of, you know, bimodal AP crystals. Let us say these are AP crystals, and we have aluminum particles.

So, how do we form this to the propellant grain if we use solid crystals? How do you form this? In order to give a structural glue or kind of a, you know, some you know binding, we need to in order to bind these the solid particles we need to use the binder. So, you need to bind them. You need some kind of a binder, and they are going to act as structural glue, just like, you know, normal glue. It is holding all the solid particles, and they are going to form this type of solid block of material which is containing our fuel as well as the oxidizers. So, within this grain, we are actually holding the solid crystals. Solid crystals are fuel and oxidizers. So, the binder will act as the structural glue to keep this composite matrix bound together. Now, what are the different types of binders? Let us talk about that.

So, binders are generally, you know, polymeric pre-polymer or monomer, you know, after we cure them and make it like, you know, grain type, which once we make the solid fuel grains. So, they become solidified. So, what is our preferred, you know, choice of binder because the binder will also act as fuel? We have to remember that we can write it here. So, if we recall from our previous lectures that heat of combustion if you recall in order to increase the heat of combustion what we said we have said that the heat of formation of reactants is supposed to be positive or small negative. This was our criteria for the heat release from the chemical reaction because the heat release from the chemical reactions we said this would depend on the summation of the heat of formation of the products minus the summation of the heat of reaction of the heat formation of the reactants.

$$\Delta Hc = -\left\{\sum mi\, H^0 f - \sum ni\, H^0 f\right\}$$

From that analysis, we understood that the heat of formation of the reactants should be small, negative, or somewhat positive. So, the binders, since they are kind of like fuel, are preferred if they have small negative values of heat of formation. So, in that respect, you know we can prefer the choice of simple aliphatic compounds, which can have very straight, simpler bond structures. But you know, most of the aliphatic compounds have methane, propane, or butane; they are actually gases.

So, gases cannot actually bind the particles together. So, we need to use some kind of a polymer, which is basically cyclobutane, sorry, cyclobutadiene, that will have a linear chain structure. They are called polybutadiene, and they will be like many of them like. So, there will be many of them, you know, from the, you know, chain structure, and this will form the butadiene groups. So, these butadiene groups will form polybutadiene, and they can end up with either hydroxyl or carboxyl. Depending on that, there are different types of butadiene, like hydroxyl-terminated polybutadiene or carboxyl-terminated polybutadiene. Basically, they are the polymer that will provide the structural glue for the grain.

So, they provide the structural glue to hold the solid fuels plus the oxidizers. Remember, solid fuels mean we have aluminum particles or even boron particles, and the oxidizers are ammonium percolate or ammonium nitrate. They are solid crystals. So, the polymers will provide the structural glue to hold the solid fuels and oxidizers. Now, there are different types of polymers that have been used as binders. The very common one is called hydroxyl-terminated polybutadiene, or very commonly, it is known as HTPB. You may find in much literature that HTPB is the common binder for composite propellant.

For example, like the booster stage, where we need to, you know, launch the vehicle. So, the first stage, the solid propellant rocket, generally has the binder as the HTPB or the hydroxyl-terminated polybutadiene binder. There are other binders. So, I think we will discuss those binder types in the following lectures. All right, like the ends of the end of the polybutadiene, maybe with carboxyl terminated instead of hydroxyl. It can have carboxyl terminated.

So, you can have it like it is called CTPB. There are other binders called polybutadiene acrylic acid acrylonitrile, which is PBAN. So, we will talk about those binders briefly in the following lecture. Thank you.