Energy Conversion Technologies (Biomass and Coal)

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Lecture 8

Solid fuels (Part I)

Good morning everyone.

Welcome to part 1 of the lecture 1 under module 2. In this lecture we will discuss about the concept of solid and the liquid fuels and basic understanding of various properties of the fuels. In that we will discuss about the solid fuel first. Where, we will discuss about the heating value of fuel, ultimate analysis and the proximate analysis.

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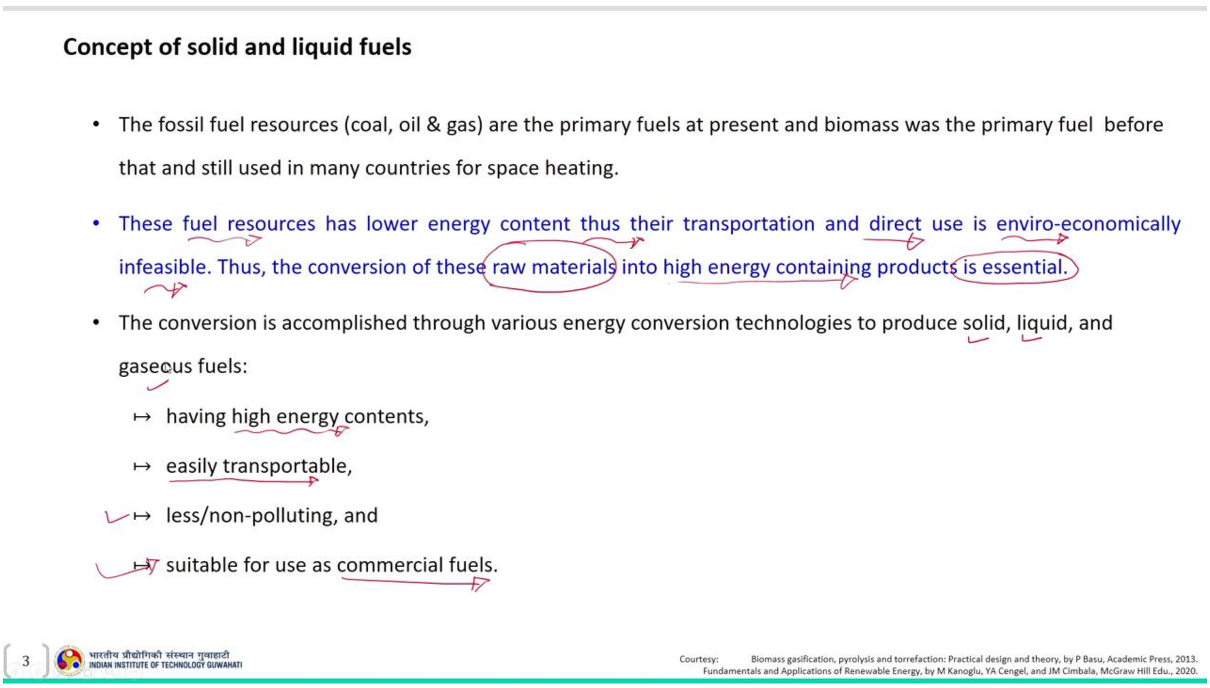

Concept of solid and the liquid fuels: The fossil fuel resources that is coal, oil and gas is the primary energy source at present and biomass was the primary fuel before that and still being used in many countries for space heating purpose. So, if you remember in one of the lecture in the previous module, I discuss about this concept of biomass, where I mentioned about biomass is no more counted in the classification of conventional energy sources and now it is accounted under the non-conventional energy sources.

The issue associated with the source material is that these particular materials have low energy content. And thus their transportation and direct use is enviro-economically infeasible and because of that the conversion of these raw forms of energy into high energy containing product is essential. And this can be accomplished through various energy conversion technologies or processes to produce gas, liquid and solid as a product. But there are also certain checks we need to take into consideration. The produced product also should have high energy content and it should be easily transportable, less-polluting and suitable for use as commercial fuels.

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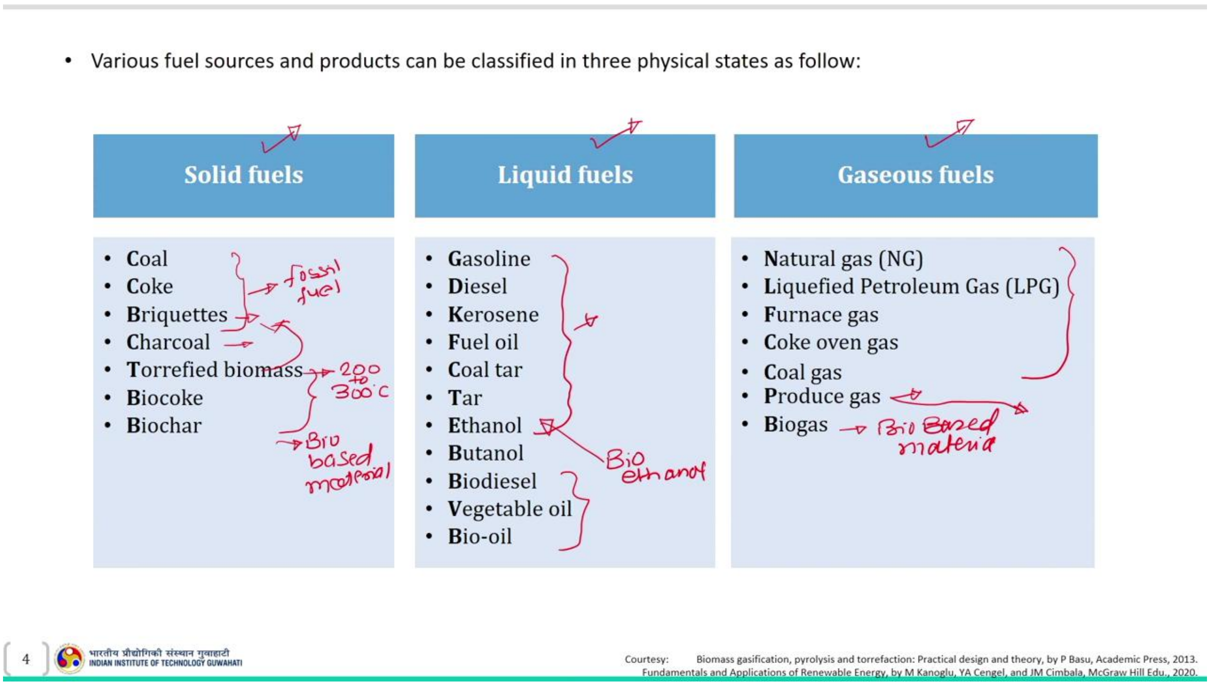

So, these various fuel sources and their products can be classified in three physical states as follows that is solid fuel, liquid fuel and gaseous fuel. So, solid fuel includes coal, coke, briquettes, charcoal, torrefied biomass, biocoke and the biochar. So, in that coal, coke, briquettes source from the fossil fuels or you can say the fossil source material. Torrefied biomass, biocoke and biochar are sourced from the bio base materials.

So, biquette in the sense is like it is a block of compressed combustible material. So, it may be charcoal, biomass or the waste material and the charcoal is produced in presence of insufficient quantity of air. And the torrefied biomass is produced in absence of air and the temperature would be between 200 to 300 °C. So, likewise this torrefied biomass further can be converted into the briquettes as well. The liquid fuels include gasoline, diesel, kerosene, fuel oil, coal tar, tar, ethanol, butanol, biodiesel, vegetable oil and the bio-oil.

So, in that this gasoline to even ethanol these are source from the again fossil fuel materials. And biodiesel vegetable oil and the bio oil are basically derived from the biobased materials are nowadays produced using the biobased materials. And the gaseous fields includes natural gas, liquefied petroleum gas, furnace gas, coke oven gas and the coal gas again which are sourced from the fossil materials and producer gas also it is being produced from the fossil material that is coal and the biogas is produced from the biobased material, and the producer gas as I mentioned earlier also. Nowadays, it is also being produced using the bio-based material by which by the process called as gasification where the biomass is gasified to convert it into a producer gas.

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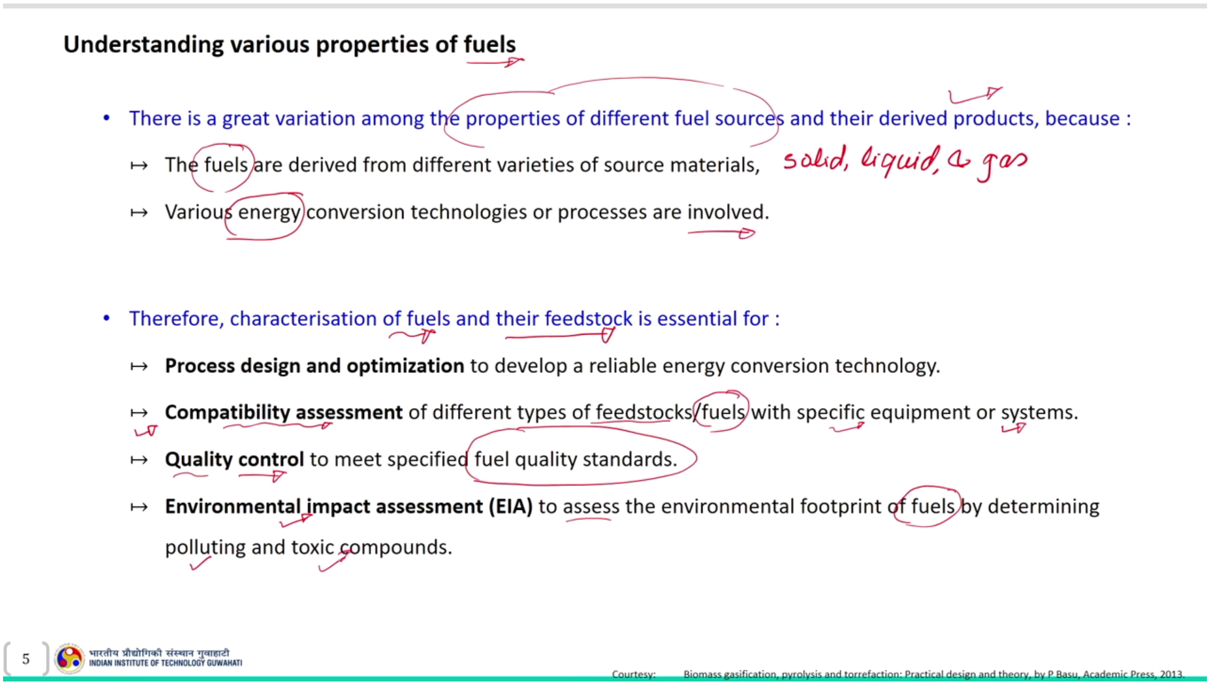

So, now let us understand the properties of these various fuels. As discussed before these fuels are produced from the source material as a result there is a great variation among the properties of these different fuel sources as well as the product derived from this particular source material. Because these fuels are derived from different varieties of the source materials like solid, liquid and gas and apart from that various energy conversion technologies or the processes or the systems are being used to convert these source material into a usable product. Because of that there is a great variation among the properties of these different fuels which are produced from the even different source material. Hence, characterization of the fuels and their feedstock is essential for designing a reliable energy conversion process or system. As well as it is essential to understand the compatibility assessment of the different types of feedstock fuels with specific design equipment or system.

Because the design process or the equipment it should be compatible with the different or the varieties of the feedstock material as well as the source material. And it should not be compatible with any single specific fuel or as well as any specific raw material, so that it can be a sustainable in the longer run. Apart from that the characterization is essential to control the quality of the produced fuel, so that it can meet the specified fuel quality standards. And the environmental impact assessment is also essential to assess the environmental footprint of the fuels by determining the polluting and the toxic compound present in the source material. And for that reason the characterization of the fields and their feedstock is essential.

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- Some important characteristics of fuels and their feedstock include:

Physical Properties	Thermodynamic Properties	Composition
Density Permeability Diffusivity Viscosity	Thermal conductivity Hating value Specific heat Heat of combustion Heat of formation Ignition Temperature	Ultimate / elemental composition - *C, H, N, S, O* Proximate composition - *Moisture, Volatile Matter, Fixed carbon, Char, Ash* Structural / chemical composition - *Cellulose, Hemicellulose, Lignin, Extractives* - *Carbohydrates, proteins, lipids* Bio based material

Other parameters and tools are also used to characterize, classify and rank the fuels.

E.g. Various fuels are ranked as per their:
- **Atomic ratios** (H/C, O/C, N/C, etc.),
- **Ratio of lignocellulose constituents** (Cellulose, hemicellulose, lignin),
- **Ternary diagram** (showing percentage of C, H, and O).

Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

Now after understanding the necessity of characterization of the fields and the feedstock, let us discuss about some important characteristics of fuels and their feedstock which include physical properties, thermodynamic properties and composition. The physical properties include density, permeability, diffusivity and the viscosity. And this is a comprehensive list and not specific to any single given fuel. Similarly, the thermodynamic properties include thermal conductivity, value, specific heat, heat of combustion, heat of formation, and the ignition temperature. And again as I mentioned these are not specific to a single field but this is a comprehensive list of the thermodynamic properties.

And the composition include the ultimate analysis, the proximate analysis, the structural and chemical composition which includes the cellulose, hemicellulose, lignin and the extractive content in the material, apart from that the carbohydrate, protein and the lipid content. And these are specific to a bio-based material. And apart from these properties there are other tools which are also used to characterize, classify and rank the fuel which includes the atomic ratio that is H/C, O/C and the N/C ratio, which is also helpful in classifying or characterizing the fuel. Ratio of lignocellulose constituent that is cellulose, hemicellulose and lignin, this is also helpful to rank the lignocellulosic biomass. And the ternary diagram showing the percentage of carbon, hydrogen and oxygen it also useful as one of the tool to characterize or classify the fuel.

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1 Solid fuels

- **Fire**, the greatest discovery in history, was produced from biomass fuels for heating caves and cooking food in ancient times.
- As civilization advanced the utilization of solid fuels (e.g. biomass, coal and petroleum seeps) broadened to domestic use, smelting of metals, thermal power generation, etc.

- Solid fuels are grouped in three classes:
  - ↦ Biomass fuels,
  - ↦ Fossil fuels, and
  - ↦ Wastes.

Courtesy: The combustion of solid fuels and wastes, by DA Tillman, Academic Press, 1991.

Now, let us discuss about solid fuel in detail. Fire: the greatest discovery in history was produced from biomass fuel for heating caves and cooking food in ancient times. And with advancement of civilization the utilization of the solid fuels has broadened to domestic use, smelting materials as well as to produce the power in the thermal power station. And these solid fuels are grouped in three classes that are biomass fuel, fossil fuel and waste.

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Classification	Sources of solid fuels	Derived solid fuel products	Uses of solid fuels
Fossil fuels	Peat, coal, oil shale, oil sands, tar sands, etc.	Peat, Coal, Coke, Briquette, etc.	Burned to supply energy to industrial processes.
Biomass	Wood, wood wastes (i.e. hogged bark and sawdust), spent pulp, rice hulls, cotton gin trash, bagasse, coffee grounds, manure, and a myriad of other biomass forms.	Pellets/Briquettes, Torrefied biomass, Biocoke, Biochar, etc.	Burned in boilers and in kilns.
Wastes	Municipal solid waste (MSW) including waste from wood, paper, food, yard, plastics etc.	Pellets/Briquettes, Refuse derived fuel (RDF), etc.	Burned for steam, electricity and for the safe disposal of society's residues.

Courtesy: The combustion of solid fuels and wastes, by DA Tillman, Academic Press, 1991.

So, now let us discuss about these source of solid fuels, their derived product and their ultimate use in the industries. The sources of fossil solid fuels include peat, coal, oil shale, oil sands and tar sand. And the products derived from these solid fuels include the peat, coal, coke and briquettes. So, here the peat and the coal are nothing but the upgraded form of this source material which can be upgraded using the suitable upgradation technology with the removal of the foreign material as well as the pollutant and it can produce a high quality coal. Apart from that, the briquettes here indicate the briquette produced from the coal dust and this particular derived product can be burned to supply energy in the industrial processes. Similarly, the biomass source material include wood, wood waste, spent pulp, rice husk, cotton trash, bagasse, coffee grounds, manure and other forms of biomass.

And this particular biomass can be converted into pellets and briquettes or it can be converted into the torrefied biomass, biocoke and also biochar. The pellets and the briquettes as I mentioned earlier, it is a block of a combustible material, so here it is a biomass-based material. Similarly, the pellet which is smaller in size can also be obtained from the combustible based material that is a biomass. The torrefied biomass, as we already discussed about the torrefied biomass in the previous slide. These particular materials again can be burned in the boiler and in the kilns.

And the waste material, the sources include the municipal solid waste including the waste from the wood, paper, food, yard and the plastic. Again, this particular source material can be converted into pellets and the briquettes as well as the refuse derived fuel. And these derived fuels can be burned for the steam generation, electricity and for the safe disposal of the society's residues. This can be converted into a suitable form of the energy.

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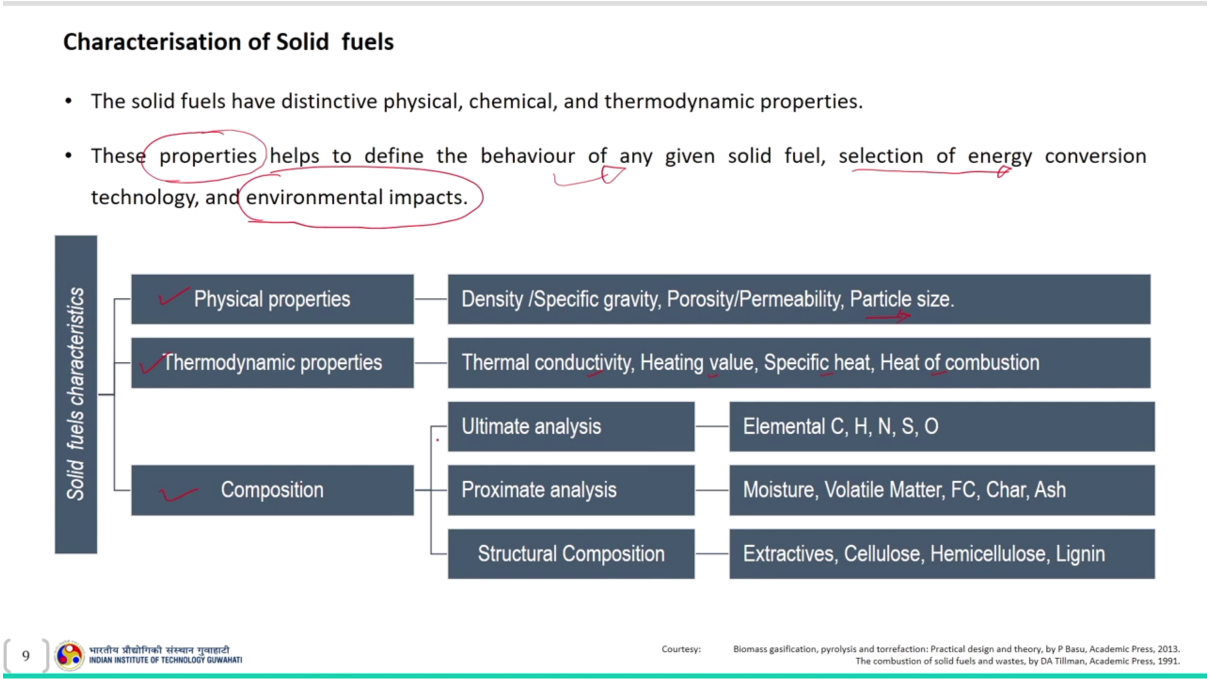

As discussed earlier the solid fuels are source from the distinct source material as a result they have the distinct physical, chemical and the composition characteristics. And it is essential to characterize these particular solid fuels which eventually helps to define the behavior of any given solid fuel, as well as it will helps to select a proper energy conversion technology or system. And also it will help in understanding the environmental impact by the utilization of these particular source materials for the energy generation. And it includes the physical properties, thermodynamic properties and the composition as we already discussed in the previous slide. The physical properties include these many properties. The thermodynamic properties include majorly thermal conductivity, heating value, specific heat and heat of combustion. And the composition includes ultimate analysis, proximate analysis and the structural composition.

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- Characteristics of various solid fuels, important in fuels analysis, are summarised bellow:

Solid Fuels	Physical properties	Thermodynamic properties	Chemical characteristics
Biomass	Specific Gravity, Porosity	Thermal Conductivity, Specific Heat, Heating Value	Proximate Analysis, Ultimate Analysis, Structural and Compositional Analysis.
Coal (fossil fule)	Specific Gravity, Porosity, Grindability.	Specific Heat (Heat Capacity), Heating Value	Proximate Analysis, Ultimate Analysis, Reactivity, Chemical Structure (Coal Ranks), Chemical Component Analysis (Organic Matter, Inorganic/Mineral Matter, etc.).
Wastes	Bulk Density, Porosity	Thermal Conductivity, Heat Capacity, Heating Value	Ultimate Analysis, Trace Metals Content

So, here the characteristics of various solid fuels important in the fuel analysis are summarized in the tabular form, which will be very easy to understand even. So, for the biomass based source material the physical properties include the specific gravity and the porosity. Thermodynamic properties include thermal conductivity, specific heat and the heating value. And the chemical characteristics include proximate analysis, ultimate analysis and the structural and the composition analysis of the biomass.

And in case of coal Physical properties include specific gravity, porosity and grindability. And majorly thermodynamic properties include the specific heat and heating value. Along with that the chemical characteristics include the approximate analysis, ultimate analysis, chemical structure, even the reactivity, chemical component present in the coal in the form of organic matter and the inorganic matter. And the waste includes bulk density and the porosity, thermal conductivity, heat capacity and the heating value and ultimate analysis along with the trace metal content. So, we will discuss about these properties one by one.

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1. **Density** *(Physical property)*

Density is an important design parameter for any fuel conversion processes and system.

There can be three characteristics densities: true, apparent, and bulk density.

(a) True density:

Weight per unit volume occupied by the solid constituent of biomass is the True density.

$$\rho_{true} = \frac{\text{total mass of fuel}}{\text{solid volume excluding pore volume}}$$

(b) Apparent density:

This considers the internal pores of a particle but not the interstitial volume between particles packed together.

As it is easiest to measure and most commonly used for design calculations, and it gives the actual volume occupied by a particle in a system.

$$\rho_{apparent} = \frac{\text{total mass of fuel}}{\text{apparent volume including solids and internal pores}}$$

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

So, first the density, density is an important design parameter for any fuel conversion process or system. There can be three characteristic densities that is true density, apparent density and the bulk density. So, the true density here it is the ratio of total mass of fuel by solid volume excluding the pore volume of the material. So, while calculating the true density it is basically considered as the total mass of fuel that is weight per unit volume by solid constituents of the biomass is the true density. So, in this calculation the pore volume of the specific source material is excluded.

Whereas, if you see the apparent density, so this consider the internal pores of particle but not the interstitial volume between the particles which are packed together while estimating the apparent density. And it is the easiest to measure and most commonly used density for the design calculation and it gives the actual volume which is occupied by particle in a system. And it can be calculated using the following equation that is total mass of a fuel by apparent volume including the solids and the internal pores, but it does not account the interstitial volume between the particles.

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(c) Bulk density:

Bulk density of a sample can be estimated based on the overall space occupied by an amount or a group of particles:

$$\rho_{bulk} = \frac{\text{total mass of fuel}}{\text{bulk volume occupied by fuel}}$$

The bulk density can be estimated by ASTM E-873-06 method. (ASTM: American Society for Testing and Materials)

These three types of densities are related as follows:

$$\boldsymbol{\rho_{apparent}} = \boldsymbol{\rho_{true}}(\mathbf{1} - \boldsymbol{\varepsilon_p})$$

$$\boldsymbol{\rho_{bulk}} = \boldsymbol{\rho_{apparent}}(\mathbf{1} - \boldsymbol{\varepsilon_b})$$

Where,

ε_p = porosity or voidage

ε_b = bulk porosity

Fuel	Bulk density (kg/m³)
Anthracite coal	800–929
Bituminous coal	673–913
Lignite coal	641–865
Wood	390–640
Cereal straw	100–170
MSW	500–8000

Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013. Synthetic fuels handbook: Properties, process, and performance, by JG Speight, The McGraw-Hill Companies, 2008.

And the bulk density it is simply a ratio of total mass of field divided by the bulk volume which is occupied by amount or a group of particles. And this bulk density can be estimated as per this ASTM standard method as well. Even these three densities are related as per this following equation that is apparent density equal to true density into 1 minus porosity. And even the bulk density can be related with the apparent density into 1 minus bulk porosity.

So, for the estimation of this apparent and the bulk density we need to know the porosity and the bulk porosity of the given sample. And in this particular table, the bulk density of the various solid fuels is compared. Now, if you see here the anthracite coal, the bituminous coal and the lignite coal, these samples have relatively a higher bulk density compared to the wood and the cereals. In fact, the municipal solid waste is having relatively a higher density than that of the wood and the cereal straw.

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2. **Porosity**

Porosity is an important characteristic of solid fuels including biomass, fossil fuels, & MSW.

- **Porosity:**
  Porosity, ε_p is defined as the ratio of pore volume to the total volume of a solid fuel.

$$\varepsilon_p = \frac{\text{pore volume}}{\text{total volume}}$$

- **Bulk porosity:**
  Bulk porosity, ε_b is defined as the ratio of interstitial volume to the total packed volume of a solid fuel.

$$\varepsilon_b = \frac{\text{interstitial volume}}{\text{total volume}}$$

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

So, the porosity, as we have discussed this concept of the porosity just now, so this porosity it is an important characteristics of solid fuel including biomass, fossil fuels and MSW. And this porosity can be estimated by this simple equation where we need to know the pore volume of a material as well as the total volume of a sample. So, once we know these two values, so the porosity can be estimated accordingly and it is defined as the ratio of pore volume to the total volume of a solid fuel.

Similarly, the bulk porosity is defined as the ratio of interstitial volume to the total packed volume of a solid. So, in the bulk porosity basically the interstitial volume between the particles is considered with that of the total packed volume of a solid fuel. And once we know this bulk porosity and the porosity then easily we can estimate the apparent density and the bulk density of a solid fuel.

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3. **Thermal conductivity** *(Thermodynamic property)*

Thermal conductivity (k) is a measure of a material's ability to conduct heat.

Thermal conductivity of a material can be defined as the rate of heat transfer through a unit thickness of the material per unit area per unit temperature difference.

$$Q = kA\frac{\Delta T}{\Delta x}$$

Where, Q is the rate of heat transfer, k is the thermal conductivity of the fuel,

A is the surface area of the fuel particle, Δx is the thickness or size of particle,

$\Delta T = T_1 - T_2$ is the temperature difference across the surface of the fuel particle.

- High k value: material is a good conductor of heat; Low k value: material is appropriate for thermal energy storage.
- Thermal conductivity of fuel depends on its composition, moisture content, density, porosity, & temperature.

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013. Fundamentals and Applications of Renewable Energy, by M Kanoglu, YA Cengel, and JM Cimbala, McGraw Hill Edu., 2020.

And the next in the list includes the thermal conductivity. Thermal conductivity is a measure of materials ability to conduct the heat. And thermal conductivity of the material can be defined as the rate of heat transfer through unit thickness of the material per unit area per unit temperature difference.

And once we know these quantities, we can calculate the thermal conductivity of a given material. High k value it indicates that the material is a good conductor of heat. Similarly, low k value it indicates that the material is appropriate for thermal energy storage. And the thermal conductivity of the fuel, it depends on its composition, the moisture content, density, porosity and temperature.

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4. **Heating value (Calorific value)**

Higher Heating Value (HHV), also known as gross calorific value (GCV), is defined as the amount of heat released by the unit mass or volume of fuel (initially at 25 °C) once it is combusted and the products have returned to a temperature of 25 °C.

For a fuel containing moisture:

- ✓ HHV includes the latent heat of vaporization of water.
- ✓ If the latent heat of vaporization of water is not recovered, the effective heat available for use is less than the chemical energy stored in the fuel. Therefore, Lower heating value (LHV) is introduced.

Lower heating value (LHV), also known as net calorific value (NCV), is defined as the amount of heat released by fully combusting a specified quantity less the heat of vaporization of the water in the combustion product.

$$LHV = HHV - h_g\left(\frac{9H}{100} - \frac{M}{100}\right)$$

Where, H = % hydrogen, M = % moisture, h_g = latent heat of steam

Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

And next in the list of the properties is the heating value. The higher heating value is also known as a gross calorific value. It is defined as the amount of heat released by unit mass or the volume of fuel which was initially at 25 °C and once it is combusted and products have returned to a temperature of 25 °C. In case if the fuel contains moisture, then the higher heating value includes the latent heat of vaporization of water. And if the latent heat of vaporization of water is not recovered, then the effective heat which is available for use is less than the chemical energy which is stored in the fuel.

And therefore, lower heating value is introduced here. The lower heating value is also known as the net calorific value. It is defined as the amount of heat released by fully combusting a specified quantity of fuel but less the amount of heat of vaporization of water in the combustion product. And this LHV can be estimated using the following expression.

LHV is equal to higher heating value minus Hg that is called as a latent heat of steam into 9 H by 100 minus M by 100 in the bracket. Where H is the hydrogen percent and M is the moisture percentage. And if these values are known then we can calculate the lower heating value of a sample. And as I mentioned earlier the higher heating value of a given fuel can be estimated using the calorimeter that is also widely known as a bomb calorimeter.

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Heating value needs to be defined on the basis of different moisture and ash content of fuel:

If M_f kg of fuel contains: Q kJ of heat,

M_w kg of moisture, and

M_{ash} kg of ash,

then, HHV can be presented in different bases as follows:

On as received (ar) basis: $HHV_{ar} = \frac{Q}{M_f}$ kJ/kg

On dry basis (db): $HHV_{db} = \frac{Q}{M_f - M_w}$ kJ/kg

On dry and ash free (daf) basis: $HHV_{daf} = \frac{Q}{M_f - M_w - M_{ash}}$ kJ/kg

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Even the heating value, this also needs to be defined on the basis of different moisture and the ash content of a fuel. If M_f kg of fuel contains Q kilo joule of heat, M_w kilogram of moisture and M_{ash} kilogram of ash then higher heating value can be presented in a three different basis as follows. That is on as received basis the amount of heat which is released on combusting M_f kilogram fuel.

So, by that way we can calculate the high reading value. Similarly, on dry basis the high reading value can be estimated as Q divided by M_f minus moisture contained in the fuel. That means mass of the fuel minus the moisture contained in the fuel it will gives the net mass of the fuel which is taking part in the combustion process. So, that is on the dry basis where we have not accounted the moisture and on dry and ash free basis. So, here it is basically mass of the fuel minus moisture minus ash. So, by that way we can calculate the high rating value on dry-and-ash-free basis.

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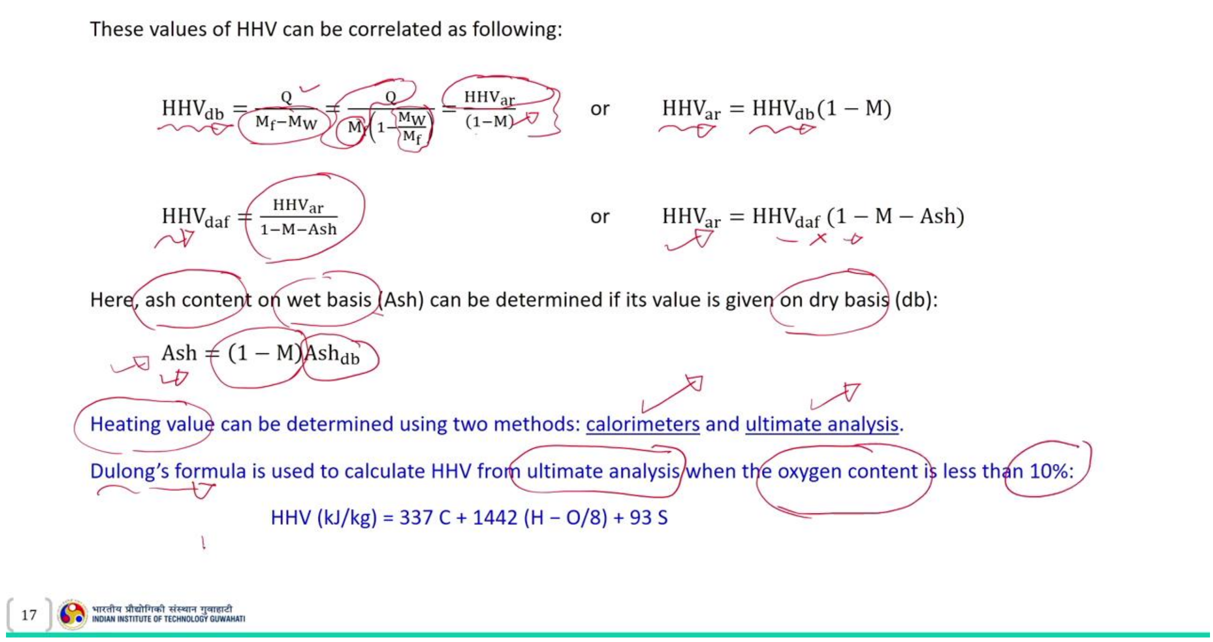

Even these high heating values can be correlated as follows that is once we know the high rating value on dry basis that is Q by M_f minus M_w, so you just simply take out this mass of the fuel common that is 1 minus mass of moisture divided by the mass of fuel which can be represented as M here onward. So, once we know the high reading value, because this Q by M_f is nothing but the higher heating value on the as received basis. So, you can just replace this Q by M_f as higher heating value on as received basis and the remaining expression will remain as it is. So, it is the ratio of these two terms where higher heating value on as received basis can be also calculated as higher heating value on dry basis into 1 minus M.

And higher heating value on dry and ash free basis, it is simply the ratio of again these terms. And similarly the high reading value on the as received basis can be also calculated where we can simply multiply these two terms to get the high reading value on the as received basis and the ash content on weighed basis. It can be also determined if the value of this ash content on the dry basis is known. So, the ash is equal to 1 minus M into ash on dry basis. So, once we know these two terms we can calculate the ash content.

Similarly, the heating value can be determined using two methods, as I mentioned the calorimeter that is called as a bomb calorimeter and also using the ultimate analysis. So, while calculating the heating value using the ultimate analysis this Dulong's formula can be used to calculate the high heating value of the any given fuel once the ultimate analysis of the given fuel is known. But there is a condition that the oxygen content in the fuel or in the feedstock should be less than the 10 percent. Then using this expression we can calculate the higher heating value.

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Heating value is one of the most important properties of fuels.

Compared to most fossil fuels, the heating value of biomass is low, especially on a volume basis, because its density is very low and it is a high oxygen containing fuel.

Fuel type	Bulk density (kg/m^3)	Heating Value (MJ/kg)
Wood	390–640	14-21
Cereal straw	100–170	16-17
Peat	100–300	7-9.3
Lignite coal	641–865	14-19
Subbituminous coal	-	19-27
Bituminous coal	673–913	27-32
Anthracite coal	800–929	32-34
MSW	500-8000	10-29

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013. Energy Sources, by B Viswanathan, Elsevier, 2017.

As I mentioned earlier as well the higher heating value is one of the important characteristics of fuel as well as the feed material. Compared to most fossil fuels, the heating value of biomass based material is low, especially on volume basis because its density is very low and it is a high oxygen containing fuel.

So, if you see this table here it represents the heating value and the bulk density of the source material, so in that the bulk density of the wood and the cereal straw, if you can see, the range of the bulk density it is relatively low compared to that of the coal sample. Even the heating value is low compared to that of the coal sample because the biomass contains relatively high amount of oxygen in its composition whereas the oxygen content in the coal sample is relatively low.

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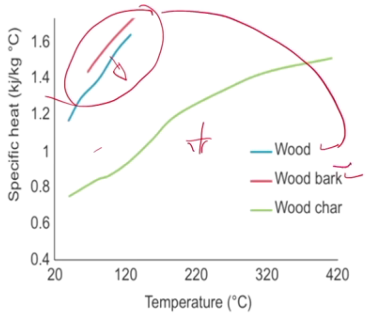
5. **Specific heat (Heat capacity)**

- *Specific heat is the amount of energy required to raise a fuel from ambient conditions to reaction temperature.*
- It is an indication of the heat capacity of a substance.
- Specific heat is an important property of fuels used for thermodynamic calculations.
- Specific heat of fuel depends on temperature, moisture, and to some extent on the type of fuel.

- The specific heat of fuel increases with temperature (see Figure).
- The wood species and its mass density do not have much effect on the specific heat.
- The char produced from the wood has much lower specific heat.



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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

So, the next in the list is the specific heat. And the specific heat is the amount of energy required to raise the fuel from ambient condition to reaction temperature. And it is indication of the heat capacity of a substance. And the specific heat is important property of a fuel which is used for the thermodynamic calculations.

Now if you see the specific heat versus temperature plot here, it shows that the specific heat of the fuel it increases with the temperature. And for the wood species for example wood and the wood bark and its mass density if you see, it do not have much effect on the specific heat. However, when this wood is converted into a wood char, then it has much lower specific heat compared to that of its original wood and the wood bark material.

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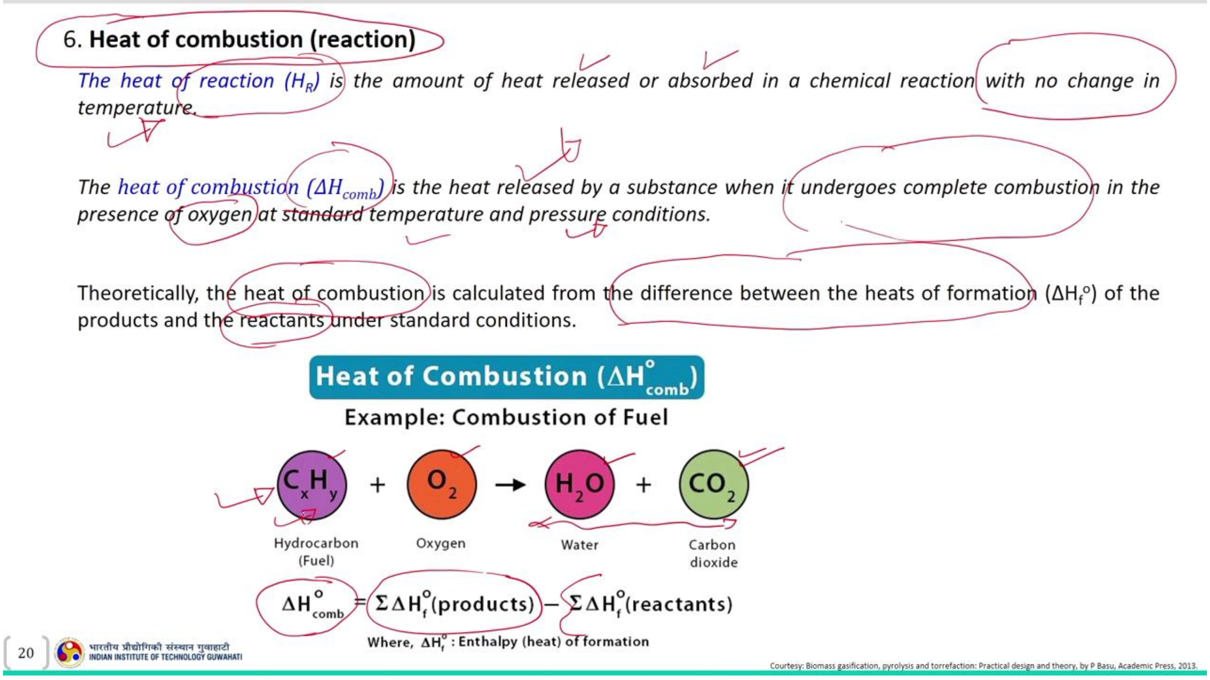

And most important property of the solid fuel is the heat of combustion, or we can say the heat of reaction. Because the heat of reaction is the amount of heat released or absorbed. Because it depends on the endothermic and exothermic nature of the reaction with no change in temperature. Similarly, the heat of combustion is the heat released by substance when it undergoes the complete combustion in the presence of oxygen at standard temperature and the pressure condition. And theoretically we can calculate the heat of combustion of a given reaction by using the difference between the heat of formation of the product and reactant under the specific condition. For example, the combustion of the hydrocarbon in presence of oxygen produces water and CO_2 as a product.

So, once we know the heat of formation of these compounds, then we can easily calculate the heat of combustion. For example, the heat of combustion as I discussed earlier, it is the difference between the summation of the heat of formation of products that is water and the CO_2 minus the heat of formation of the reactant that is hydrocarbon and the oxygen. And once we know these values, we can easily calculate the heat of combustion.

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ΔH_{comb} can be calculated from the heat of formation (H_f).

For example:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$$

heat

$$\Delta H_{comb} = 2\Delta H_{H2O} + \Delta H_{CO2} - \Delta H_{CH4} - 2\Delta H_{O2} = -801.7 \text{ kJ/mole} \ (-ve \text{ sign} \Rightarrow \text{exothermic})$$

+ve sign

Heat of formation some important compounds. (Source: Basu, 2013)

Compound	H_2O	CO_2	CO	CH_4	O_2	$CaCO_3$	NH_3
Heat of formation at 25 °C (kJ/mole)	-241.5	-393.5	-110.6	-74.8	0	-1211.8	-82.5

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So, now let us discuss one small example here to calculate the heat of combustion of this specific reaction where the methane is combusted in presence of oxygen to produce water and CO_2 as a product, as the heat of formation of this compound is given here in this table. So, the heat of combustion as we discussed earlier, it is the summation of the heat of formation of product compounds that is water and CO_2 minus the heat of formation of the reactant.

So, here as 2 moles of waters are produced, so 2 into heat of formation of the water plus this is 1 mole of CO_2, heat of formation of CO_2. Once we take the summation of this and minus the summation of heat of formation of methane and heat of formation of the oxygen. So, these values are given here, once we replace these values in this equation we will get the final answer in the form of -801.7 kJ per mole. And the negative sign here indicates the exothermic process right, as already we know the combustion is the exothermic process as it releases significant amount of heat. And that is also depicted here in this form of the heat of combustion of the reaction. In case if the sign is positive, then it is called as an endothermic process.

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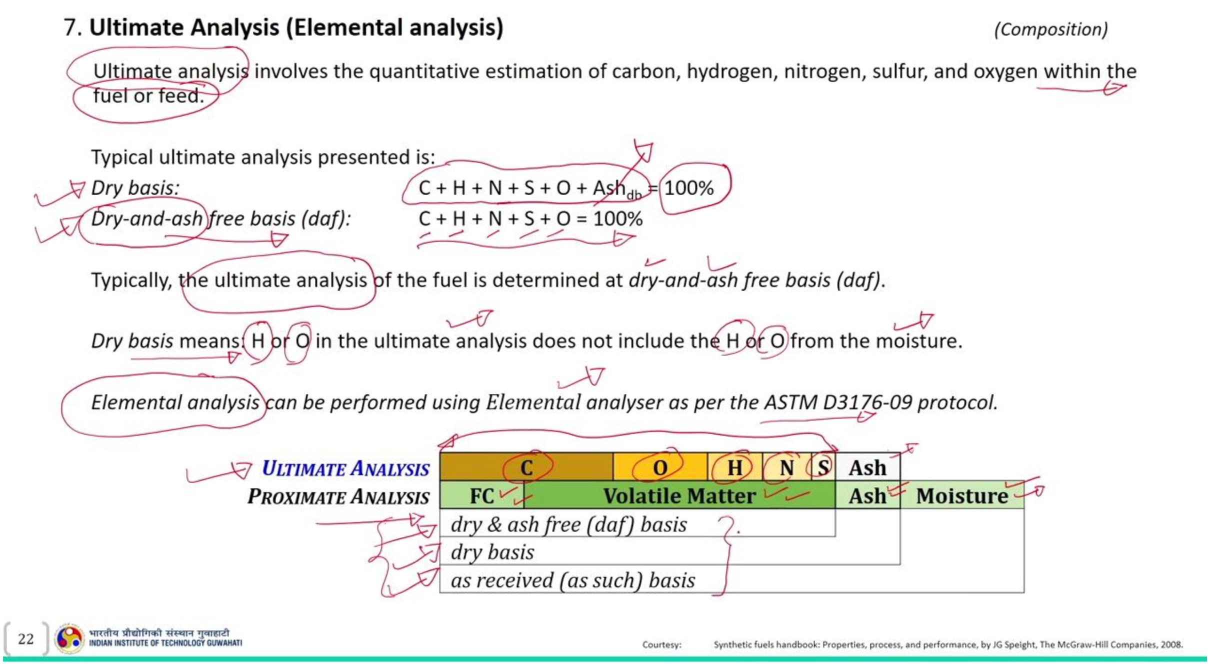

So, the next point in the properties is the ultimate analysis. Ultimate analysis, it involves the quantitative estimation of carbon, hydrogen, nitrogen, sulphur and oxygen within the fuel or the feed material. So, typically the ultimate analysis is presented in the following way that is on dry basis and dry and ash free basis. When it is on the dry basis then it includes carbon, hydrogen, nitrogen, sulphur, oxygen and the ash, which accounts to be 100 percent.

And when it is dry and ash free basis then the ash is neglected and it only presented in the form of carbon, hydrogen, nitrogen, sulfur and oxygen, which accounts to be around close to 100 percent. And typically this ultimate analysis of the fuel is determined at dry and ash-free basis. So, normally when we try to estimate the ultimate analysis of any source material we try to estimate the ultimate analysis on dry and ash free basis. Dry basis means the hydrogen and oxygen in the ultimate analysis does not include the hydrogen and oxygen from the moisture.

And this ultimate analysis or also known as the elemental analysis can be performed using the elemental analyzer and that is as per the ASTM standard protocol. This ultimate analysis as I mentioned earlier also, it includes the carbon, oxygen, hydrogen, nitrogen and sulfur. In case if we are considering on the dry basis then we have to include the ash as well. But as I mentioned earlier also the ultimate analysis are normally determined on dry and ash free basis.

So, it includes only these elements. Similarly, the proximate analysis it includes the fixed carbon, volatile matter, ash and the moisture content in the specific raw material as well as the produce product. If its need to be estimated on dry and ash free basis, then it includes only the fixed carbon and the volatile matter. If it needs to be estimated on the dry basis, then it includes the ash. And as on the received basis then it includes again the moisture. So, likewise the proximate analysis can be presented based on the following three conditions.

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Table: Ultimate analysis of different fuels (daf basis)(coutesy: Viswanathan, 2017; Speight et al., 2008)

Fuel type	Heating Value (MJ/kg)	C%	H%	N%	S%	O%	H/C Ratio	O/C Ratio
Wood	14-21	49	7	0.1	0.1	44	1.7	0.67
Cereal straw	16-17	48	5	0.4	0.1	47	1.3	0.73
Peat	7-22	60	6	1	0.4	33	1.2	0.41
Lignite coal	14-19	70	5	1	1.4	24	0.9	0.26
Bituminous coal	27-32	85	5	0.9	1	9	0.7	0.08
Anthracite coal	32-34	93	3	0.9	0.7	3	0.4	0.02
MSW	10-29	48	6	1.2	0.3	33	1.5	0.52
RDF	17-23	52	7	0.6	0.3	40	1.6	0.58

- **S** in the fuel contributes to SO_2 emission.
- To reduce SO_2 emissions one can use limestone (slurry) flue gas desulfurization (FGD):

$$SO_2 + (CaCO_3 + 2H_2O) + \tfrac{1}{2}O_2 \rightarrow (CaSO_4 \cdot 2H_2O) + CO_2$$

Here, reduction of 1 mole of SO_2 produce 1 mole of CO_2.
Therefore, S must be removed from the fuel before the combustion (*deep-desulphurisation*).

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.
Synthetic fuels handbook: Properties, process, and performance, by JG Speight, The McGraw-Hill Companies, 2008.
Energy Sources, by B Viswanathan, Elsevier, 2017.

So, the ultimate analysis of different fields is tabulated here in the tabular form along with its H/C ratio and the O/C ratio. And if you see here the H/C and the O/C ratio of biobased material is relatively high compared to that of coal material. However, the sulfur content in the biomaterial is less than that of the coal material. And hence the sulfur in the fuel needs to be removed before being used in the combustion process because the sulfur in the fuel it contributes to SO_2 emission.

Therefore, to reduce the emission of the sulphur dioxide we can scrub this sulphur dioxide gas using a flue gas desulphurization unit. Where the limestone is used as slurry in the scrubber, where this sulphur dioxide gas is scrubbed with this limestone slurry and produces calcium sulphate dihydrate that is also known as the gypsum along with the CO_2. So, if you see this particular reaction, so for reducing 1 mole of sulphur dioxide, it produces around 1 mole of carbon dioxide. And therefore, the sulphur must be removed from the fuel before using the feedstock in the combustion process.

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Atomic H/C and **O/C ratios** are calculated from the ultimate analysis for the ranking of fuels.

- Atomic H/C and O/C ratios are calculated in the form of molar fractions of the respective elements.

$$\text{H/C ratio} = \frac{\left(\frac{\%w_H}{MW_H}\right)}{\left(\frac{\%w_C}{MW_C}\right)}$$

$$\text{O/C ratio} = \frac{\left(\frac{\%w_O}{MW_O}\right)}{\left(\frac{\%w_C}{MW_C}\right)}$$

Where, %w is percent weight of given element,

MW is molecular weight of given element,

Subscript C, H, O represents carbon, hydrogen, and oxygen, respectively.

Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

Apart from the ultimate analysis, the atomic ratio that is H/C ratio and the O/C ratio can also be calculated to rank the fuels. The atomic H/C and the O/C ratios are calculated in the form of molar fractions of the respective element. That is if you see here, this H/C ratio, it is the ratio of molar fraction of hydrogen to the molar fraction of the carbon. That is percentage weight of hydrogen divided by its molecular weight and here it is percentage weight of carbon divided by its molecular weight. And similarly the O/C ratio can be calculated.

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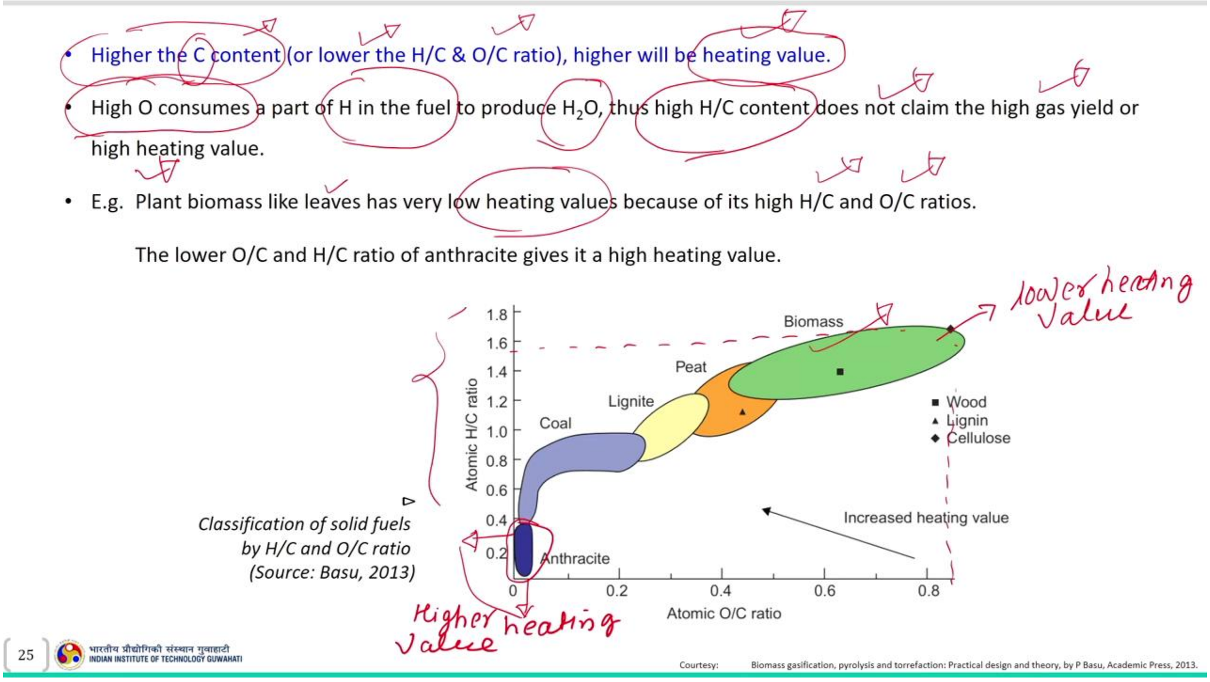

So, as we discussed earlier the higher the content of carbon that means the H/C ratio will be lower, also the O/C ratio will be lower, higher will be the heating value. And that is what we have seen in the previous slide where we have seen in the table that the H/C ratio and the O/C ratio of coal is relatively low than that of the biomass. And that is the reason the feedstock or the source material which has higher carbon content ultimately its heating value is relatively higher.

So, the high O in the source material consumes the part of the H_2 in the fuel as well as in the source material to produce H_2O. And thus high H/C ratio content does not claim that the high gas yield or high heating value. For example, if you see here the biomass like leaves has very low heating value, because it has very high H/C and the O/C ratio which can be seen here from this graphical representation as well.

If you can see here this biomass which is shown in the green color, it has relatively higher H/C ratio and higher O/C ratio, ultimately it has a lower heating Now, if you compare this biomass with the coal that is the anthracite, so it has relatively very lower H/C as well as the O/C ratio, but the higher heating. So, these ways even this H/C ratio as well as the O/C ratio that is also called as the atomic ratios are useful to classify the fuel as well as to rank the fuel.

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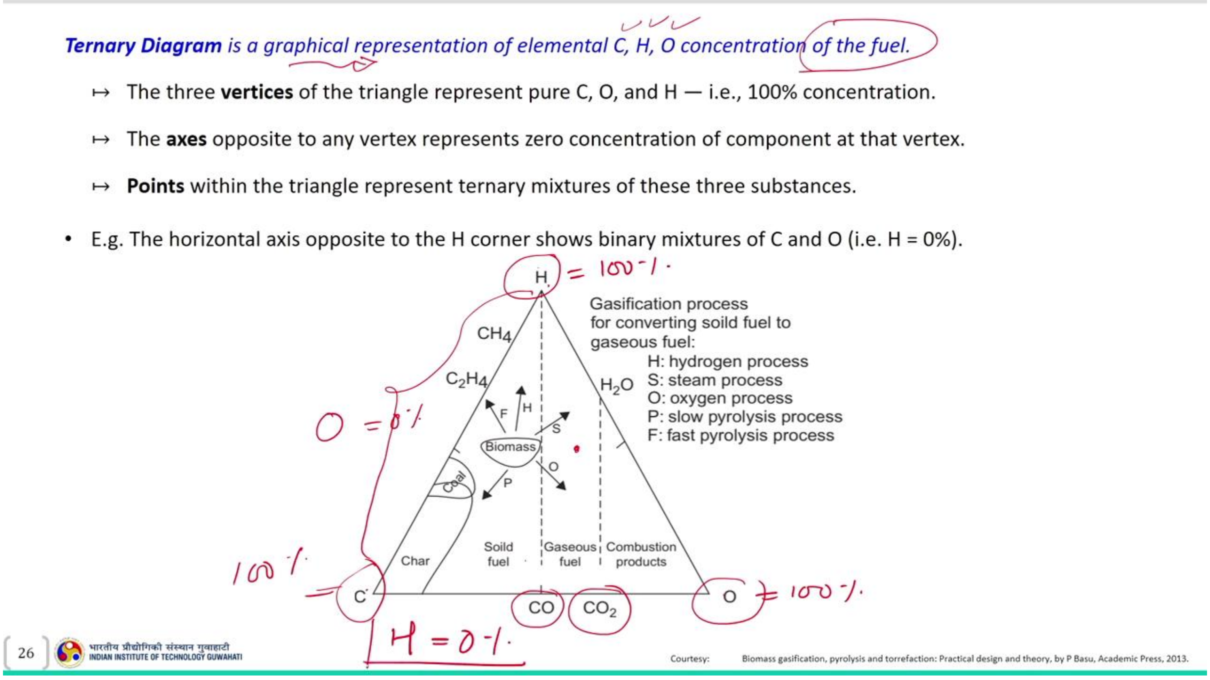

Even the ternary diagram is also useful in ranking the fuel. Because ternary diagram here it is a graphical representation of elemental like carbon, hydrogen and oxygen concentration of the fuel. So, these three vertices, if you see here, these three vertices of the triangle element, it represents the carbon, oxygen and the hydrogen and it is nothing but the 100% concentration of carbon, hydrogen and the oxygen, and the axis opposite to the vertex represents the zero concentration of the component at that vertex.

So, for example, if you see here this particular axis which is opposite to the vertex that is O, so here the concentration of O is 0%. And points within this particular triangle it represents the ternary mixture of these three substances. So, for example, here the horizontal axis which is opposite to the edge corner shows the binary mixture of carbon and oxygen and 0% of H.

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- Ternary diagram is an useful tool for the classification of fuel:

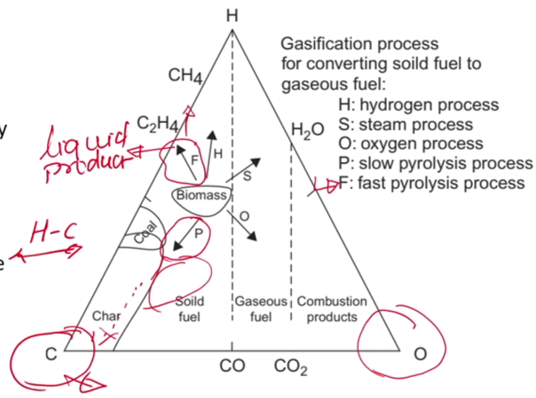
  E.g. Coal is located toward the C-vertex and closer to H-C axis, suggesting that it is much richer in carbon.

- It is also useful to illustrate the fuel conversion processes:

  For example:

  Fast pyrolysis moves the products toward hydrogen and away from oxygen, which implies higher liquid product.

  Slow pyrolysis moves the product toward carbon through the formation of solid char.



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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

So, likewise this ternary diagram it is a useful tool for the classification of the fuel. So, for example, if you see here the coal which is located towards the C vertex and it is closer to the H-C axis, suggesting that it is a much richer in carbon. And also it is very well known that the high grade coal is much richer in the carbon content.

Similarly, this ternary diagram is also useful to illustrate the fuel conversion processes. For example, if you try to see the fast pyrolysis process first. So, in case of fast pyrolysis process that is F here, the product moves towards the hydrogen and away from oxygen which implies that the process will produce higher liquid product. And in case of slow paralysis process suppose for example P here, which indicates the slow paralysis process it moves the product towards the carbon through solid char right through formation of the solid char which indicates the formation of a specific product. Likewise this ternary diagram is also useful tool for the classification of a fuel.

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- **Calculating heating value from ultimate analysis:**
  - ↦ The ultimate analysis of solid fuel on dry basis: C + H + N + S + O + Ash_{db} = 100%.
  - ↦ Among these combustible constituents are carbon C, hydrogen H, and sulfur S.
  - ↦ Thus, the heating values of given fuel can be approximated from the mass fractions (x, dry basis) of C, H and S present in the given fuel.

$$\mathrm{HHV} = x_C \times \mathrm{HHV}_C + x_H \times \mathrm{HHV}_H + x_S \times \mathrm{HHV}_S$$

$$\mathrm{LHV} = x_C \times \mathrm{LHV}_C + x_H \times \mathrm{LHV}_H + x_S \times \mathrm{LHV}_S$$

Fuel (Phase)	HHV, kJ/kg	LHV, kJ/kg
Carbon (*s*)	32,800	32,800
Hydrogen (*g*)	141,800	120,000
Sulfur (s)	9,160	9,160

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Apart from that the ultimate analysis as we discussed earlier, it is also useful for calculating the heating value of a source material as well as the produced fuel. The ultimate analysis of the solid fuel on the dry basis as we discussed earlier, which includes carbon, hydrogen, nitrogen, sulfur and the oxygen along with the ash and it accounts to 100 percent. And among these constituents only carbon, hydrogen and sulfur are only the combustible constituents. And thus the heating value of a given fuel, it can be approximated from the mass fraction of these constituents that is carbon, hydrogen and sulfur but that is on the dry basis, as we have assumed it is on the dry basis.

So, once we know the mass fraction of these constituents then we can easily calculate the higher heating value of the given fuel. Once we know the mass fraction of carbon, mass fraction of hydrogen and mass fraction of sulphur and their higher heating values then we can easily calculate the high heating value of the given fuel. On the similar basis we can calculate the low heating value of a given fuel, but for that we need to know the high heating value of carbon, hydrogen and sulphur which are given here in the tabular form.

And once these values are known along with their mass fraction we can easily calculate these values. And if you recollect we discuss the same concept in one of the lecture in the module 1, there we have estimated the higher heating value of a given composition of a fuel. So, once the composition of the fuel is known then we can easily calculate the higher heating value as well as the lower heating value of a given fuel. So, this in total completes the ultimate analysis of a source material as well as the fuel.

So, with this we will end our lecture here. And in the next lecture we will discuss about the remaining properties that is the approximate analysis and the structural composition of a source materials as well as the fuel.

Thank you.