Fundamentals of Combustion for Propulsion
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Lecture – 16
Statistical representation of composite propellants in HeQu1D – geometry and thermochemistry

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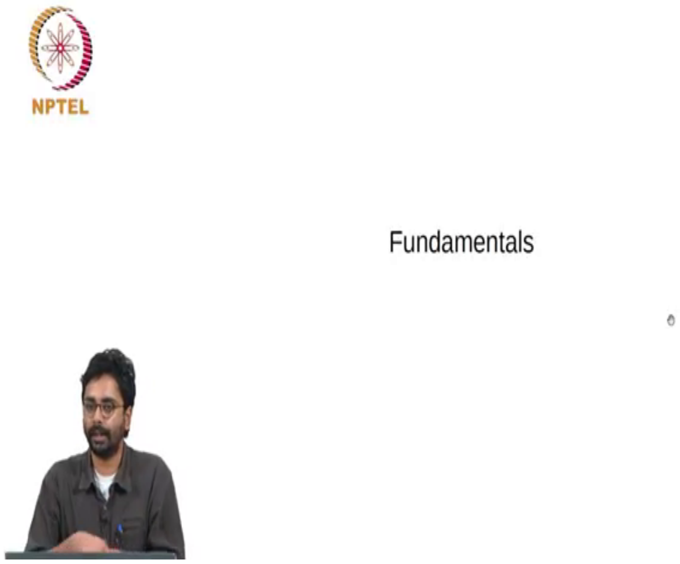

Fundamentals

Let us continue with the discussion of a solid propellant modeling. Let us look at some basics first. I just want to remind that we are looking at AP HTPB composite propellants and a model to predict the steady burn rate, and the burn rate of these propellants when subjected to pressure perturbations.

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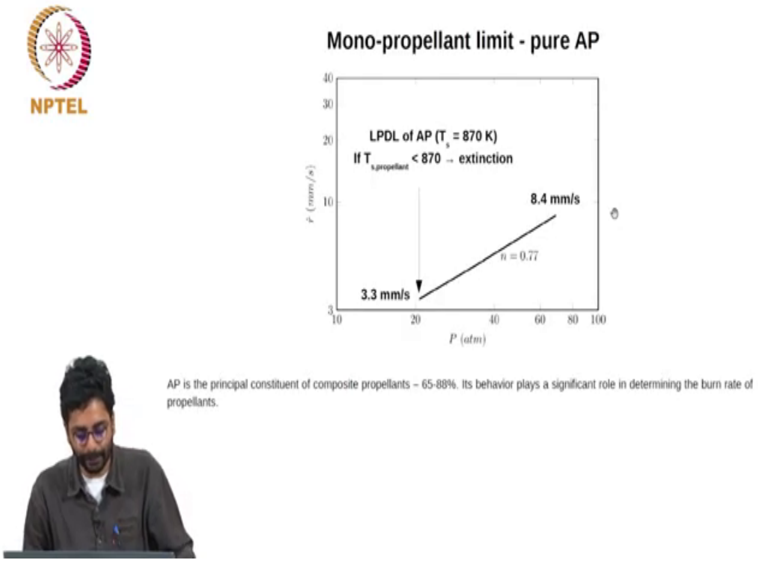

Mono-propellant limit - pure AP

AP is the principal constituent of composite propellants – 65-88%. Its behavior plays a significant role in determining the burn rate of propellants.

And start from some fundamentals. Most of what constitutes composite propellant is AP, it is 68 percent in the case of aluminize propellants, it is up to 85, 86 percent in non aluminize propellants. So, AP shows the following AP shows the following burn rate behavior. AP starts burning only at 20 atmospheres, AP can ammonium perchlorate can undergo self-sustain deflagration only starting from 20 atmospheres. This is of course, true for pure AP, with impurities this limit can get shifted a little bit.

But the important thing is that whatever be the limit of pressure when it starts burning; it starts burning at around 3.3 millimeters per second ok. And at and then it burn rate the AP rise to n, for AP is A is 3.3 millimeters per second at 20 atmospheres, the n value is 0.77 ok. This is characteristic of deflagration that is controlled by a premixed flame ok.

Remember that when the index is closed to 1, the behavior is controlled by premixed flames. We will formally see this a little later, but index is close to 1, when it is controlled by a premixed flame and lower index usually means there is effect of diffusion, effect of lateral diffusion.

So, at the reason why AP starts burning at only 20 atmospheres is because the surface temperature that is required for AP to undergo self-sustain deflagration is should be equal to at least the melting temperature of AP, unless it melts it cannot undergo exothermic decomposition. And if it does not undergo exothermic decomposition, it cannot self undergo self-sustained deflagration.

So, the low pressure deflagration limit which is the LPDL of AP is 20 atmospheres, because it is only at 20 atmospheres, the surface reaches the melting temperature, which is approximately 870 Kelvin. So, AP is the principle constituent of composite propellants 65 to 88 percent of all composite or of the mass is AP. And therefore, its behavior plays a significant role in determining the burn rate of the propellants. So, this is first thing.

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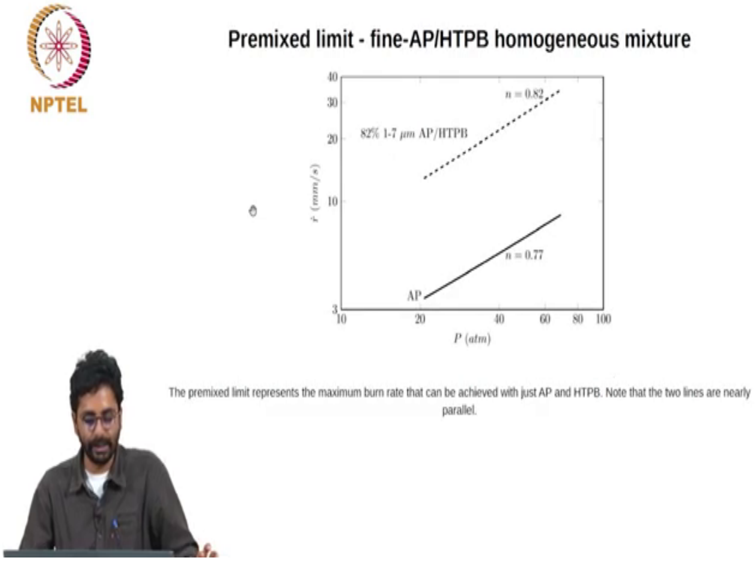

Premixed limit - fine-AP/HTPB homogeneous mixture

The premixed limit represents the maximum burn rate that can be achieved with just AP and HTPB. Note that the two lines are nearly parallel.

The next limit which is important to understand, it is what is called the homogeneous limit. AP-HTPB propellants are in general heterogeneous composite propellants, but imagine that the heterogeneity results from the fact that AP particles of variety of sizes are used. You have large particles and you have small particles. And in zones which have large particles the AP concentration is higher, and in zones where small AP particles are used the fuel concentration is higher.

But now imagine that you use only very very fine AP particles as to how fine it should be will be precisely defined later, but let us say you use a uniform AP particle size and all AP particle size are very very small ok. If you assume that you are working with let us say 1 micron AP particle or 5 micron AP particle, they distributed in the; distributed in the binder-matrix ok. Then everywhere in the propellant, the oxidizer to fuel distribution there is roughly the same.

So, this is the homogeneous limit of a heterogeneous propellant. What do you essentially done is you started with a heterogeneous propellant sort of broken down, imagine breaking down AP into very fine sizes and distributing it uniformly. A homogeneous propellant heterogeneous propellant will become a homogeneous propellant in this limit, yeah.

Student: (Refer Time: 04:41) result to the actual propellant or.

It is an actual propellant.

Student: (Refer Time: 04:47). Yeah 1 to 7 micron in the size (Refer Time: 04:52)

Correct, yeah. So, when you do this, what do you end up with is a propellant like this which has a 82 percent AP of very fine sizes 1 to 7 micron, there has to this HTPB. This is the homogeneous limit of a heterogeneous propellant, and then this limit the burn rate is controlled again by a premixed flame. Since there are no heterogeneity in the condense phase, the flame also will be a homogeneous premixed flame without any variations of the kind that we saw in the picture in the CFD simulation for an actual propellants.

So, when you homogenize the entire AP with the binder the flame in the gas phase will also become a homogeneous premixed flame ok. So, in these two limits, the burn rate behavior is controlled by a premixed flame and therefore, the index is close to 1 ok. And this is also the limit that this is the limiting burn rate, because the homogenous limit is where you can get the maximum possible burn rate from AP-HTPB composition.

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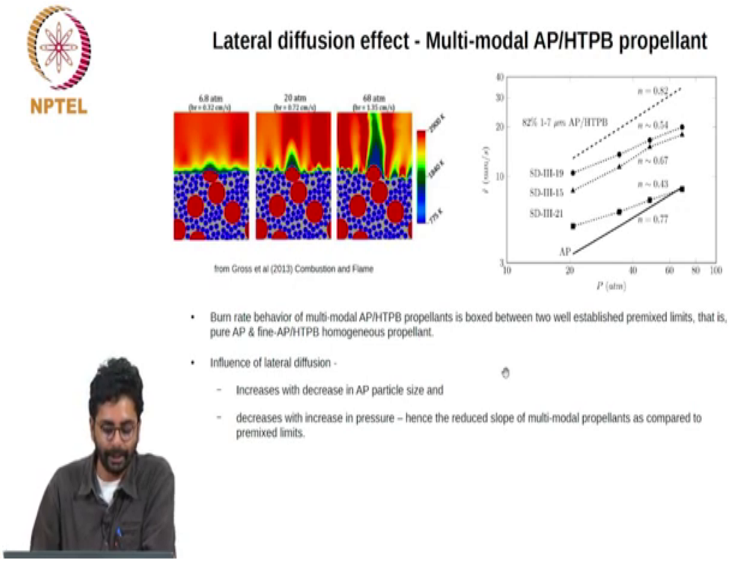

Lateral diffusion effect - Multi-modal AP/HTPB propellant

from Gross et al (2013) Combustion and Flame

- Burn rate behavior of multi-modal AP/HTPB propellants is boxed between two well established premixed limits, that is, pure AP & fine-AP/HTPB homogeneous propellant.
- Influence of lateral diffusion -
    - Increases with decrease in AP particle size and
    - decreases with increase in pressure – hence the reduced slope of multi-modal propellants as compared to premixed limits.

Effect of lateral diffusion we have already discussed this in some detail. So, when you are neither at the AP limit nor at the homogeneous limit, in reality you are somewhere in between. You have particles of variety of sizes sitting inside a matrix of HTPB. And therefore, you have local pockets giving of AP decomposition products surrounded by pockets of fuel rich conditions giving of fuel vapors. And the oxidizer is trying to diffuse laterally into the fuel; the fuel is trying to diffuse laterally into the oxidizer. And depending on the distance that it can laterally move before it starts reacting, the flame structure will be determined by the conditions of lateral extent of lateral diffusion.

So, what does the effect of lateral diffusion? The effect of lateral diffusion is as can be seen from the burn rate data for several propellants that are shown in this plot is to bring down the index from close to 1 to about a minimum of 0.43. So, the limits at the limits AP burns at 0.77 at the homogeneous limit it burns with an index of 0.82. When you add particles of disparate sizes or by model as a discalced, you have two modes of distribution that are added because of the effect of lateral diffusion. There are zones which are controlled by premixed flame, there are zones that are controlled by non premixed flames. And therefore, the index comes down from 0.82 or about 0.8 to as low as 0.43 ok.

So, burn rate behavior of multi model AP HTPB propellants is boxed between the two well-established premixed limits, I am referring to the AP and the homogeneous limit. Influence of lateral diffusion increases with decrease in AP particle size. We have seen this, this is equivalent of reducing the diameter of the ethyl inject that is the simplest way to remember this. So, the extent of or the influence of lateral diffusion will be significant when the diameter is smaller ok. When the diameter becomes comparable to the distance that it can move in the lateral direction and the influence of lateral diffusion will decrease with increase in pressure. Why is that? Because the reaction rate increases with pressure, and therefore, the distance that the oxidizer and fuel can move laterally before it starts reacting is smaller ok.

Therefore, this reduces the slope of multi model AP propellants is compared to premixed limits. The last point also means the following. For the same composition the influence of lateral diffusion is higher at lower pressures and lower at higher pressures. At lower pressures reaction rates are lower, and therefore the extent of lateral diffusion is higher. Therefore, the propellant for example SDIII-19 that you see here is closer to the homogenous limit at lower pressures. When the pressure increases, the extent of lateral diffusion decrease the extent of lateral diffusion decreases and it becomes controlled by other factors, and therefore, the increase in burn rate because of lateral diffusion is not as high and higher pressures as it is at lower pressure. Therefore, the slope comes down that is the reason the slope comes down.

So, in if I have to summarize it, what I would say is when there are several particle sizes, the behavior is close to the homogeneous limit at lower pressure and the behavior is close to AP limit at higher pressures ok. So, the slope comes down ok.

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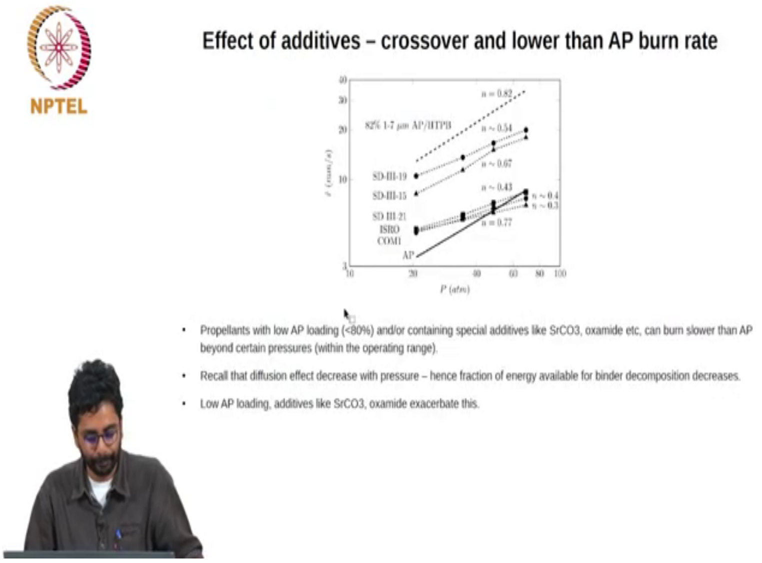

Effect of additives – crossover and lower than AP burn rate

- Propellants with low AP loading (<80%) and/or containing special additives like SrCO3, oxamide etc, can burn slower than AP beyond certain pressures (within the operating range).
- Recall that diffusion effect decrease with pressure – hence fraction of energy available for binder decomposition decreases.
- Low AP loading, additives like SrCO3, oxamide exacerbate this.

Now, that is only the cases that we saw are only with AP and HTPB, of course, there are several other additives that are used. So, what can happen with several other additives is propellants with low AP loading less than 80 percent, and or containing special additives like strontium carbonate, oxomide, etcetera can burn slower than AP beyond certain pressures within the operating range. One example is shown here. This is the a COMI composition with crosses over and burns slower than AP composition, AP burn rate at pressures as low as 50 atmospheres.

And recall the diffusion effect decreases with pressure. Hence fraction of energy available for binder decomposition also decreases with pressure. And therefore, low AP loading and additives like strontium carbonate, oxomide can exacerbate this effect of heat flux coming to the surface of the propellant ok. You can reduce the heat flux coming to the surface of the propellant, in fact, increase in pressure reduces the heat flux coming to the binder, and in adding strontium carbonate can make it worse. Of course, these are all not serious issues at high solid loading of AP, at but at moderate or low solid loading of AP these effects can be significant.

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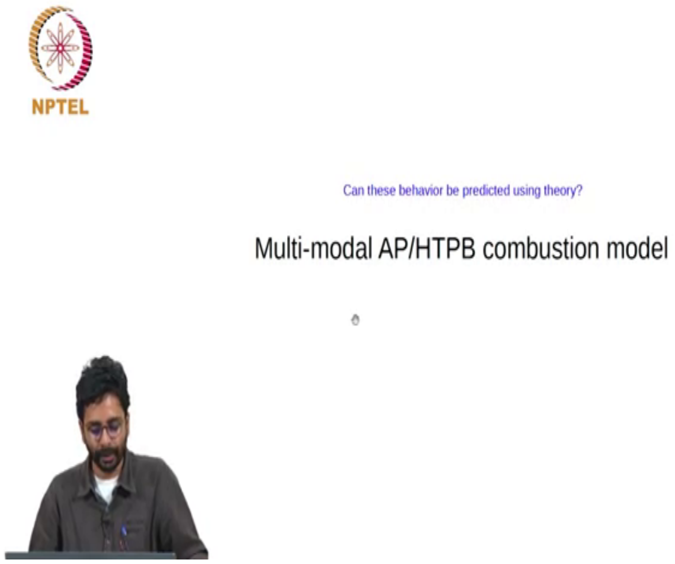

Can these behavior be predicted using theory?

Multi-modal AP/HTPB combustion model

So, the broad question is can the variety of behavior that we just saw be predicted using a theory.

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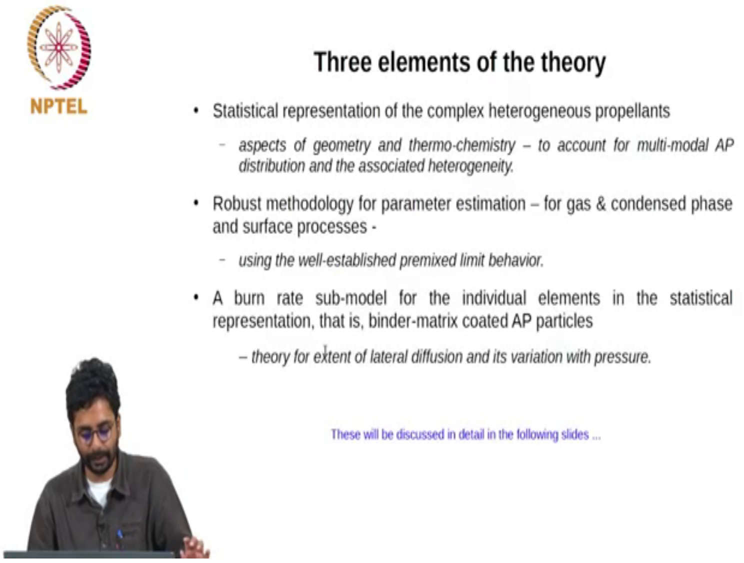

Three elements of the theory

- Statistical representation of the complex heterogeneous propellants
  - *aspects of geometry and thermo-chemistry – to account for multi-modal AP distribution and the associated heterogeneity.*
- Robust methodology for parameter estimation – for gas & condensed phase and surface processes -
  - *using the well-established premixed limit behavior.*
- A burn rate sub-model for the individual elements in the statistical representation, that is, binder-matrix coated AP particles
  - *– theory for extent of lateral diffusion and its variation with pressure.*

These will be discussed in detail in the following slides ...

And yes, and there are three elements to the theory. One is the static statistical representation of the complex heterogeneous propellant. You have wide variation in the oxidizer to fuel ratio inside the composite solid propellant. Therefore, you need some statistical way of representing what the average behavior is that is the first part.

The second part is parameter estimation. This is the critical part in propellant modeling because the processes are so complex especially in the presence of additives and other ingredients, that it is not very easy to fix parameters for various processes that happened in the condense phase, surface and the gas phase ok. And it is also important that we do not introduce too many parameters.

See if you have too many parameters which we can arbitrarily change, then there is no you cannot claim that the results are predictions ok. In fact, with two to three adjustable constants, you can explain away any burn rate variation. The idea is to not have any adjustable constants and make predictions o k.

So, the second part is the important part for parameter estimation and it is done using the well established premixed limits. The third is a burn rate sub model for individual elements in the statistical representation; it will become clear what I am referring to in a few moments ok.

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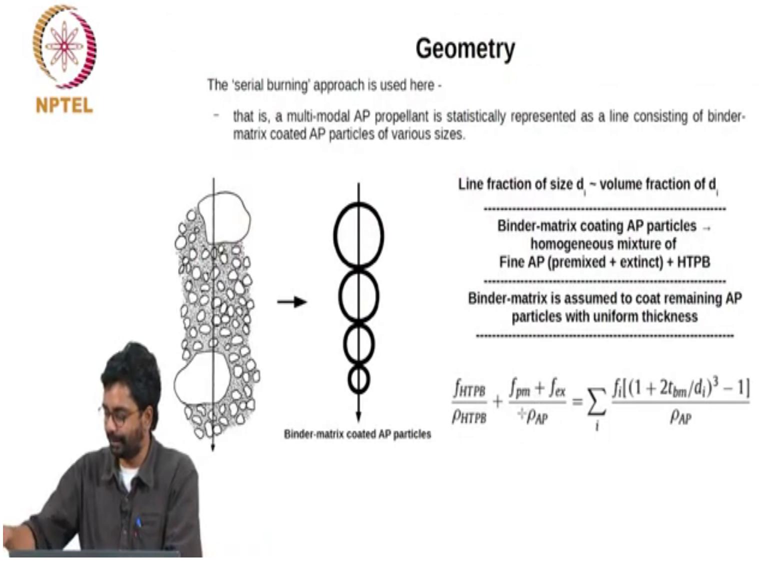

Geometry

The 'serial burning' approach is used here -

- that is, a multi-modal AP propellant is statistically represented as a line consisting of binder-matrix coated AP particles of various sizes.

Line fraction of size d_i ~ volume fraction of d_i

Binder-matrix coating AP particles → homogeneous mixture of Fine AP (premixed + extinct) + HTPB

Binder-matrix is assumed to coat remaining AP particles with uniform thickness

$$\frac{f_{HTPB}}{\rho_{HTPB}} + \frac{f_{pm} + f_{ex}}{\rho_{AP}} = \sum_i \frac{f_i[(1 + 2t_{bm}/d_i)^3 - 1]}{\rho_{AP}}$$

So, let us look at the geometry part first. The serial burning approach is used here that is what it means is that the multi-modal AP propellant is statistically represented as a line consisting of binder-matrix coated AP particles of various sizes. The cross section of a typical propellant will look like this. And this is converted into a statistical representation of the following kind ok, where imagine a large number of random lines drawn through the propellant ok.

And the propellant the such lines cut through particles of different sizes and binder-matrix. And then you can calculate what does the intersection of such lines with particles of different sizes for a large number of random lines. Collect that data and then when you average it, when you have what is called as statistical particle path ok. And the way that is binder is distributed is we are assuming that the binder coats, particles – AP particles on a statistical particle path with constant thickness ok.

So, such a line, in fact, it may sound very complicated, but the simplest the simple way of saying it is if you draw a random line through a propellant of this kind the probability that it intersects a particle of size d is proportional to the volume fraction of that particle. Imagine a box containing particles of different sizes. The question that is being asked is that if you draw a random line through that box, the probability, what is the probability that it will intersect the particle of certain size? The simple the answer to that question is that, that probability is equal to the volume occupied by particle of that size ok.

So, the line fraction as this is called the fraction of the length of such a statistical line occupied by particle of size d is proportional to the volume fraction of d i of particles of size d i. And the binder-matrix is distributed; we are assuming that it coat each particle with constant thickness. So, the binder-matrix coating AP particles is a homogeneous mixture of fine AP and HTPB, what fine AP is I will describe in describe a little later ok.

So, the binder-matrix is assumed the coat AP remaining AP particles with uniform thickness, which you can calculate by simply equating the volume of the binder-matrix which is this mass fraction of HTPB by density of HTPB plus whatever AP is there in the binder-matrix to the volume of this thickness surrounding the AP particle. A sphere surrounded by binder-matrix coating of size t b will have a volume which is pi by 6 d plus t b q minus pi by 6 d q.

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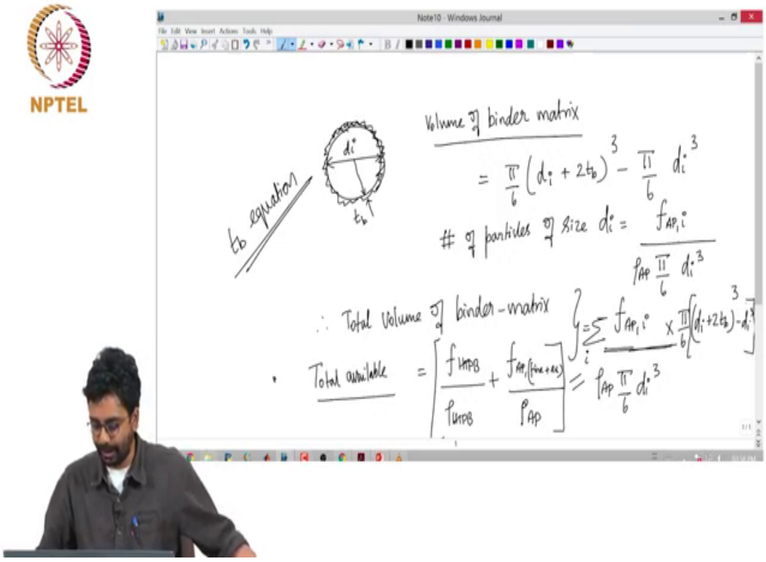

Volume of binder matrix

$$= \frac{\pi}{6}\left(d_i + 2t_b\right)^3 - \frac{\pi}{6} d_i^3$$

$$\# \text{ of particles of size } d_i = \frac{f_{AP,i}}{\rho_{AP} \frac{\pi}{6} d_i^3}$$

$$\therefore \text{ Total Volume of binder-matrix } \Big\} = \sum_i \frac{f_{AP,i}}{\rho_{AP} \frac{\pi}{6} d_i^3} \times \frac{\pi}{6}\left[\left(d_i + 2t_b\right)^3 - d_i^3\right]$$

$$\text{Total available} = \left[\frac{f_{HTPB}}{\rho_{HTPB}} + \frac{f_{AP,(fine+ex)}}{\rho_{AP}}\right]$$

I think let me maybe write this what I am trying to see is that you have this is important because it later is used for calculating the oxidizer to fuel ratio and extinction. So, you have AP of size d i ok, and the thickness of the coating, the thickness of the coating is t b. So, the volume of binder-matrix is equal to pi by 6 d i plus 2 t b cube, these are assumed to be spherical particles minus pi by 6 d i cube ok. This is the volume of the binder-matrix over one particle ok.

Now, there are a large number of particles. So, the number of particles of size d i is equal to the mass fraction of that size divided by the mass of one particle which is the density of AP into the volume of one particle ok. Therefore, the total volume of binder-matrix for particle size d i is the mass fraction of that size divided by this is the number of particles multiplied by this quantity which is the volume occupied by one particle ok. Now, you sum this over particles of all sizes, you will get the total volume of the binder-matrix is correct. This is for one size.

Without the summation, it is binder volume of the binder-matrix around one particle of size d i. When you multiply it by the number of particles of size d i, you get volume for that particle size, then sum over all the sizes. This is the total volume of the binder-matrix coating all particles with uniform thickness ok. The total available binder-matrix, the available binder-matrix is volume is the mass fraction of HTPB divided by the density of HTPB plus mass fraction of fine AP as to what this is I will explain fine plus x t, both I will explain later divided by the density of AP.

So, this is the total volume that needs to be coated this will be the volume if it is coated with thickness t b by equating these two, you can get t b equation is it clear ok, small. You will see exactly the whatever I have written at the bottom of this page, you will see written the slide also ok. What you see here is exactly that of course, the pi by 6 has been canceled out and the expression has been simplified a little bit. But essentially what is there on the left is the total volume of the available binder-matrix what is on the right is the volume if it is coated with a thickness t b ok. So, using this equation, you can calculate get an estimate for the binder thickness ok.

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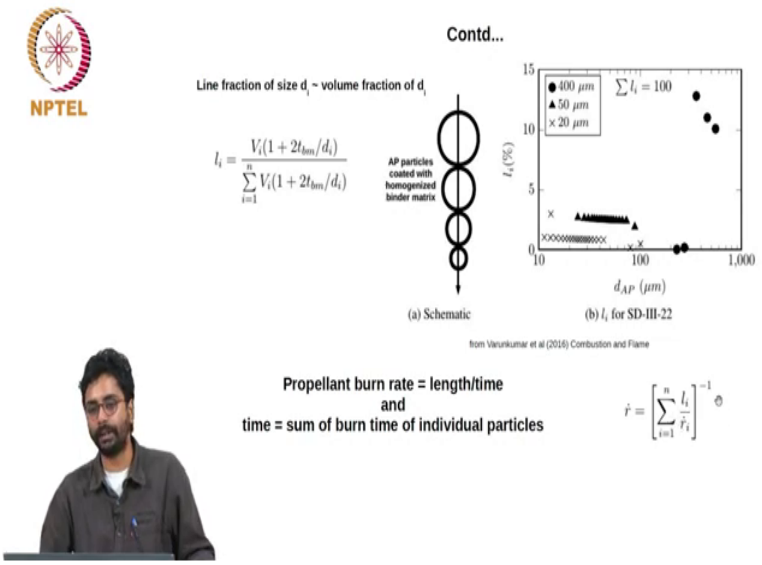

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Line fraction of size d_i ~ volume fraction of d_i

$$l_i = \frac{V_i(1 + 2t_{bm}/d_i)}{\sum_{i=1}^{n} V_i(1 + 2t_{bm}/d_i)}$$

(a) Schematic

(b) l_i for SD-III-22

from Varunkumar et al (2016) Combustion and Flame

Propellant burn rate = length/time
and
time = sum of burn time of individual particles

$$\dot{r} = \left[\sum_{i=1}^{n} \frac{l_i}{\dot{r}_i}\right]^{-1}$$

And the lined fraction occupied by particle of size d i which I imagine again imagine random line going through a propellant pack, the probability of an intersection is proportional to the volume fraction. So, the line fraction of size d i is proportional to the volume fraction of d i and that is what is used here to calculate. If you imagine line of unit size, what fraction of it will be occupied by a size of particle size d i is calculated using this formula and corrected for the binder thickness ok. Correct the calculated value is shown for a representative propellant here called SD-III-22 from Miller 1982 ok.

So, what we have done using this procedure is that we had a certain random distribution of AP particles of different sizes in the propellant. It has be now converted into a averaged line containing particles of various sizes proportional to their representation in the actual propellant, and the fuel has also been distributed in a certain fashion around these particles ok. Now, moving on from here, the propellant burn rate is simply calculated as the length of this line divided by the time it takes for such a line to burn ok. And the time for this line to burn will be the sum of the times for each one of these particles to burn.

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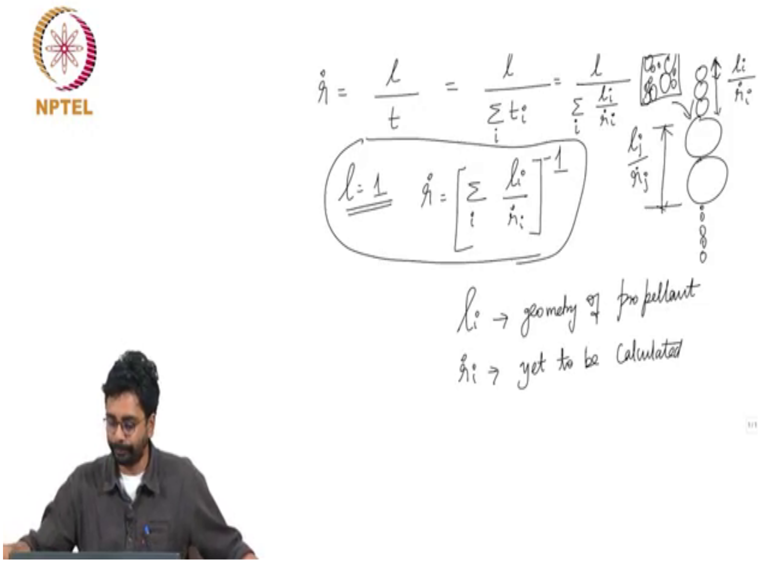

$$\dot{r} = \frac{l}{t} = \frac{l}{\sum_i t_i} = \frac{l}{\sum_i \frac{l_i}{\dot{r}_i}}$$

$$\boxed{\underline{\underline{l = 1}} \quad \dot{r} = \left[\sum_i \frac{l_i}{\dot{r}_i}\right]^{-1}}$$

l_i → geometry of propellant

$\dot{r}_i$ → yet to be Calculated

So, the burn rate of the propellant is the length of the statistically averaged path divided by the time, the length is l and the time is sum of time for particle of size d i to burn ok. So, you have small particle, several small particles, you have a large particle and some small particles ok. So, the burn rate is the time it takes for this particle to burn is the diameter of that particle, I am sorry, yeah, the time that is required for this entire batch of particles to burn is the length occupied by that particle divided by the burn rate of that particle. The time that is required for this batch of particles to burn is the length occupied by this particle divided by the burn rate of this particle. So, this will become sum over l i over r dot i ok.

l is arbitrary I can take l as 1 a unit line, and therefore, r dot this sum over i, so this is the this is how the burn rate is calculated. l i is known from the geometry of the propellant r dot i, yes, it will be calculated ok. This is the basic idea of calculating the propellant burn rate. We calculate we converted certain random distribution into this ok. And from there we can calculate the burn rate of the propellant. Again you see the formula here, it is the same formula sum over all particles l i over r dot i inverse.

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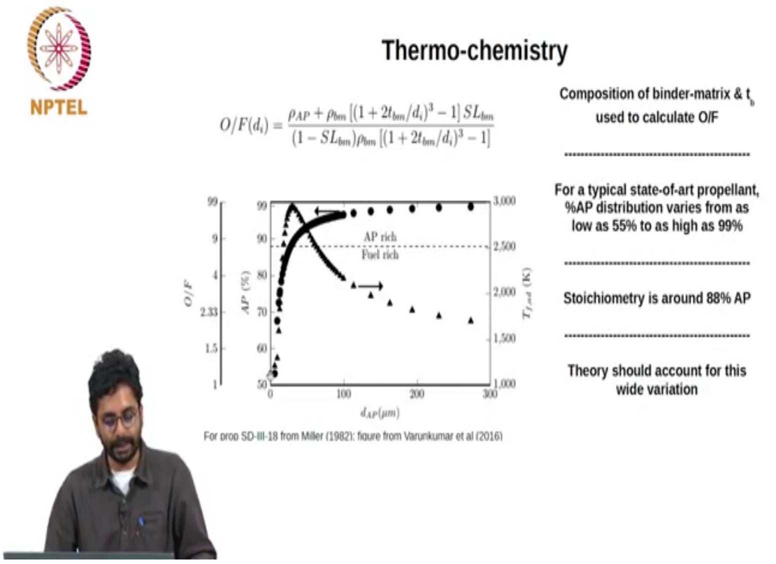

Thermo-chemistry

$$O/F(d_i) = \frac{\rho_{AP} + \rho_{bm}\left[(1+2t_{bm}/d_i)^3 - 1\right] SL_{bm}}{(1-SL_{bm})\rho_{bm}\left[(1+2t_{bm}/d_i)^3 - 1\right]}$$

For prop SD-III-18 from Miller (1982); figure from Varunkumar et al (2016)

Composition of binder-matrix & t_b used to calculate O/F

For a typical state-of-art propellant, %AP distribution varies from as low as 55% to as high as 99%

Stoichiometry is around 88% AP

Theory should account for this wide variation

Now, having calculated the statistical particle path, we know how much AP is surrounded by how much of binder, and therefore, we can calculate the local distribution of oxidizer to fuel ratio. And the oxidizer to fuel ratio distribution in a heterogeneous propellant in a typical heterogamous propellant is like what it is shown here in this plot. What is on the x-axis is the diameter of the AP particle and what is on the y-axis is the percentage AP in each one of those particles which can also be expressed as oxidizer to fuel ratio.

The important thing take away from this is same as what I mentioned earlier, packets containing smaller AP particles are fuel rich ok, and larger AP particles are oxidizer rich. This is the intuitive conclusion we came to by looking at the cross section of the propellant pack and that conclusion is burn out by the calculations also. 88 percent is where around 88 percent is where AP HTPB is stoichiometry and has maximum flame temperature. Anything above that line is AP rich, anything below is fuel rich.

And what I want you to notice again is that larger particles are AP rich smaller particles are fuel rich ok. And the flame temperature reaches a peak around 88 percent AP, and it is decreases on both the sides on the right side it approaches the AP mono propellant limit.

So, composition of binder-matrix and binder thickness is used to calculate the oxidizer to fuel ratio. For a typical state of the art propellant percentage AP distribution varies from as low as 55 percent here as you can see to as high as 99 percent for larger particles ok. Stoichiometry is around 88 percent. And any theory that is developed to predict the burn rate of the propellant should account for this heterogeneity in distribution of oxidizer and fuel.