


Fundamentals of Combustion
Prof. V. Raghavan
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Lecture – 03
Fuel and Their Properties – Part 3 Liquid and Solid Fuels

(Refer Slide Time: 00:14)

Liquid fuels




Latent heat of vaporization is the energy that is required for converting the liquid to its vapor. A higher value of latent heat would indicate that higher amount of heat is required for the phase change at a given pressure and that the liquid may be less volatile.

The liquid fuel is usually at a temperature less than the boiling point to begin with. Heat is required to increase its temperature close to the boiling point. The heat supplied for this process is termed as **sensible heat**. This depends on the **specific heat** of the liquid. Then for the phase change, the latent heat has to be supplied.

Therefore, the **volatility** of the liquid fuel is generally governed by the liquid-phase specific heat, boiling point and the latent heat of vaporization.

Dr. V. Raghavan, IIT Madras 11

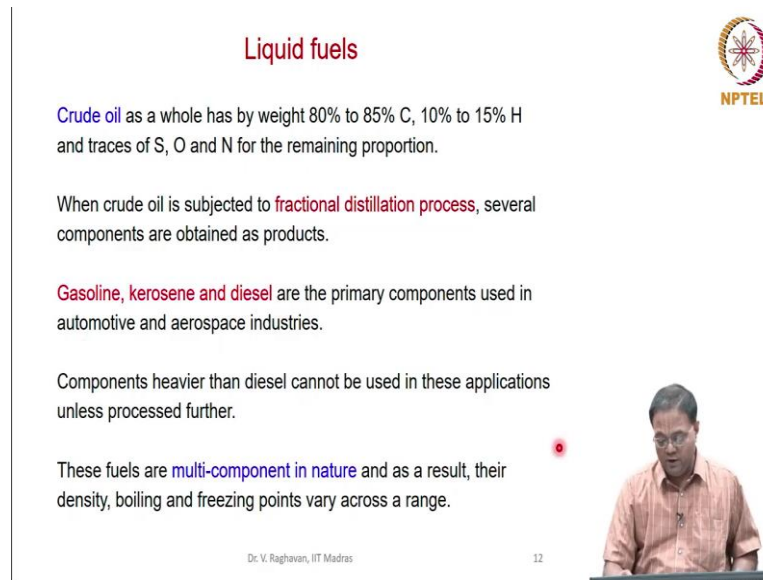


Latent heat of vaporization is the energy that you have to supply to convert the liquid into vapor. This is very important as you can see that in some cases; latent heat may be higher, boiling point may be lower. So, in combination only we have to see, whether the fuel is volatile or not. Specific heat is the property which is useful in supplying the sensible heat.

From the atmospheric temperature, towards the boiling point, you have to heat it. For that the important property is specific heat. The latent heat has to be supplied to vaporize the liquid fuel. Specific heat, latent heat of vaporization and boiling point, these three govern the volatility together.

These are the three important characteristics. So, to classify liquid fuels, you have fire point and flash point. Volatility can be defined based on these three properties mentioned above.

(Refer Slide Time: 01:22)



Liquid fuels

Crude oil as a whole has by weight 80% to 85% C, 10% to 15% H and traces of S, O and N for the remaining proportion.

When crude oil is subjected to **fractional distillation process**, several components are obtained as products.

Gasoline, kerosene and diesel are the primary components used in automotive and aerospace industries.


Components heavier than diesel cannot be used in these applications unless processed further.

These fuels are **multi-component in nature** and as a result, their density, boiling and freezing points vary across a range.

Dr. V. Raghavan, IIT Madras

12

NPTEL



Now, fossil fuels, the main liquid fossil fuel is crude oil. When you do an ultimate analysis of crude oil; ultimate analysis is done to understand what are the elements constituting the fuel. We can see that crude oil contains 80 to 85 percent of carbon, 10 to 15 percent of hydrogen and traces of sulfur, oxygen, nitrogen atoms and so on.

So, sulfur is present in liquid fuel. If you take a gaseous fuel; we can avoid these impurities. Now, we can see that we cannot avoid impurities in the liquid fuel, and in the solid fuels you will see more impurities like minerals etcetera. Even in liquid fuels, minerals would be present.

Now, the crude oil cannot be used for any practical applications; because it is a very thick and black oil, with very high viscosity and so on. It cannot be used and it cannot be even vaporized easily. It has to be subjected to a process called fractional distillation by which you get lot of components; like petrol, gasoline, kerosene, diesel, etcetera.

These have increasing molecular weights and densities. Now, these are the components which we get by processing crude oil by through a fractional distillation process. These

fuels can be used in automotive and aerospace applications; even in industrial burners, we use diesel-based fuels, so diesel oils, heavy diesel oils etcetera.


See for example, fuels heavier than diesel cannot be directly used in automotive application; but we can use it in industrial applications. We can actually preheat or supply steam along with it, so that you can atomize it. So, for atomization, you have to bring down the viscosity.

So, heating the liquid or adding steam to it is primarily done in several industries. Please understand that, every component which is generated from crude oil is multi component in nature; it is not a single liquid, it is multiple liquids mixed together.

So, multi-component nature is another main point we have to understand. When we analyze these fuels; we have to understand, what are the constituents of this fuel, So, fuel characterization should be done.

But one fortunate thing is, when they burn; they do not display the multi component nature, they burn as though they are single component fuel. That is the advantage of these three fuels, what we use in day-to-day applications.

(Refer Slide Time: 04:05)




Liquid fuels

Alternative (non-fossil) liquid fuels are alcohols, liquefied solid fuels and vegetable oils.

Ethanol (ethyl-alcohol) is obtained from sources such as sugarcane and corn. Ethanol is blended with gasoline and used directly in engines.

Oils extracted from vegetable seeds such as rapeseed, sun flower seed, neem, jatropha and karanja, have very high viscosity and are subjected to a process called **transesterification**, using alcohols such as methanol or ethanol.

The processed vegetable oil with much lesser viscosity is called **biodiesel**.



Dr. V. Raghavan, IIT Madras 13

Alternative or manmade, synthetic liquid fuels are alcohols. You can use solid fuels to make liquid fuel, liquefied solid fuels and vegetable oils. Vegetable seeds are produced,

grown and they can be converted into vegetable oils. Vegetable oils can be processed through a process called transesterification, where you will get biodiesels.

So, normally you take solid fuels and convert them into alternative liquid fuels. Solid fuels can be converted into gaseous fuels or liquid fuels. If we take alcohols like ethanol, methanol etcetera; methanol is produced from natural gas. We can also use CO and H₂, synthetic gas, to produce methanol. From solid fuels you can also produce synthetic gases and from synthetic gas you can produce methanol.

Ethanol can be produced from sugarcane bagasse. Sugarcane industries produce ethanol in large quantities. So, alcohols like methanol, ethanol etcetera can produce from solid fuels or gaseous fuel. Solid fuels can also be liquefied.

Now, in case of rice straw, you just gasify it, take in gas and through Fischer-Tropsch process you get liquid fuels. But the conversion efficiency is under research; the scaling up and conversion efficiency etcetera are not thoroughly understood, but it is producible.

So, liquid fuels are produced from solid fuels and from gaseous, by gasifying it. For vegetable oils you can grow, for example, there are edible and non edible crops we can have. For example, sunflower, corn, etcetera or jatropha, karanja.


These vegetable seeds can produce vegetable oils and you can use them to produce biodiesels, ok. Ethanol is obtained from sugarcane bagasse and corn and it can be blended with gasoline and used directly in engines. Please understand that, directly we cannot use bio diesel or ethanol in an engine; because engine is designed for using diesel or petrol.

So, directly using ethanol in engine may be possible; but we do not know the long-term consequence of that. For example, what will happen in terms of corrosion and other thing, we do not know. However, blending has worked very well; blending ethanol say 20 percent or 30 percent ethanol with petrol and using that; that means, we are bringing down the usage of the fossil fuel to that extent. Similarly, biodiesels can be blended with diesels and used.

So, you can produce vegetable seeds like rapeseed, sunflower seed, neem, jatropha, karanja, etcetera. There are edible and non edible seeds from which you can extract oils.

These oils cannot be used directly, because they are very viscous. To bring down the viscosity what you do is, you do transesterification with alcohols like methanol or ethanol; so, you get methyl esters. They are called biodiesels and that can be used with diesel in engines.

(Refer Slide Time: 07:43)




Solid fuels

Solid fuels like liquid fuels have higher energy density when compared to gas fuels. They are, however, much complicated than liquid fuels because of their **heterogeneity**. Coal and wood are common examples. Coal a naturally processed material is got from underground.

Solid fuels have four typical components, **moisture**, **gaseous substances called volatiles**, **fixed carbon** called **coke or char** and **mineral content called ash**, in some proportions. Thus, they are heterogeneous in nature.

Proximate analysis is used to determine these fractions. Some solid fuels have **sulphur** in addition. The calorific value of a solid fuel depends on its volatile and fixed carbon content.



Dr. V. Raghavan, IIT Madras 14

Now, coming to the solid fuels, in solid fuels there are four important components; first of all, solid fuel can be classified into two categories, one is called charring fuel and another is called non charring fuel.

When you take charring fuel, what happens is, when you just heat it moisture goes out and volatiles goes out and you get some carbonaceous material, carbon plus some minerals. When heating a solid fuel; if you get a carbonaceous material, then such a fuel is called charring fuel.

On the other hand, if you take plastic bags etcetera; you just heat it, it will melt and vaporize and then it will burn. There is no carbonaceous materials or minerals left as a residue. Those fuels are called non charring fuels. But mostly for industry and cooking applications, we use coal and wood. These are charring fuels; that means they leave the char as a residue upon heating up.

So, there are four components present in the solid fuels, charring solid fuels; moisture which is a trapped water vapor, then gaseous substances which are called volatiles. So, when this wood is transformed to coal, lot of things are happening under the ground.

So, moisture, volatile gases, everything is trapped inside. The third content is fixed carbon, you will have carbonaceous material and ash, ash is the mineral component. So, these are the four main component which we get.

But the rank of coal is mainly estimated with the fixed carbon content. If you have a coal with very high fixed carbon content, say 90 percent above; then we call it anthracite. It is the highest rank coal. When the carbon content decreases, we go towards wood. So, anthracite bituminous etcetera and we go towards wood that has the least carbon content.

In that case, now you will get more volatiles. So, volatiles will be higher or moisture may be higher and so on. These are the four components which we get in charring solid fuel; moisture, gaseous substances called volatiles, fixed carbon and ash. The fixed carbon and ash together is called char. So, you can see the heterogeneity or heterogeneous nature of the solid fuel.

It has liquid like moisture, then it has gases, and it has minerals. These are inert and porous substances, and it also has a carbon graphite. Now, we can see that solid fuel is a complex fuel, it is not very easy to burn this. So, even for burning wood, we need lot of things; lot of analyzes you have to use and design your wood stove properly.

It is not so easy to burn it efficiently. We have to do lot of research and so, the easiest way is to gasify this and produce gases, and use the gases to produce liquids and so on. But if you want to burn it, you have to really carefully burn it. And if there is any variation in the contents, like in these four contents; then we are going to get different set of results. So, how to get these four contents; moisture, volatiles, fixed carbon and ash? you do what is called proximate analysis; proximate analysis is basically when you try to heat this solid fuel, gradually. You can set some heating rate and heat this in a proximate analyzer.

First we can use inert gas like nitrogen. So, hot nitrogen gas can be used to heat it slowly. Now, what happens? when the solid is heated to say temperature about 100 degrees, the moisture escapes; above 100 degrees the moisture escapes, then further continue the

heating. So, when the temperature reaches in between 300 and 500 degrees; slowly the trapped gases are going to come out of that.


Now, you know the original mass and as these moisture and volatiles escape; you can continuously measure the mass and you can see that there will be change in the mass loss curve, by tracking that we will know what will be amount or what is the percentage of moisture present, what is the percentage of volatiles present and so on. When you just pass nitrogen continuously; you will not see any change, after the moisture and volatiles leave the material.

Now, you will see that their mass loss does not change at all; the mass loss curve becomes constant. Now, you have to shift to a oxidizing medium. So, you supply air or oxygen. When you do so what happens is, the fixed carbon starts burning; after it reaches a particular temperature, say 800 to 900 degree centigrade, these fixed carbon starts to burn. Then you will see that there will be mass loss again.

Now, after a particular point, only ash will be left and that will not burn at all. Ash will be inert. So, the heating will not have any effect. You will see that will be the percentage of ash. By this analysis, we can get all the weight percentages of all these components; moisture, volatiles, fixed carbon and ash, so this is the proximate analysis. As I told you, solid fuel is ranked based upon the fixed carbon content.

(Refer Slide Time: 13:39)

Solid fuels


NPTEL


Solid fuel is classified as per its fixed carbon content.

Typical mass based percentages of carbon present in various solid fuels based on moisture-, ash- and sulfur-free basis

Fuel	Fixed carbon %
Wood	45 – 55
Peat	50 – 65
Lignite	60 – 72
Sub-bituminous	70 – 80
Bituminous	80 – 90
Semi-anthracite	90 – 95
Anthracite	92 – 98

Dr. V. Raghavan, IIT Madras

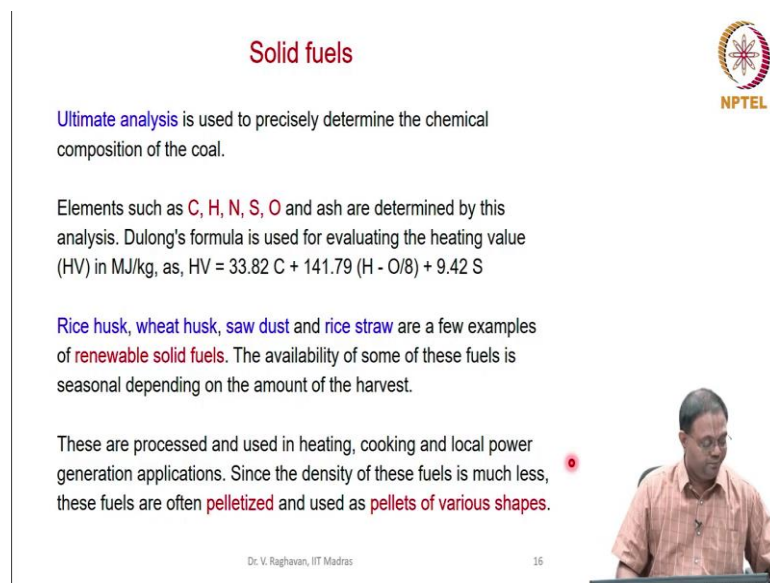
15



As I told you, wood has 45 to 55 percentage of fixed carbon. Anthracite is the highest rank coal, 92 to 98 percent of fixed carbon, then semi anthracite and so on. So, when you reduce the fixed carbon content, you go towards the wood. Lignite has 60 to 72 percent of fixed carbon and so on.

Please understand that, these are all the typical variations and these fuels depend upon the region, where they are available and so on. It is not available everywhere, for example, lignite available in say Tamil Nadu, Neyveli is different from lignite available elsewhere. So, we have to understand the composition of the coal, or any solid fuel before using it in any application. It is very tough to really use it, because of the complex nature. Also please see that, you can also have, for example, when you mine the coal at one place, you will get some property; if you just change your mines, then the property will change and that may affect the performance of the combustion. So, that is another important and complex nature of these fuels.

(Refer Slide Time: 15:12)



Solid fuels

Ultimate analysis is used to precisely determine the chemical composition of the coal.



Elements such as C, H, N, S, O and ash are determined by this analysis. Dulong's formula is used for evaluating the heating value (HV) in MJ/kg, as, $HV = 33.82 C + 141.79 (H - O/8) + 9.42 S$

Rice husk, wheat husk, saw dust and rice straw are a few examples of renewable solid fuels. The availability of some of these fuels is seasonal depending on the amount of the harvest.

These are processed and used in heating, cooking and local power generation applications. Since the density of these fuels is much less, these fuels are often pelletized and used as pellets of various shapes.

Dr. V. Raghavan, IIT Madras

16



Now, there is another analysis which we normally do with the solid fuels which is called ultimate analysis. Ultimate analysis will give you the percentages of the elements contained; like as we already saw in the crude oil, how much C, H, N, S, O are present.

Similarly, the same ultimate analysis can be done for coal or biomass, where you will get the percentage of elements such as C, H, N, S, O etcetera. And please understand that

when you do this normally; this carbon what you get is, carbon which is present in the volatiles plus the carbon which is present in the fixed carbon.

So, ultimate analysis will give the total carbon content; but by proximate analysis, you will know what is the amount of fixed carbon and what is the amount of volatiles. So, now, what is the carbon content in the fixed carbon and volatiles can be separately determined by using the combination of ultimate and proximate analysis.

Now, once you know the ultimate analysis, you can find the heating value of the solid material. For example, you have formula called Dulong's formula which can be used to find the heating value in mega Joules per kg. For example, if carbon percentage, hydrogen percent etcetera is known; then you substitute those in this to get the value in mega Joules per kg.

When you get this C, H values etcetera; this should be done on a dry and ash free basis. For example, you know what is the ash content and moisture content. So, you have to subtract and make the calculations in dry and ash free bases and those values are substituted here to get the higher heating value for the solid material.

Or you can also use bomb calorimeter. So, this is the formula; theoretically you can use this correlation which we got from literature and we can use this. So, coal, wood etcetera are the bio masses which we use for several applications. Now, the vegetation say, rice husk, rice straw, saw dust, wheat straw, wheat husk etcetera; they are all renewable solid fuels.

If we take India, for example; we produce rice and wheat to very large amount. We are producing that abundantly. So, rice husk, rice straw etcetera is available and we are just throwing it away, we can use it for producing liquid and gaseous fuels. We can also burn it in furnaces; some grate burners etcetera and produce power straightaway.


But instead of that, we can also store this by converting this into liquid and gaseous fuels. May be converting into liquid fuel will be easier for us to store this. So, these are the alternative solid fuels which can be used for several applications.

What is the difference between coal and say saw dust or rice husk? It is the density. Coal has a very high density, say for example, it is a very heavy material. So, density can be

about say 1600 kilogram per meter cube to 2800 kilogram meter cube. So, when you have a denser fuel, you pulverize it and use it. When you have very light fuel, you cannot just use that as the same way as you use coal.

So, normally what you use it, you pelletize this and make pellets, to increase density; and you can use that as a feed for your burners. So, lot of applications are there; directly you can burn this or gasify it to produce gases or liquefy that to produce liquid fuels and so on.

(Refer Slide Time: 19:06)



Fuels for space applications


Hydrazine (N_2H_4), decomposes by itself exothermally, at high temperatures (600°C). Exotic catalysts made of Iridium and Molybdenum are used to decompose N_2H_4 to gases almost instantaneously at ambient conditions. These are called monopropellants.

Unsymmetrical dimethyl hydrazine [$N_2H_2(CH_3)_2$], on contact with a small amount of **red fuming nitric acid** produces bright flame (hypergolic or self-igniting). They react in liquid-phase releasing components which react in gas-phase exothermally within 15 milliseconds.

Liquid hydrogen, a cryogenic fuel, boils off at -253°C (20 K), is an excellent fuel with low molecular weight and high energy

Dr. V. Raghavan, IIT Madras

17



Now, so far what we have seen is the fuels for industrial applications, domestic applications and so on. Now, some special fuels, what we use for a space application is listed here; I am not going into the details, just telling about some fuels. See for example, hydrazine N_2H_4 , decomposes by itself exothermally at high temperature.


When it is heated to about 600 degree centigrade, it decomposes and when it decomposes; it is an exothermic decomposition. The exotic catalysts made of iridium and molybdenum are used to decompose this. So, catalyst based decomposition can happen and gases are produced and these are called monopropellant, which are used in rockets, small rocket engines, monopropellants.

Then for example, you say unsymmetrical dimethyl hydrazine; and red fuming nitric acid, this combination can produce chemical reactions and this is used in liquid rockets

basically. Similarly, in cryogenic liquid rocket applications, you can use liquid hydrogen and liquid oxygen as the fuel and oxidizer. So, these are the fuels which are specially used for space applications.


(Refer Slide Time: 20:33)


Fuels for space applications



Several liquids having excess oxygen like nitric acid (HNO_3), Red fuming nitric acid (12% - 14% nitrogen tetroxide (N_2O_4) mixed with nitric acid), nitrogen tetroxide, liquid oxygen (LOX) are used as **oxidizers**. N_2O_4 is liquid at near ambient conditions, should be kept below 21°C for it to be liquid. LOX needs good insulation; its boiling point is -183°C .

Polymers like polybutadiene with hydroxy, carboxy termination (HTPB [$\text{OH}-(\text{C}_4\text{H}_6)\text{-OH}$]) (CTPB [$\text{COOH}-(\text{C}_4\text{H}_6)\text{-COOH}$]) **composite propellants** are used in **solid fuelled rockets**. **Ammonium perchlorate** (NH_4ClO_4) is used as oxidizer.





Dr. V. Raghavan, IIT Madras 18

The oxidizers, as I told you liquid oxygen is one of the thing. Instead of only liquid oxygen; you can also use nitric acid, red fuming nitric acid etcetera. This can be used where the oxygen content is more, those can be used as oxidizer in the space applications.


Similarly, solid propellant rockets use polymers. So, polybutadiene with hydroxy or carboxy determination, these fuels ok; complex polymers can be used for solid propellants. Ammonium perchlorate can be used for oxidizer in those applications.

So, these are the fuels which are used for special applications. For others we can, see for example, for power plants etcetera, we use different types of fuels; liquid fuels as well as solid fuels.

For automotive applications, predominantly we use liquid fuels; and for industry heating purposes etcetera or domestic cooking, domestic and commercial cooking, we use gaseous fuels.

(Refer Slide Time: 21:43)


Course Contents



- (1) Fuels and their properties
- (2) Review of basic thermodynamics of ideal gas mixtures
- (3) Stoichiometry
- (4) First and Second Laws of Thermodynamics applied to combustion;
Heat, temperature and composition of products in equilibrium
- (5) Mass transfer basics
- (6) Fundamentals of combustion kinetics
- (7) Governing equations for a reacting flow
- (8) General characteristics of combustion flame and detonation
- (9) Laminar flame propagation-Flammability limits and quenching of
laminar flames-Ignition-Flame stabilization
- (10) Gas jets and combustion of gaseous fuel jets
- (11) Turbulent premixed and non-premixed flames
- (12) Droplet evaporation and combustion
- (13) Combustion of a carbon particle.

Dr. V. Raghavan, IIT Madras

19



So, this is the end of the first topic, fuels and their properties. We will continue with the second topic later. Review of basic thermodynamics especially for the ideal gas and mixtures.