

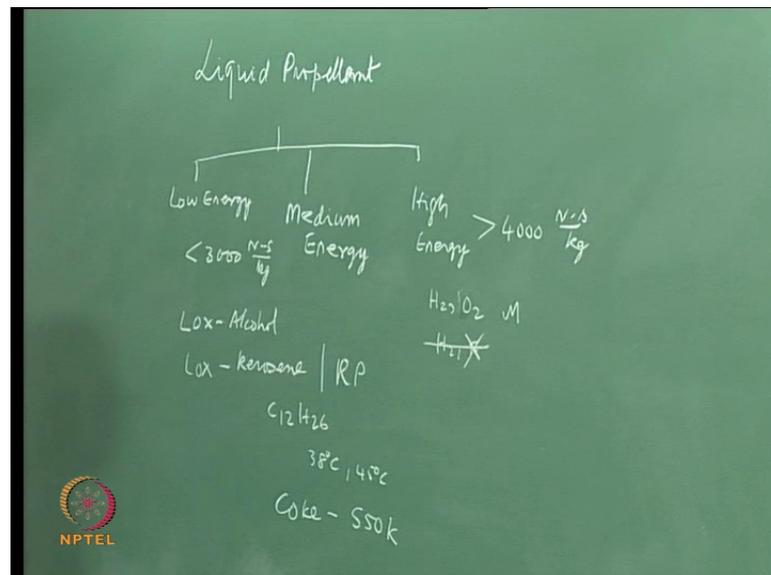
Rocket Propulsion
Prof. K. Ramamurthi
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Lecture No. # 19

Low energy liquid propellants and hybrid propellants

Good morning. In the last class we were dealing with the liquid propellants and we continue on it. But before continue on it, I would like to clarify that the classification of liquid propellants was distinctly different from the way we classified solid propellants. While we classified solid propellants into double base, composite, mixture of composite and double base i.e., composite modified double base and nitramine propellants, we had somewhat different classification for liquid propellants.

(Refer Slide Time: 00:47)



The liquid propellants were classified as low energy propellants, medium energy propellants and high energy propellants. In today's class, we continue with this classification and also we will try to see whether any other classification is also possible, so as to cover the entire spectrum of the different liquid fuels and liquid oxidizers. These liquid fuels and liquid oxidizers comprise the liquid propellants. For high energy liquid propellants, we found that hydrogen and oxygen, which generate products with low

molecular mass, give high Isp not because it has a high energy, but due to the low value of the molecular mass of the products.

Hydrogen with oxidizer fluorine will also have high energy but fluorine being very reactive cannot be used as a propellant. This was about high energy propellants and we said that high energy propellants are those which have specific impulse greater than 4000 Newton second by kilogram. We then came to the low energy propellants. We said these are propellants which have specific impulse is less than about 3000 Newton second by kilogram. And for this we considered liquid oxygen LOX with alcohol which was used in the V 2 rocket in 1945. It was developed by the Germans. I always take this is an example but alcohol contains oxygen also in addition to hydrocarbon and it is not that energetic.

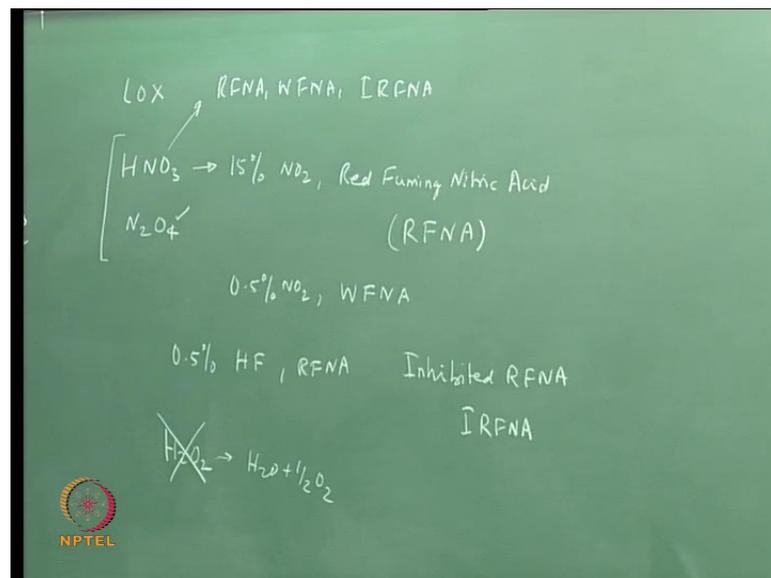
From LOX alcohol, we went to LOX kerosene. When we look at kerosene we find well, kerosene is something like an aliphatic compound; we said something like $C_{12}H_{26}$ and since it comes from a petroleum base, it also contains some other constituents and is not a pure chemical. And therefore, while using it we need to be careful. Raw kerosene has a flash point around $38^{\circ}C$. And we wanted it to increase it for which we added additives. Additives are also added to modify other properties of kerosene. The resulting kerosene used with liquid oxygen was called as rocket propellant (RP).

Flash point temperature is the temperature of the liquid fuel at which the vapor forms a flame when mixed with air but the flame cannot persist since the vapor gets consumed. Fire point is the temperature of the liquid fuel wherein so much of copious vapour is produced such that flame persists even when you remove the ignition source. The flash point of kerosene is around 38 degrees Celsius and we increase by adding additives. Further, when you heat liquid kerosene in the absence of oxygen it should not form solid residues like coke and coking temperature is the temperature at which such residues are formed. By adding additives we make sure the no such coking takes place till a temperature of around 550 Kelvin. This is because during the passage of kerosene in cooling channels or injection ports, it should not block the flow due to the coking if it is heated.

Though, basically when we say LOX kerosene propellant, we refer to it as rocket propellant RP. It is not correct to say a combination because we could use it at different mixture ratios.

Let us see what are the other combinations of liquid oxidizers and liquid fuels which could be the low energy propellants.

(Refer Slide Time: 04:56)



We considered LOX as an oxidizer. Why should LOX alone be an oxidizer? Any substance which has excess oxygen could be an oxidizer. We could have HNO₃, nitric acid. And if you see HNO₃, it consists of one H and one N. N any way is inert. We have three of oxygen what you need is half O to form H₂O. That means we still have two of oxygen. Therefore, nitric acid can be used as an oxidizer and it is used as an oxidizer. We could also consider the other substance maybe N₂O₄ which have more oxygen in it than HNO₃. In the case of HNO₃, we saw while we looking at the heat of formation it has something like minus 170 kilo joules per mole for the heat of formation. Whereas, N₂O₄ had slightly positive heat of formation. We also noted that for propellant, if the fuel and oxidizer have slightly positive or small negative values of heat of formation, it is to be preferred as the energy released in the reaction increases. Therefore, N₂O₄ tends to a better oxidizer compared to nitric acid.

In HNO_3 you are losing some oxygen to the hydrogen whereas, in the case of N_2O_4 all the oxygen is available for the burning. N_2O_4 is also used as an oxidizer. Let us go a little deeper into HNO_3 as it was used extensively and is still used in strategic rockets.

HNO_3 is used as such; but if we add NO_2 to it, we add more oxygen to it and it becomes more energetic. Therefore, HNO_3 is sort of energised by addition of something like fifteen percent NO_2 and what happens? You know you have fumes of NO_2 coming out the moment you open the lid of the HNO_3 tank and therefore HNO_3 with NO_2 added to it is known as red fuming nitric acid or rather RFNA. These fumes of NO_2 coming are orangish or reddish in colour and hence the name RFNA. We will see some photographs of some test firings and the fumes. You will see some orangish fumes in the plume. If you add a smaller amount of NO_2 say 0.5 percent, the HNO_3 still fumes but not as red fumes. It is known as white fuming nitric acid WFNA.

Both RFNA and WFNA are used in practice as oxidizers; but then this acid is very corrosive. Both the red fuming nitric acid and white fuming nitric acid are extremely corrosive it tends to corrode the vessel in which it is stored. Therefore, what is done is that we add something like 0.5 percent of hydrofluoric acid to say RFNA and this inhibits the corrosive nature of the oxidizer. This inhibited RFNA is known as inhibited red fuming nitric acid IRFNA.

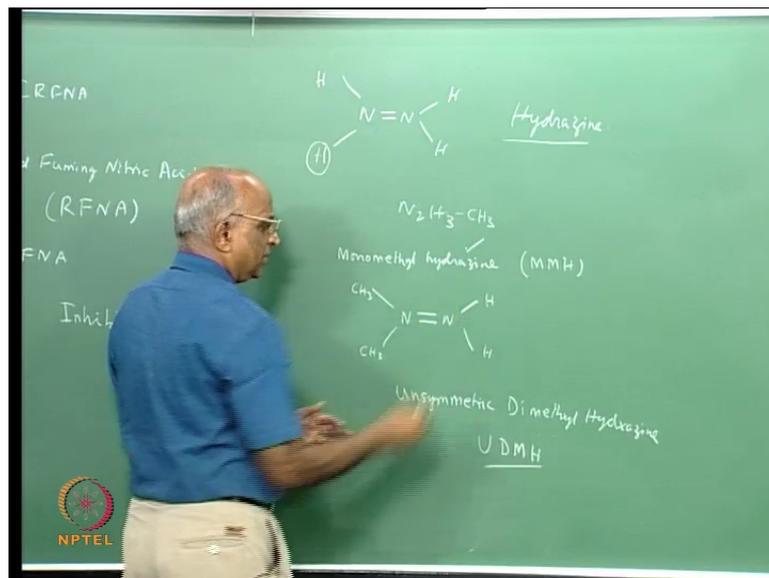
Therefore, you have nitric acid as red fuming nitric acid, white fuming nitric acid and with additive hydrofluoric acid HF added to it such that the corrosion of the tank is suppressed it becomes IRFNA or IWNA. Therefore, while considering nitric acid let us keep in mind RFNA, red fuming nitric acid; WFNA, white fuming nitric acid and may be modified or inhibited red fuming nitric acid. You could also have inhibited white fuming nitric acid. These are the different forms in which nitric acid is used. It was used extensively in defense and in other establishments but now the preferred oxidizer is N_2O_4 . This is more energetic considering the slightly positive heat of formation of N_2O_4 . Well these are about the only oxidizers which are used in addition to liquid oxygen.

Hydrogen peroxide H_2O_2 is also an oxidizer because we find there is still excess oxygen over hydrogen H_2O . We are still left with one O; but it is a very mild oxidizer with small oxygen content. It has a heat of formation which is again terribly negative. Something like -180 kJ/mole and therefore, it is not an effective oxidizer. In fact H_2O_2 can directly

also dissociate into $\text{H}_2\text{O} + 1/2 \text{O}_2$ and this reaction is exothermic. It is used more as a single propellant i.e., mono propellant; as a single in built explosive consisting of oxygen and fuel rather than as an oxidizer.

Therefore, the two oxidizers other than LOX which we can consider are HNO_3 and N_2O_4 . Now, let us list the fuels which they are used with. We note that these oxidizers will not be as strong as liquid oxygen for the simple reason you are having some little bit of nullifying effect of hydrogen and nitrogen. When we use HNO_3 with kerosene or N_2O_4 with kerosene the performance is going to be even poorer than LOX with kerosene and therefore, combination of these oxidizers with the fuels what we considered like kerosene will be still be low energy propellants. Let us take look at fuels, other than kerosene.

(Refer Slide Time: 11:10)



We can talk in terms of what we talked earlier hydrazine, N_2H_4 . It is a very popular fuel. You know this also had a slightly positive heat of formation and therefore is a good fuel. You have lot of hydrogen in it and therefore, you could have molecular mass of the products which could still be small.

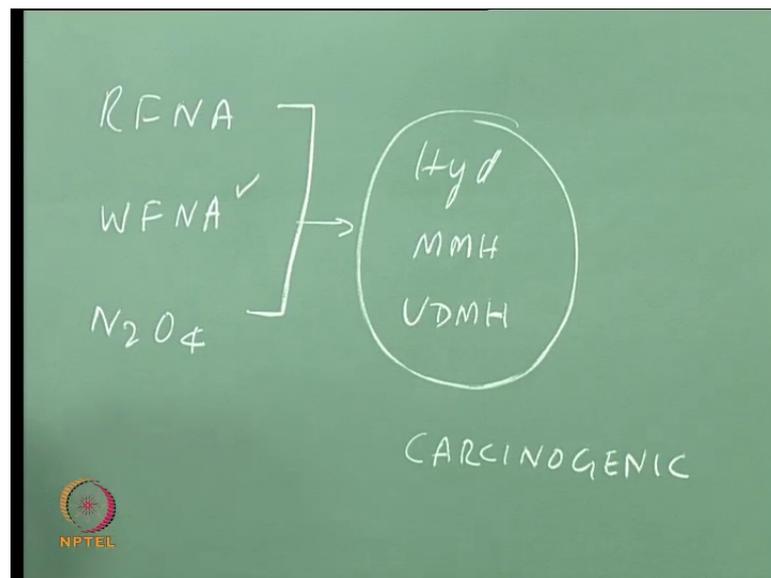
We can take one of the H from hydrazine and substitute it with a methyl radical. In other words from N_2H_4 , we take one of the H out, we are left with 3 H, and we substitute the H with CH_3 . In other words we substitute one methyl radical in hydrazine and we get what is known as mono methyl hydrazine $\text{N}_2\text{H}_3\text{CH}_3$ (MMH). While talking of different

chemicals you will recall, we said hydrazine is an explosive in the sense it can directly dissociate whereas, mono methyl hydrazine is also about the same. It has about the same heat of formation around -50 kJ/mole but it has a higher specific heat and it is not as reactive as hydrazine. Therefore, the preference is to use mono methyl hydrazine rather than hydrazine. But hydrazine is also used. Being more reactive requires some more care as it is more prone to combustion instability.

Hydrazine tends to be a little unstable compared to mono methyl hydrazine. We can keep on evolving around hydrazine. Instead of taking one hydrogen atom in hydrazine and substituting it by a methyl radical, on one side of itself i.e., unsymmetrically we put one more methyl radical here – two of them, and this is known as unsymmetrical dimethyl methyl hydrazine UDMH ($N_2H_2(CH_3)_2$]. It is not as strong as hydrazine because now you are adding more carbon molecules to it but it is a very powerful fuel. Most of the liquid propellant boosters that we are using in our country make use of unsymmetrical dimethyl hydrazine for fuel.

Therefore, the fuels which we have considered so far are UDMH, MMH and hydrazine. These three fuels can be used with RFNA or with white fuming nitric acid which is quite rare or with N_2O_4 .

(Refer Slide Time: 14:18)

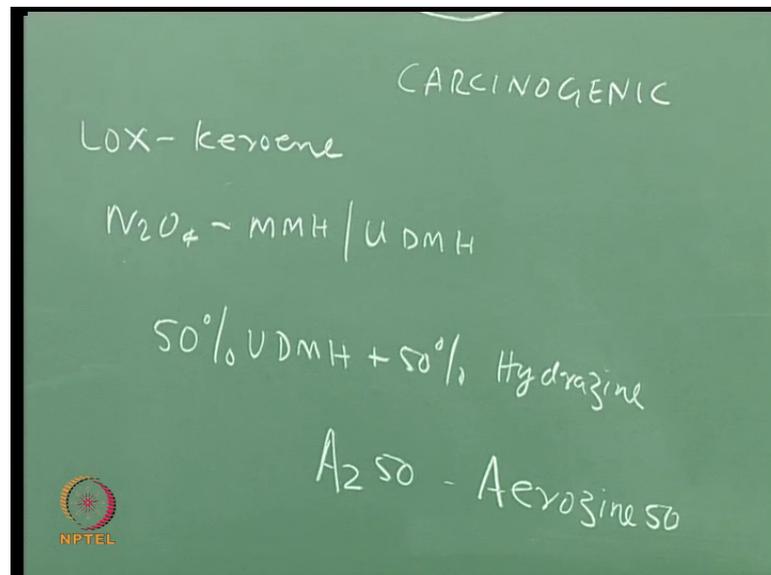


We use these oxidizers with hydrazine or mono methyl hydrazine or UDMH. Mono methyl hydrazine has a high specific heat and more expensive compared to UDMH.

Therefore, wherever smaller quantities of hydrazine fuel are required we use mono methyl hydrazine like in upper rocket stages where we do not want to use so much of fuel. Hydrazine is also used especially in spacecrafts, but as I told you it is little more reactive whereas UDMH is more widely used for wherever large propellant requirements are there.

All these three fuels can cause cancer and there is a trend in today's world to get back and substitute it by kerosene or some other fuel. We call these fuels as carcinogenic. But in rocketry since only small quantities are required we take adequate precautions, we continue to use these fuels.

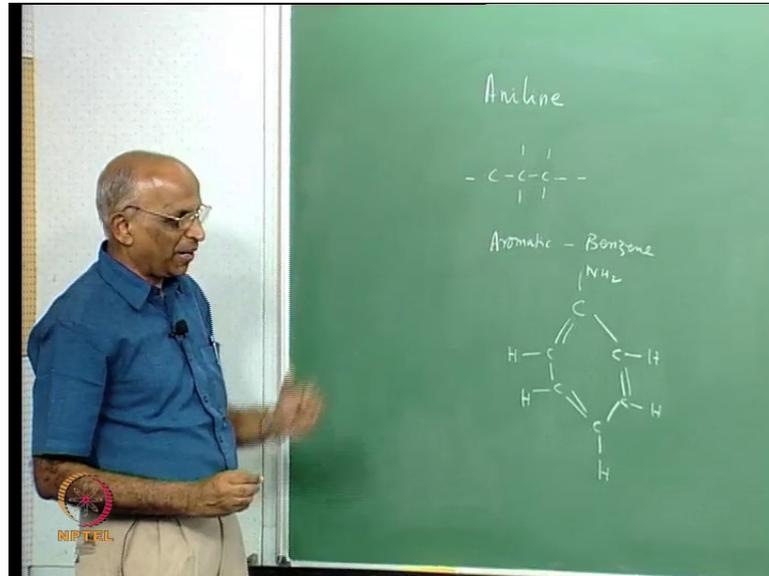
(Refer Slide Time: 15:40)



Therefore, we summarize the low energy fuels: In addition to LOX kerosene, we could have N_2O_4 with mono methyl hydrazine or with unsymmetrical dimethyl hydrazine i.e., either MMH with N_2O_4 or UDMH with N_2O_4 . There is also one last fuel which we call as a mixture of fifty percent UDMH plus fifty percent hydrazine. This is known as AZ fifty and is used with N_2O_4 . It is used in some of the rockets developed in US. Therefore, the low energy propellants could be LOX alcohol, well this is outdated and alcohol is replaced by kerosene. HNO_3 in the form of red fuming nitric acid and N_2O_4 which more energetic, and fuels hydrazine, MMH and UDMH. These are the low energy liquid propellants.

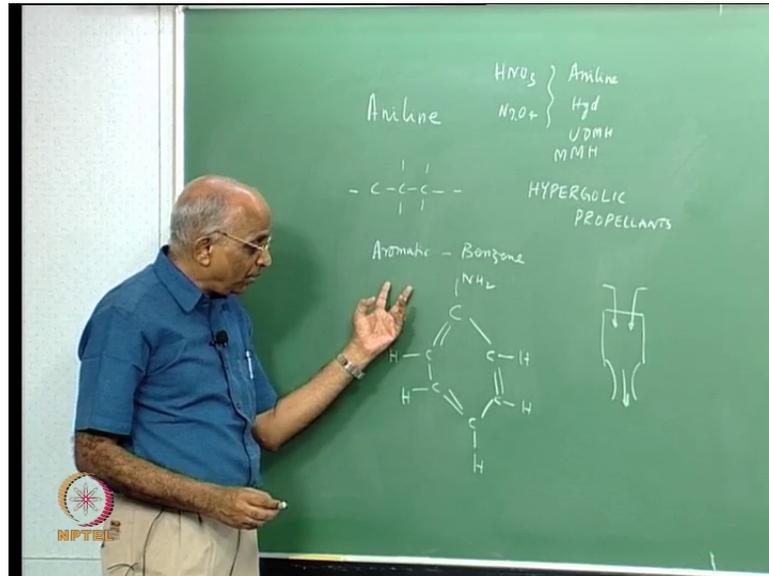
It may be useful to go back in history and address a few other fuels used in rockets for missiles. We still see some other fuels being used earlier especially at DRDL when they were making missiles.

(Refer Slide Time: 17:28)



One is known as aniline. See, while all the fuels what we considered were somewhat based on aliphatic compounds like kerosene we say C C all in the straight chain, aniline is derived from an aromatic compound. Aromatic compound corresponds to the benzene chain. You have six carbon atoms with alternate double bonds. What do you do in aniline is to substitute one of the hydrogen atoms in the benzene molecule by the amine radical NH₂. This becomes aniline. Let us keep this in mind because we will come back to this NH₂ amine radical. We have NH₂ in hydrazine and NH₂ in MMH and UDMH. This amine radical is very reactive and gives an important property to the propellant.

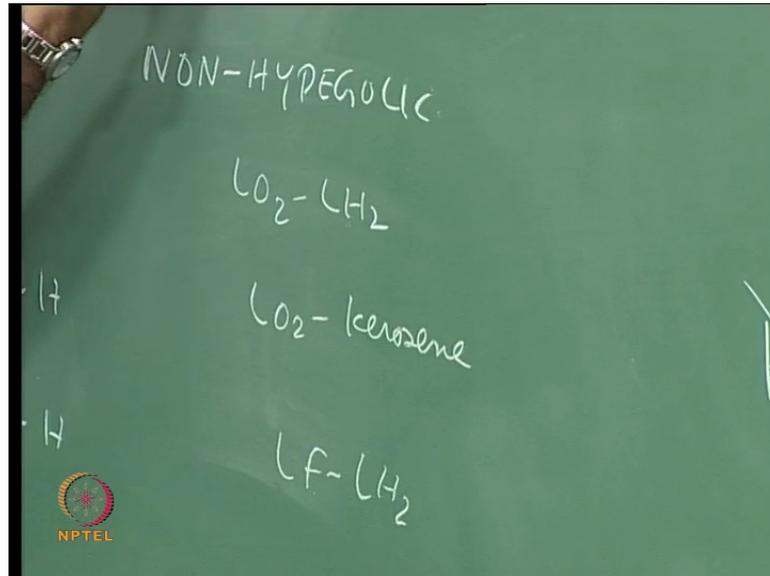
(Refer Slide Time: 18:56)



That the moment the fuel containing NH_2 comes in contact with let us say HNO_3 or with N_2O_4 , it ignites and reacts. Such of the propellants which contain this amine radical readily react with HNO_3 and N_2O_4 . And such propellant combinations of N_2O_4 or HNO_3 with a fuel like aniline or with hydrazine or UDMH or MMH will not therefore, require an ignition source to start the combustion process.

All what we do is to introduce the fuel, one of these fuels with the oxidizer into the chamber. Immediately by itself it will ignite and these are known as hypergolic propellants. Why is it hypergolic? The amine radical in these fuels readily reacts with the acid or the N_2O_4 to form hot combustion products. Therefore, the design of the rocket become much simpler. All what we need to do is to push this fuel having the amine radical in the chamber, push the oxidizer into the chamber and when the two mix it burns and releases hot gas. We do not even need to ignite it extraneously. We do not need an auxiliary igniter whereas, if we consider even liquid hydrogen or kerosene with liquid oxygen and N_2O_4 , we need to ignite it because we have to overcome the energy barrier before a chemical reaction can take place. These are all hypergolic low energy propellants.

(Refer Slide Time: 20:48)

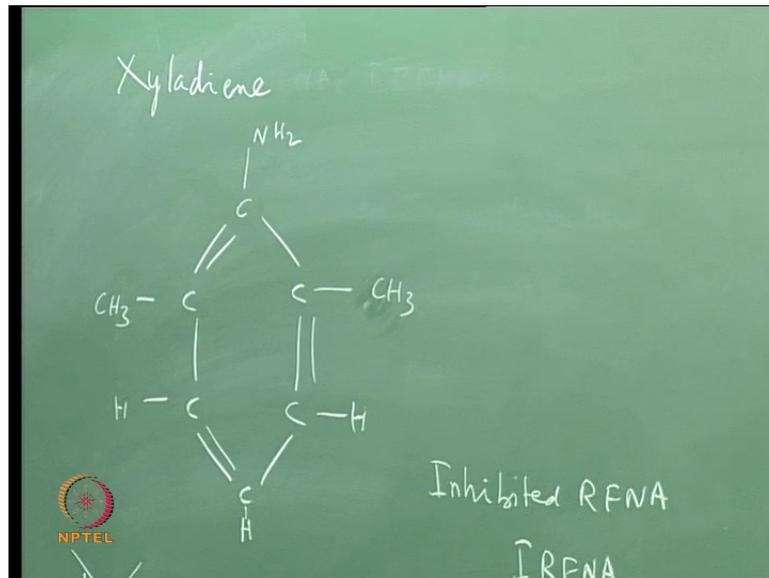


And we call those propellants which require an ignition source for initiating reactions or combustion as being non-hypergolic. These are liquid oxygen with liquid hydrogen, liquid oxygen with kerosene.

The only exception is liquid fluorine and liquid hydrogen. Liquid fluorine is so reactive that it will react with anything including the container in which it is stored. Therefore, it is also comes in the category of hypergolic propellant. But mind you, it does not contain an amine radical. It comes from the reactivity of fluorine itself.

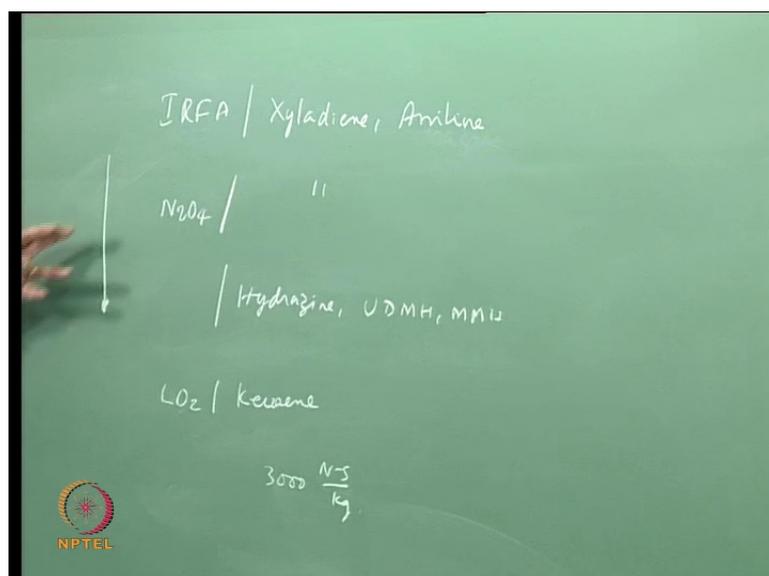
Aniline was extensively used in the seventies and eighties. As a slight improvement over aniline one very last fuel of which we talk is known Xyladiene.

(Refer Slide Time: 21:40)



And in xyladiene we have the same aromatic structure of benzene, you have alternate double bonds, you have NH_2 here as in aniline. We take two more of the hydrogen atoms and replace it by methyl radicals as shown. This substance is known as xyladiene. Again it consists of an amine radical and therefore, it is hypergolic with N_2O_4 , RFNA and WFNA. Aniline and xyladiene are used as liquid fuels for some the missiles. They are low performing with low energies.

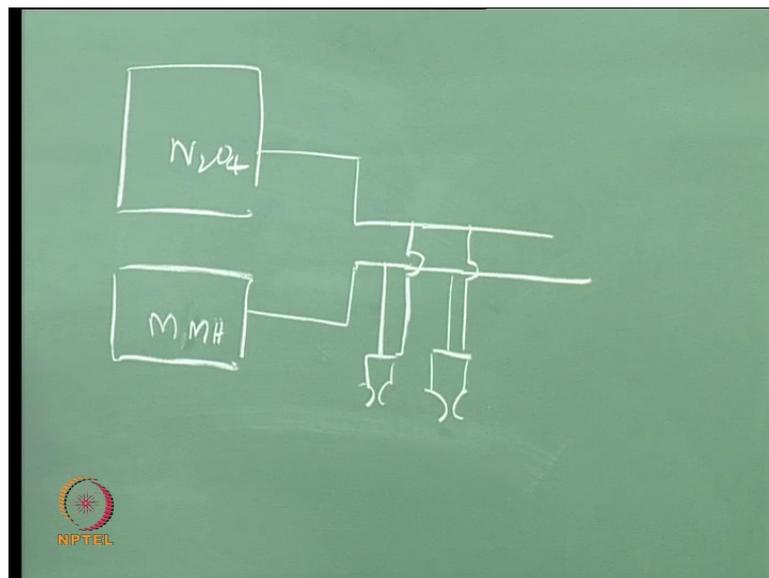
(Refer Slide Time: 22:49)



We can say that IRFNA with xyladiene or aniline or better still with N_2O_4 and N_2O_4 with hydrazine and UDMH and with MMH and LOX with kerosene are the low energy propellants with progressively increasing Isp values. However, the maximum Isp is less than about 3000 Newton second by kilogram.

These are the low energy propellants and many of these low energy propellants especially those using the nitric acid and N_2O_4 are hypergolic which means they are much easier to use. This is why we see these fuels being repeatedly used in spite of being carcinogenic and having low performance. The rocket construction gets simpler. You do not need an auxiliary igniter. We can whenever we want to you just fire it. Supposing we have a space craft; let us say that in the space craft you have a fuel tank and an oxidizer tank. The oxidizer is N_2O_4 and fuel is MMH.

(Refer Slide Time: 24:31)

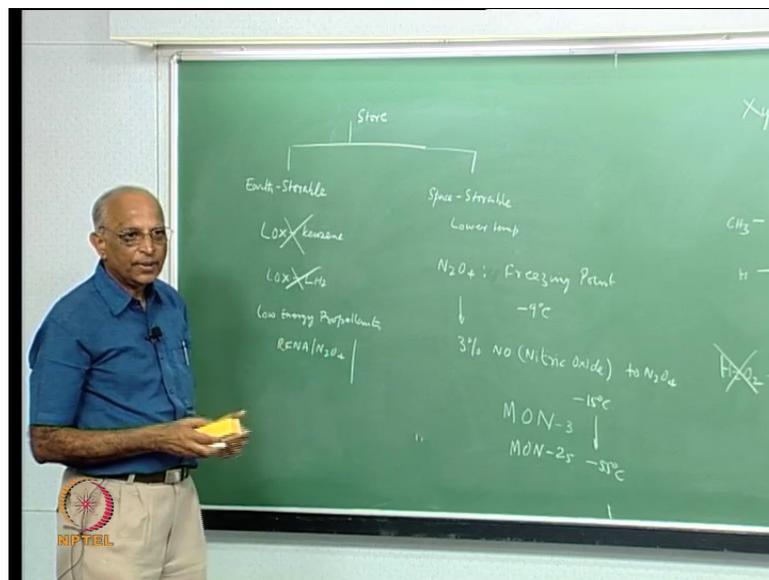


A spacecraft such as INSAT has a number of small rockets for attitude and orbit corrections. We have some 12 such rockets and these are connected to the fuel and oxidizer tanks through flow control valves and regulators. Whenever you want to have some correction to be done in the spacecraft for which a particular rocket has to operate, we feed the propellants into it. We just have to open the valve for a given duration. It will give an impulse which is used for the correction. We do not need any other ignition device to be able to initiate the combustion in the rocket and that is the advantage of many of the low energy propellants.

For large boosters for which fuel and oxidizer are required in abundance LOX and kerosene are desired. Kerosene is readily available it is a very cheap fuel again and that is why the majority of the boosters of the launch vehicles, which require large quantities of fuel make use of liquid oxygen and kerosene. We are still to start with these activities in our country. The only problem is that it becomes a semi cryogenic propellant.

At this point in time I will slightly divert the discussions and return to the medium energy propellants a little later.

(Refer Slide Time: 26:04)



We covered hypergolic, non-hypergolic propellants and this could as well be a classification of the propellants. The classification of propellants can also be done under how you can store the propellants. Why do we say storing is so important? Suppose we have a missile to take off; see a missile must be ready for launch at any point in time. That means the tanks of the missile must be always filled with the fuel and the oxidizer. If a propellant could be stored on Earth we say the propellant is Earth storable. If we want to use it in a space craft and the space craft goes round for twenty years or twenty five years, the propellant must be there in the spacecraft during the period of the orbit. That means the propellant must be storable in space. The distinction between Space storable and Earth storable is in the conditions experienced in space and on the Earth.

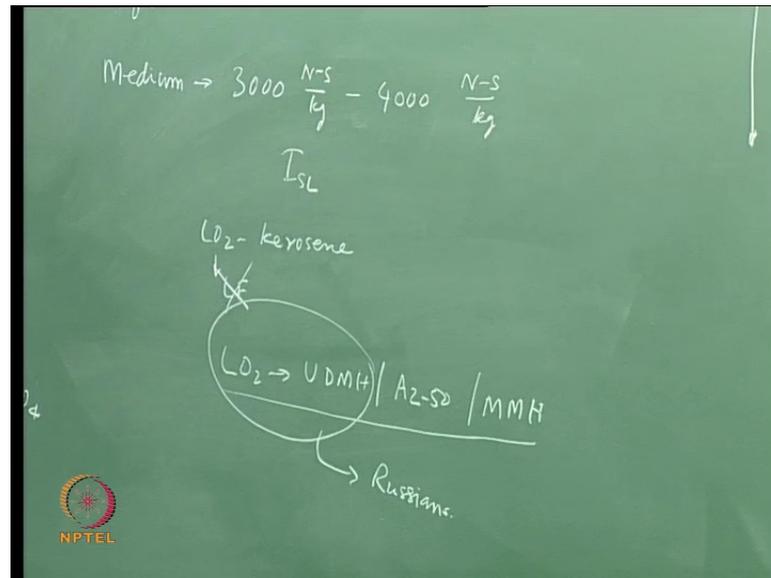
If we have LOX-kerosene we cannot keep it on ground all the time because LOX has to be kept under refrigerated conditions or under insulated conditions for a short time. Otherwise it will evaporate. Therefore, this is not even Earth storable let alone space storable. You know similarly, LOX and liquid hydrogen are cryogenic fuels requiring special storage. Semi cryogenic and cryogenic fuels are not Earth storable and only the low energy propellants, such as red fuming nitric acid or N_2O_4 as oxidizer with hydrazine, UDMH and MMH are Earth storable. Space storable poses harsher criterion; it becomes more difficult to store. In space we can get much lower temperatures and therefore, not all Earth storable propellants can be space storable. For instance let us take an example N_2O_4 as a very good oxidizer.

Let us consider the freezing point of N_2O_4 ; the freezing point of N_2O_4 is around $-9^\circ C$ and whenever we have a spacecraft, when it is not looking at the sun the temperature comes down. Therefore, we need heaters to keep this warm; but if we were to add something like three per cent of nitric oxide that is NO to it, that means three per cent nitric oxide to N_2O_4 we can decrease the freezing point. The freezing point instead of being $-9^\circ C$ can be decreased to $-15^\circ C$. Therefore, if we have to make the oxidizer N_2O_4 perform in space one of the things to be done is may be we should add some additives like nitric oxide. If we add three per cent, we have a little lower freezing point. The addition of NO to N_2O_4 makes it into mixed oxides of nitrogen and the mixture is known as Mixed Oxides of Nitrogen MON. When we add three per cent NO, we call it as MON 3.

When we use N_2O_4 as an oxidizer and if the same N_2O_4 has to be used in space for a prolonged period then we have to decrease its freezing point. We do that by adding NO to it. If we add three per cent it is known as MON 3. If I add something like 25 percent of NO to N_2O_4 we can decrease the freezing point to $-55^\circ C$, which is even better. Therefore, in space we can use the fuel as MMH, but we substitute N_2O_4 partly by NO to get MON. This is the difference between Earth storable and space storable propellants; cryogenic and semi cryogenic propellants are those which are neither earth storable or space storable. They can be used in launch vehicle and conditioned may be a day or a few days before the launch.

The cryogenic and semi-cryogenic propellants cannot be used for missiles nor for satellite propulsion and control. These are the different classification of propellants.

(Refer Slide Time: 30:46)



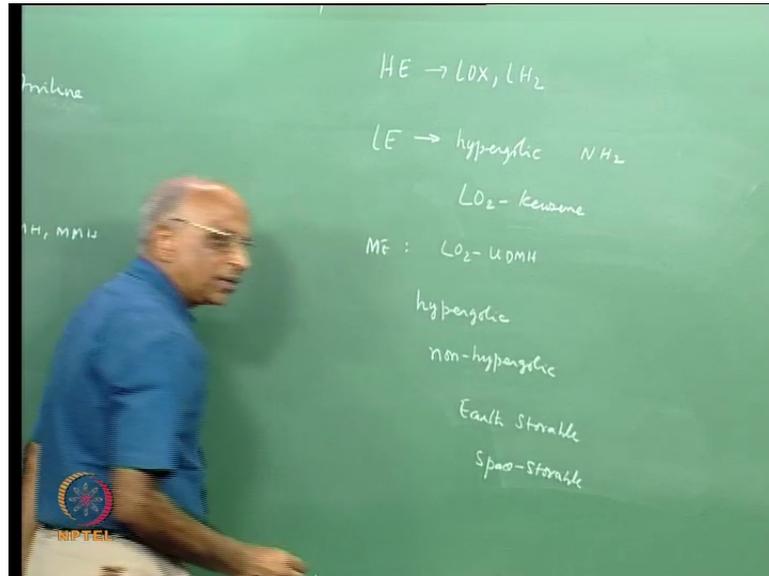
Medium energy propellants would have I_{sp} in the range between 3000 Newton second by kilogram and 4000 Newton second by kilogram. We talk in terms of sea level specific impulse because vacuum specific impulse is much higher than what we evaluate on the ground. Therefore, whenever sea level specific impulse is less than three thousand, we say it is low energy, when it is greater than 4000, we say high energy propellant. But there are hardly any good medium energy propellants.

The only exception which we can think of is instead of having LOX kerosene, if we use instead of LOX, liquid fluorine, it gives an specific impulse greater than 3000; something like 3200 and it could be a good candidate. But liquid fluorine cannot be used as it is extremely reactive.

Oxidizers like RFNA, N_2O_4 are inferior to LOX because they contain some other elements in addition to oxygen. Therefore, if we can use LOX instead of N_2O_4 with one of the fuels say UDMH or let us say combination of UDMH and hydrazine, Aerozine 50 or let us say with MMH, then we get higher performance in excess of 3000 Newton second per kilogram. And these are the medium energy propellants. But in practice this propellant combination LOX and UDMH has been used only in Russia.

Therefore, with liquid propellants, we find only a few propellants in the three categories of low energy, medium energy and high energy are used. Let us now summarize it.

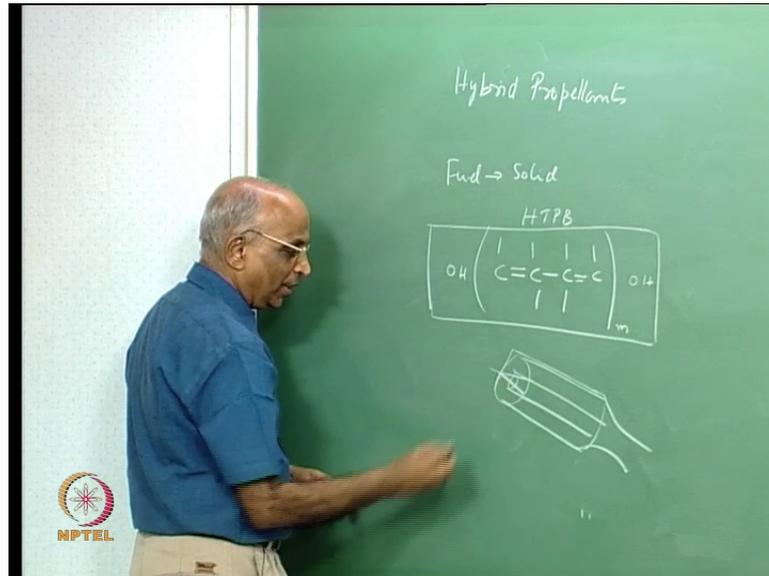
(Refer Slide Time: 33:06)



High energy propellants are neither storable on Earth or in Space. It could be LOX (liquid oxygen) and liquid hydrogen. The low energy propellants are generally storable on Earth and many of them are storable in space with little modifications such as MON 3 or MON 25 instead of N_2O_4 . These are essentially hypergolic whenever the fuel contained the amine radical in it and the oxidizer was N_2O_4 or HNO_3 . The low energy propellants liquid oxygen and kerosene is not Earth storable neither is it space storable. You have the medium energy propellants which is again semi cryogenic liquid oxygen and UDMH. This is the only propellant in the medium energy category which has been used in a rocket so far. Well, these are the classifications according to energetics of the propellant. We could classify the propellants into hypergolic or non-hypergolic. Hypergolic are ones which in which the oxidizer and the fuel when they come in contact it automatically burns. We will consider this aspect when we deal with liquid propellant rockets.

Non-hypergolic propellants need an igniter to get the combustion started in the rockets. The last classification of propellants was based on being Earth storable liquid and space storable. The semi cryogenic and cryogenic are neither earth storable nor space storable. This is all about the different liquid propellants that we considered.

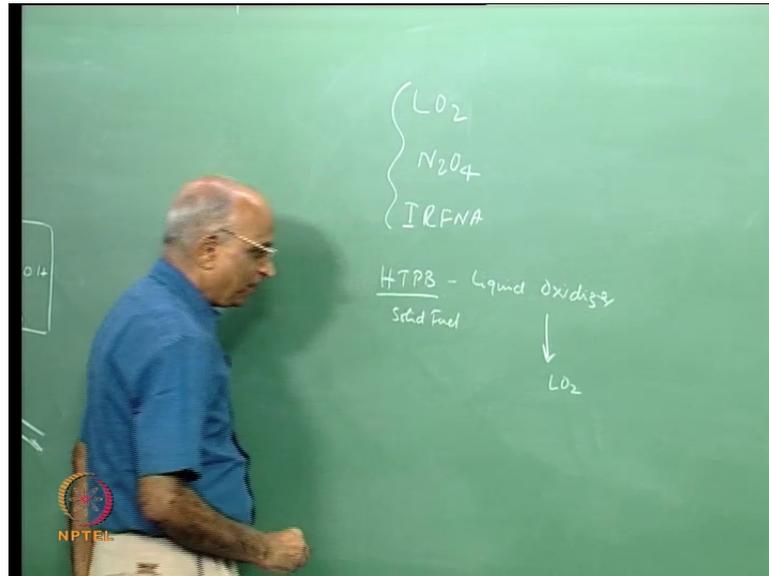
(Refer Slide Time: 35:14)



We have considered solid propellants and liquid propellants; let us take a look at what are the hybrid propellants. Thereafter, we can solve one or two small problems. What do we mean by hybrid propellants? Hybrid propellants are those propellants which are in a mixed phase: may be the oxidizer could be a solid, fuel could be a liquid whereas, the other one could be a gas or a liquid. Usually the fuels of hybrid propellants use HTPB. What was HTPB? Well! it is poly butadiene. You have C C C and C two double bonds and a single bond between C atoms and between C and H. This is what was poly butadiene and it was a chain as it is, may be m times over. The chain is terminated by hydroxyl radical and we get hydroxy terminated poly butadiene. That means we have one OH here, I have one OH here. This could be a fuel. The advantage we had with hydroxy terminated poly butadiene was lighter hydrogen in it compared to PBAN which was poly butadiene acrylic acid acrylo nitrile.

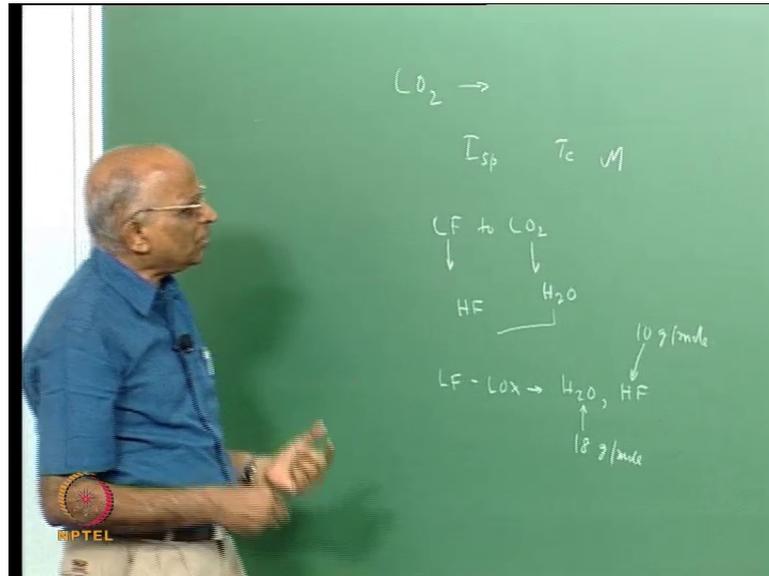
Therefore, a typical fuel solid fuel for a hybrid rocket is something like HTPB grain or solid and what is done is you form a solid as shown with a hole in it and then put it in a cylindrical case and attach it to a nozzle. The HTPB is the solid fuel. Now we require an oxidizer. We could inject the liquid oxidizer on it. The oxidizer could be anyone of the oxidizers we have considered.

(Refer Slide Time: 37:15)



The oxidizers could be liquid oxygen, could be N_2O_4 , could be red fuming nitric acid or better still inhibited red fuming nitric acid. We'll use one of these oxidizers and spray them on the solid fuel. The fuel and oxidizer begin to react and hot gases are generated. The hybrid combination is generally a solid fuel such as HTPB and one of the three liquid oxidizers. We do not use a gaseous oxidizer, because we need a large volume to store it. There was a time in 80's when there was lot of interest in hybrid rockets but again now a days we see the private companies in US developing hybrid rockets for space tourism. These are manned vehicles which will take tourists from ground to space using hybrid rockets. When we talk of liquid oxidizers, liquid oxygen is powerful enough.

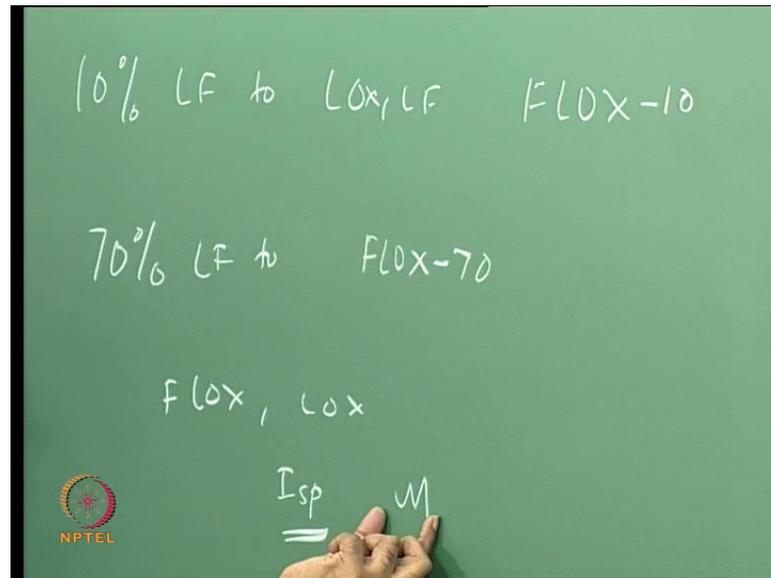
(Refer Slide Time: 38:50)



Can we make the value of the specific impulse of let us say liquid oxygen with a solid fuel to be higher in some way than by modifying the property of the liquid oxygen itself? The specific impulse can be increased by either increasing the combustion temperature or reducing the molecular mass of the combustion products. Either you increase the temperature of the combustion products or you reduce the molecular mass of the combustion products. Let us examine the following: Supposing we add liquid fluorine to liquid oxygen; then in that case, when the oxidizer is liquid oxygen and the solid fuel is hydrocarbon, the product of combustion is water from the hydrogen in hydrocarbon.

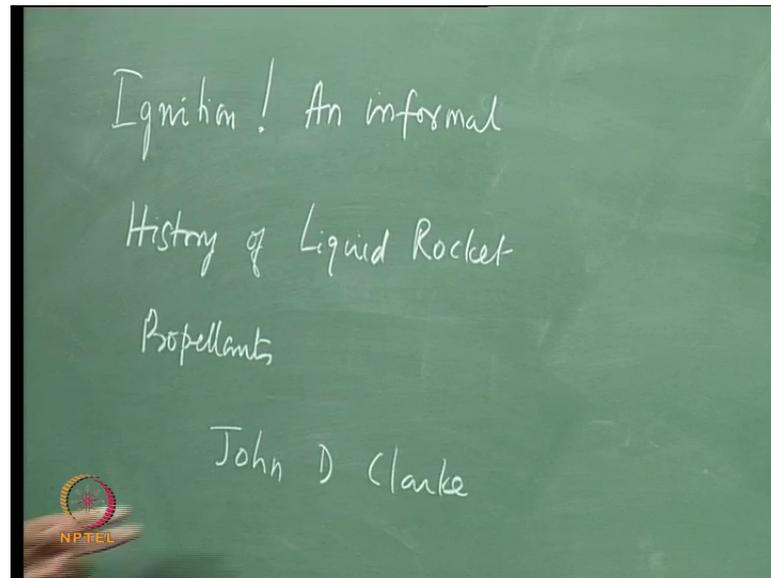
Now, with some liquid fluorine added to liquid oxygen and mind you it is quite easy to add liquid fluorine to liquid oxygen, because the boiling point of liquid fluorine and liquid oxygen are about the same in addition to getting water since I add fluorine, I also get hydrogen fluoride. Therefore, the products of combustion now with liquid fluorine added to liquid oxygen are in addition to H_2O , hydrogen fluoride HF also. The molecular mass of water namely H_2O is 18 g per mole: $2 + 16 = 18$ g/mole. The molecular mass of hydrogen fluoride is 10 g/mole. Therefore, you find that the act of adding liquid fluorine to liquid oxygen results in getting more of hydrogen fluoride as we increase the quantity liquid fluorine to oxygen and therefore the net value of the molecular mass of products that we get decreases. Therefore, since this molecular mass decreases, we get higher value of specific impulse.

(Refer Slide Time: 40:59)



Therefore, what is it that we do? May be we add liquid fluorine to liquid oxygen: say 10% of liquid fluorine to a mixture of liquid oxygen and liquid fluorine. That 10% liquid fluorine in this particular mixture; it is known as FLOX 10. FLOX stands for fluorine and liquid oxygen. If we add something like seventy percent of liquid fluorine to the liquid oxygen mixture then we call it as FLOX 70. Therefore, by using FLOX instead of liquid oxygen LOX, we get much higher specific impulses and therefore, these are considered to be higher energetic oxidizers. The main aim therefore is by using FLOX instead of liquid oxygen LOX, we get a higher value of specific impulse. The higher value of specific impulse does not come from the energetics of propellant alone. But by a reduction in the molecular mass of the products which gives us the higher value of specific impulse. Let us keep this in mind; we can improve the performance of propellants by reducing the molecular mass of the products.

(Refer Slide Time: 42:24)



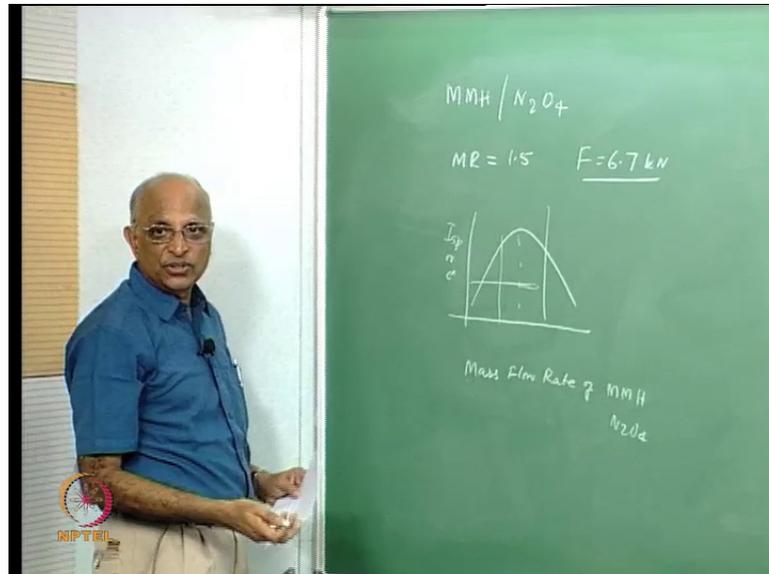
We said that propellants could either be solids, could be liquids or could be a hybrid combination of fuel and oxidizer. We classified solids into four categories and what were the four categories? We said it could be a double base or a single base, it could be a composite in which case you have crystals of solid oxidizer dispersed in fuel heterogeneously, it could be a combination of the above two: composite modified double base. It could also be a nitramine propellant. For liquid propellants liquids we said could be space storable, earth storable, hypergolic, non-hypergolic. We also said: low energy, medium energy and high energy and of course, we looked at hybrid propellants.

These are about the only propellants which are in use today. And when we consider solid rockets, solid propellant rockets, liquid propellants rockets and hybrid propellant rockets we will consider the details of how to incorporate the propellant to make these rockets. There are other factors we will be looking at; both the chemistry and the ballistics. This what we will be doing from the next class onwards.

I would like to give you one reference which is extremely fascinating to read about propellants. It is a book called Ignition. It is in our library the exact name of the book is Ignition - an informal history of liquid rocket propellants. It is by John D Clarke. Quite an old book though written up in 1962. But it provides a very comprehensive coverage. It not only deals with the performance, but storability, ability to handle, dangerousness, ignitability, corrosiveness, etc.

Let us quickly do one or two small problems such that we revise this particular area of propellants. The first one I choose is extremely simple but illustrative.

(Refer Slide Time: 45:20)

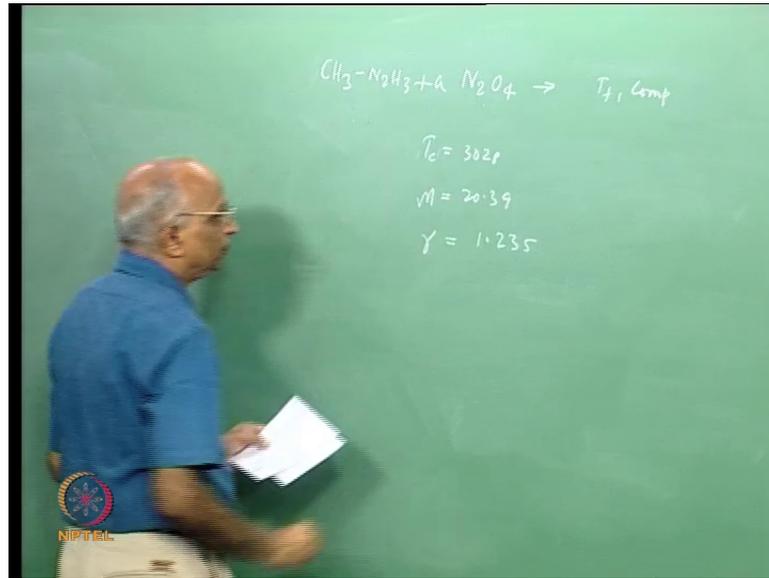


Supposing we use a MMH and N₂O₄ as propellants and we use it at a mixture ratio of 1.5 that means, the moment I choose a propellant, I also choose a mixture ratio. Why? Because choice of mixture ratio governs I_{sp} or C* value; I_{sp} and C* will be maximum in the fuel rich region. We always choose fuel rich mixture ratio. Normally even though I say 1.5, may be here we choose this because for simplicity in doing a problem. Sometimes we will use mixture ratio in which the volume quantities of the fuel and oxidizer are the same. The volume of N₂O₄ is same as MMH so that we just need to develop one tank and a similar tank can be used for both the MMH and N₂O₄.

Let us start with this problem. We need to make a rocket using MMH and N₂O₄ at a mixture ratio of 1.5; We would also be given the value of thrust. Well, the thrust is 6.7 kilo Newton. Now we ask what must be the mass flow rate of MMH into the chamber? What must be the mass flow rate of N₂O₄ in the chamber to give us a thrust of 6.7 kilo Newton? Therefore, how to estimate these quantities ?

The propellant combination is known.

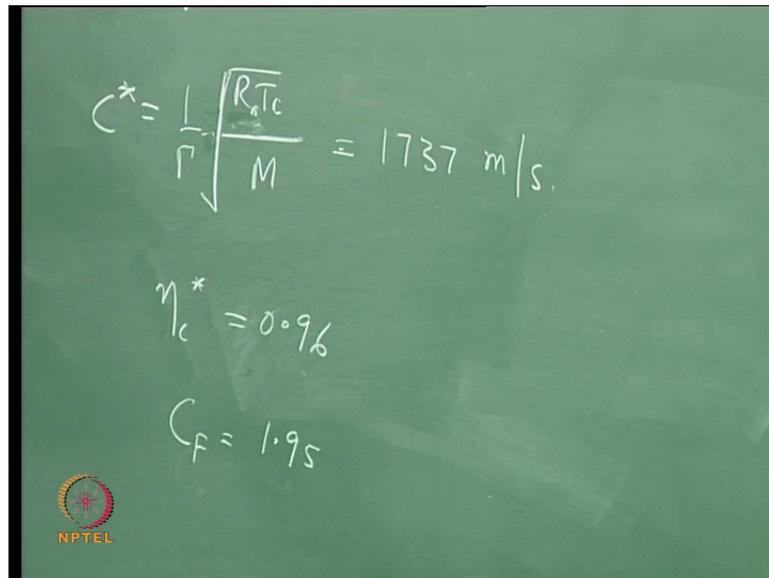
(Refer Slide Time: 47:08)



I know the formula for MMH we said it is $\text{CH}_3\text{N}_2\text{H}_3$. It reacts with N_2O_4 at the particular mixture ratio. We can write out the equation for the chemical reaction and find out the temperature of the products. We can find out the composition of the products using the methods discussed or if you want to simpler or approximate analysis one assume some products and do the problem. Assume the hydrogen to be much more reactive than carbon and therefore hydrogen first consumes the oxygen and only the balance of oxygen is left for carbon to react. The nitrogen in the substance is obtained in the products as N_2 . Therefore, the procedure is first we use the hydrogen in the fuel which searches for the oxygen, consumes it, the balance oxygen is now available for carbon to react either fully to carbon dioxide or partially to carbon monoxide. If oxygen is in short supply it may not oxidize carbon and the nitrogen in the fuel or oxidizer is available in the products as N_2 .

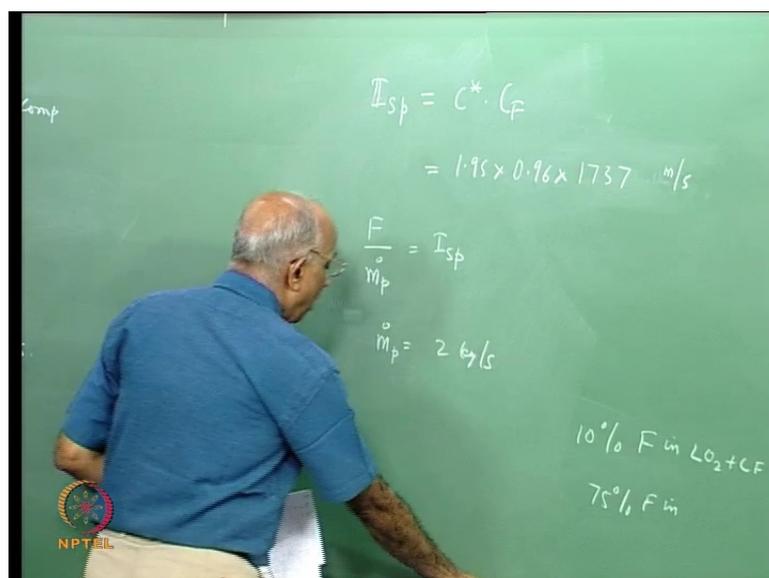
This approximate procedure is quite useful in determining the combustion products for fuel rich mixtures. However, we could do the detail problem using chemical equilibrium. We will find that the temperature of the flame or temperature of the combustion products is 3028 Kelvin; the molecular mass of the products is equal to 20.39 g per mole. The value of γ is 1.235. Once we know this, we can get the value of C^* .

(Refer Slide Time: 49:07)


$$C^* = \frac{1}{\Gamma} \sqrt{\frac{R_0 T_c}{M}} = 1737 \text{ m/s.}$$
$$\eta_c^* = 0.96$$
$$C_f = 1.95$$

$C^* = \sqrt{(R_0 T_c / M) / \Gamma}$, where $\Gamma = \sqrt{\gamma \times (2 / (\gamma + 1))^{(\gamma + 1) / 2(\gamma - 1)}}$. We substitute the values and the $C^* = 1737 \text{ m/s}$. Most of the propellants have C^* around 1800 to 2000 m/s. If we assume a C^* efficiency of 0.96 for the present since we have not yet studied how to estimate it, and also take the thrust coefficient of the nozzle to be 1.95, something which is realizable, we can calculate the specific impulse.

(Refer Slide Time: 50:33)



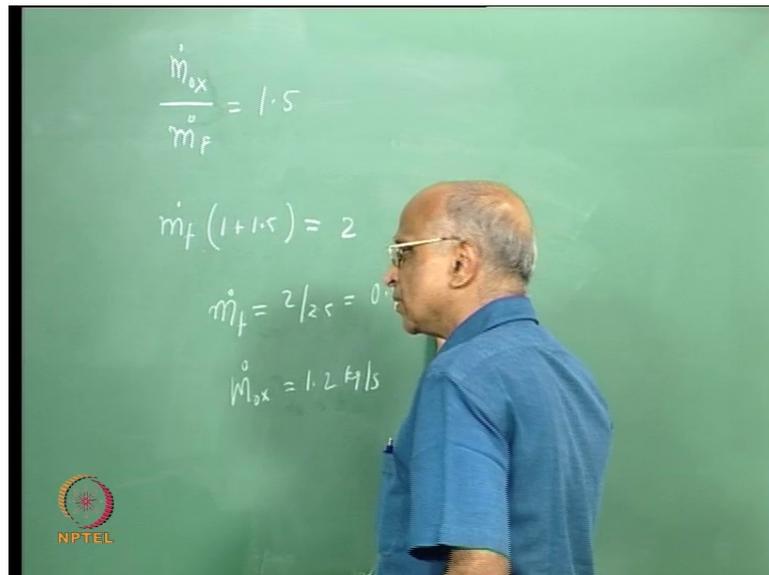
Temp

$$I_{sp} = C^* \cdot C_f$$
$$= 1.95 \times 0.96 \times 1737 \text{ m/s}$$
$$\frac{F_0}{m_0} = I_{sp}$$
$$m_0 = 2 \text{ kg/s}$$

10% F in $LO_2 + CF$
75% F in

To calculate the value of specific impulse: $I_{sp} = C^* \times C_F$ which is 1.95. C^* star is efficiency is 0.96. The theoretical value of $C^* = 1737$ m/s. Hence $I_{sp} = 0.96 \times 1737 \times 1.95$. We want a thrust = 6.7 kilo Newtons. The the value of thrust divided by the mass flow rate of the fuel and oxidizer (total propellant) is equal to I_{sp} . From this we get the value of mass flow rate of the propellant $\dot{m}^o = 2$ kg/s.

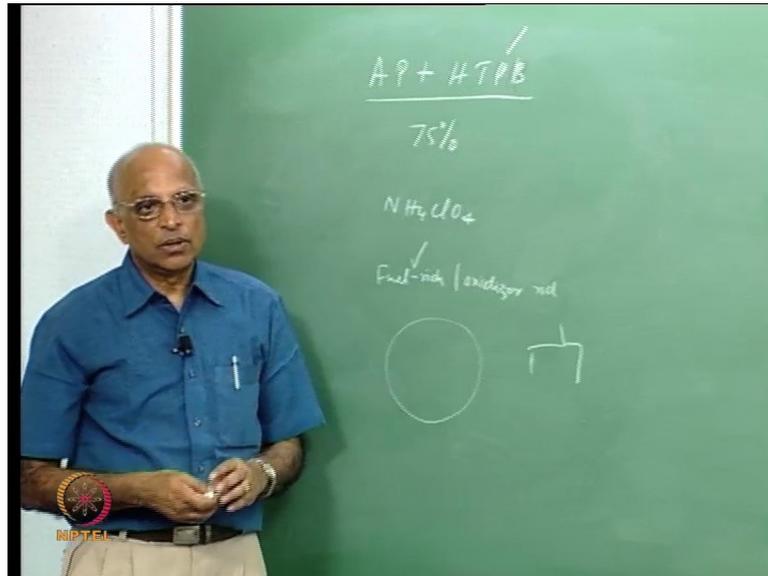
(Refer Slide Time: 51:36)



What is the flow rate of oxidizer and flow rate of fuel? You know the mixture ratio is given as 1.5. $\dot{m}^o_{ox} / \dot{m}^o_F = 1.5$. Therefore, we can get the mass flow rate of oxidizer and fuel which are 1.2 and 0.8 kg/s. This is how we solve for the propellants required in a rocket. one solves.

Let us consider another problem involving a solid propellant. Let us say I have a solid propellant which consists of ammonium per chlorate as oxidizer and HTPB as the fuel.

(Refer Slide Time: 52:49)



We specify that the solid loading in this propellant is 75 percent. We know the molecular mass of the HTPB, the molecular mass of AP namely NH_4ClO_4 and the mass of AP in the mass of propellant viz., the solid loading is given. We have to find out whether this propellant is fuel rich or oxidizer rich.

Since the molecular mass of HTPB and AP is available to us, we can find out the number of moles of HTPB and AP in 100 kg of the propellant. We divide 25 by the molecular mass of HTPB and 75 by the molecular mass of AP. From this we get the value of the number of moles of HTPB required for a single mole of AP. Then from this we write the equation for the chemical reaction and find out whether it is oxidizer rich or fuel rich. You will find even with this 75 percent solid loading the propellant is still fuel rich. All propellants tend to be fuel rich.

Please complete this problem as a homework problem?

The solid propellants are made as a solid block and in the next class we will see how to make a solid motor out of this block. Similarly, for the different liquid fuels what are the cycles which we can use such that we can get them to burn at high pressures and provide us with high values of jet velocity? And similarly, for hybrids. We will start with solid propellant rockets in the next class.