Energy Conversion Technologies (Biomass and Coal)

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Lecture 9

Solid fuels (Part II)

Good morning everyone.

Welcome to part 2 of the lecture 1 under the module 2. In this lecture we will discuss about the remaining properties of the solid fuel that is proximate analysis and composition analysis of solid fuels.

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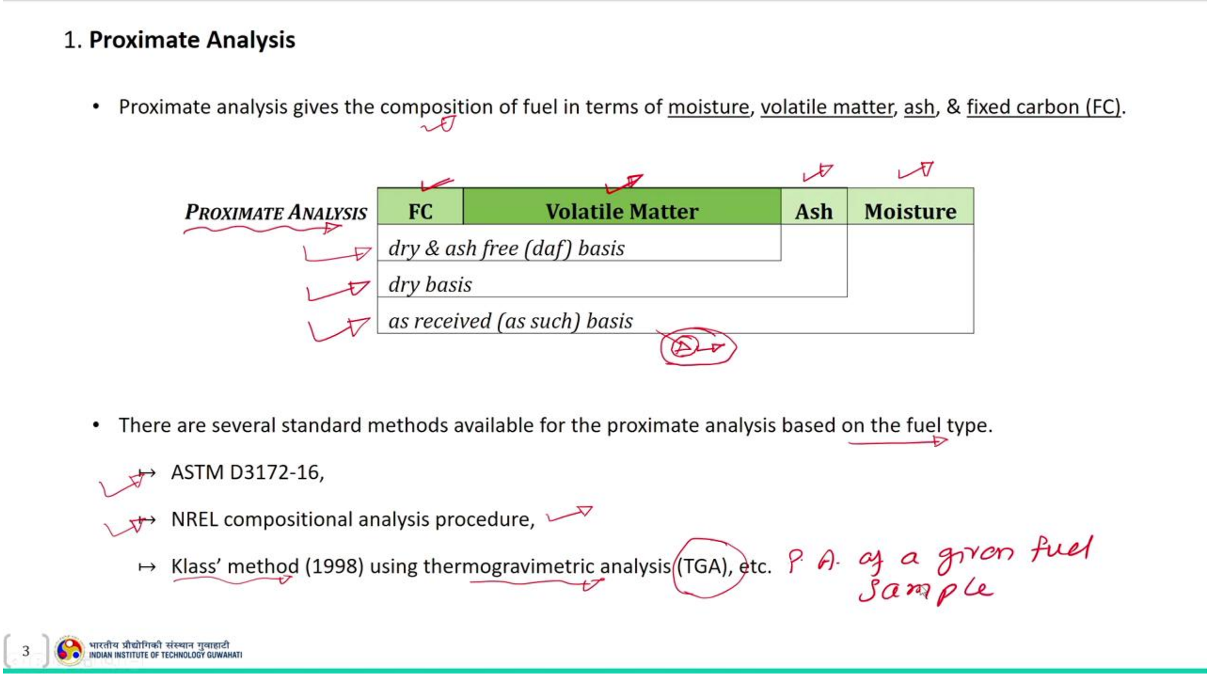

1. **Proximate Analysis**

- Proximate analysis gives the composition of fuel in terms of moisture, volatile matter, ash, & fixed carbon (FC).

PROXIMATE ANALYSIS	**FC**	**Volatile Matter**	**Ash**	**Moisture**
	dry & ash free (daf) basis			
	dry basis			
	as received (as such) basis			

- There are several standard methods available for the proximate analysis based on the fuel type.
  - ↦ ASTM D3172-16,
  - ↦ NREL compositional analysis procedure,
  - ↦ Klass' method (1998) using thermogravimetric analysis (TGA), etc.

P. A. of a given fuel sample

Proximate analysis is used to measure the composition of a fuel in terms of say fixed carbon content, volatile matter, moisture and ash content. And this proximate analysis can be expressed in the following ways.

Proximate analysis is presented on dry and ash free basis mainly includes the fixed carbon content and the volatile matter content of a given fuel. And on dry basis it includes the ash content of a given fuel. And if you are estimating the proximate analysis on as received basis then it includes the moisture content as well. And mostly we estimate the proximate analysis of a given fuel on as received basis to know the fixed carbon content volatile matter, ash and the moisture content of a given fuel.

As received basis means the material is used for proximate analysis without using any additional pretreatment or additional step that is called as a drying. So, the material which is obtained on as-received basis is used for the proximate analysis as well as to find out the composition of a given fuel. There are several standard methods are available for the proximate analysis and these are basically based on the fuel and its type.

So ASTM method which is a standard method used for the proximate analysis apart from that there is a NRL compositional analysis procedure is also available for the estimation of the proximate analysis of a given field. And newest addition is the class method using thermogravimetric analysis that is also known as a TGA is also used for the proximate analysis of given fuel sample.

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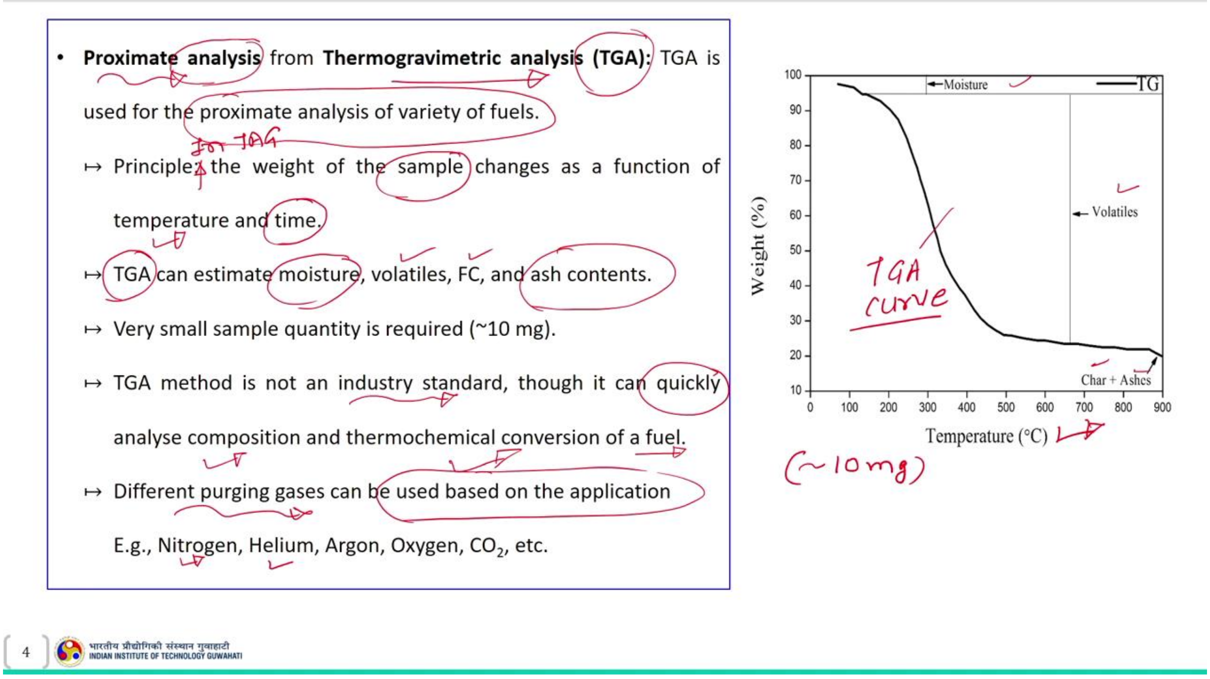

- **Proximate analysis** from **Thermogravimetric analysis (TGA):** TGA is used for the proximate analysis of variety of fuels.
  - ↦ Principle: the weight of the sample changes as a function of temperature and time.
  - ↦ TGA can estimate moisture, volatiles, FC, and ash contents.
  - ↦ Very small sample quantity is required (~10 mg).
  - ↦ TGA method is not an industry standard, though it can quickly analyse composition and thermochemical conversion of a fuel.
  - ↦ Different purging gases can be used based on the application E.g., Nitrogen, Helium, Argon, Oxygen, CO_2, etc.

for TGA

So, now let us discuss about this new method of proximate analysis from the thermogravimetric analysis also known as a TGA. So, this TGA is used for the proximate analysis of variety of fuels and in TGA the weight of the sample it changes as a function of temperature and time. So, if you see this particular curve here so in this case this thermogravimetric data which is collected from the thermal reaction is compiled into a plot of mass or percentage of initial mass versus temperature. And this plot, which is often smoothen, is referred to as a TGA curve. And once we have this TGA curve, so with the help of this TGA curve, we can easily estimate the moisture, volatile matter, char and ash content in a given sample.

TGA, as I mentioned, it can estimate the moisture, fixed carbon and the ash content of a given sample. And another advantage of utilization of this particular technique for the proximate analysis is this particular technique required very small quantity of sample that is close to only 10 milligram. And this TGA method is not an industry standard, though it can quickly analyze composition and thermochemical conversion of a fuel. Another advantage of using this technique for the proximate analysis is that this particular technique can analyze different sample even under different purging gases as well and can be used based on the application and the purging gases which can be used are nitrogen, helium, argon, oxygen and CO2. So, these are some basic advantage of using this particular technique for the analysis purpose and one of the most convenient advantages of this particular technique is it can be carried out in a short span of time.

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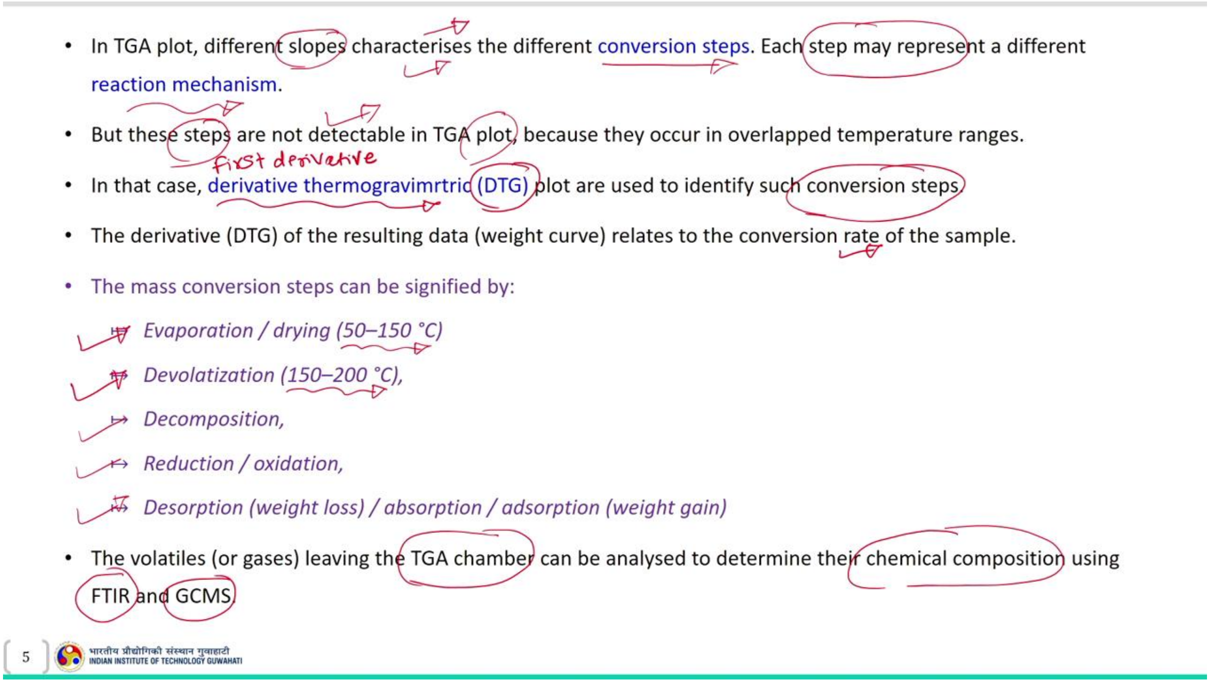

- In TGA plot, different slopes characterises the different conversion steps. Each step may represent a different reaction mechanism.
- But these steps are not detectable in TGA plot, because they occur in overlapped temperature ranges.
- In that case, derivative thermogravimrtric (DTG) plot are used to identify such conversion steps.

first derivative

- The derivative (DTG) of the resulting data (weight curve) relates to the conversion rate of the sample.
- The mass conversion steps can be signified by:
  - *Evaporation / drying (50–150 °C)*
  - *Devolatization (150–200 °C),*
  - *Decomposition,*
  - *Reduction / oxidation,*
  - *Desorption (weight loss) / absorption / adsorption (weight gain)*
- The volatiles (or gases) leaving the TGA chamber can be analysed to determine their chemical composition using FTIR and GCMS.

However, there are certain issues associated with this particular TGA plot as well. Because in TGA plot different slope characterizes the different conversion steps and each step may represent a different reaction mechanism, because it all depends on the characteristics of a given fuel. So, if the fuel has different constituents then each step may represent a different reaction mechanism based on the different composition or I would say different constituents of a given fuel. But these steps are not detectable in a TGA plot as I shown earlier because if you see this TGA plot these different steps are difficult to detect in the TGA plot. Because they occur in overlapped temperature ranges.

We take the example of the biomass. So, hemicellulose contained in the biomass may get overlap with the decomposition pattern of the cellulose because of these overlap temperature ranges of the decomposition pattern of this different compound. And hence it is very difficult to detect this step in a TGA curve. In that case first derivative that is also known as the derivative thermogravimetric plot that is DTG plot are used to identify such conversion steps. The derivative of the resulting data relates to the conversion rate of the sample based on this composition and this conversion step can be signified in the following step.

For example, the evaporation and the drying step which mainly occurs between 50 to 150 °C as well as the devolatilization step which occurs between 150 to 200 °C followed by the decomposition, reduction and desorption step in TGA analysis. The volatiles which are leaving the TGA chamber can be analyzed to determine their chemical composition. And for that purpose the TGA equipment can be coupled with either FTIR or GC-MS.

So, the gases which are leaving the TGA chamber can be passed on to the GCMS analysis where we can easily find out the chemical composition of those gases as well as these gases can be easily detected using the coupled FTIR. So, this is one of the convenient method to analyze the volatile matter leaving the TGA chamber using FTIR or GCMS.

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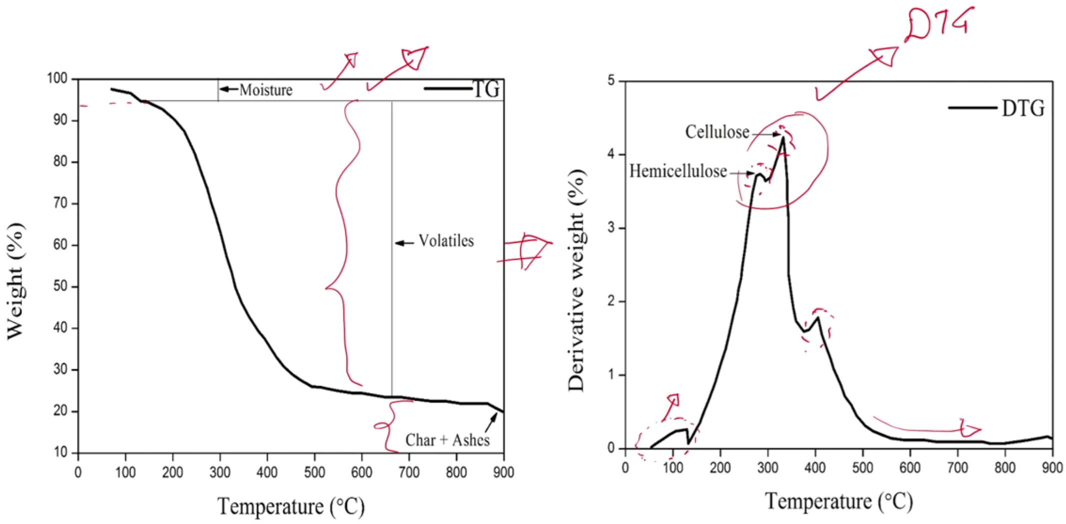

So, this particular schematic here represents the TGA curve. And this represents the DTG curve of the resulting thermogravimetric data. So, in this case if you see here this particular portion on the graph indicates the moisture, this particular portion indicates the volatiles and the remaining part indicates the fraction in the form of char and ash.

Now, as we discussed in the previous slide, it is difficult to identify these steps in the TGA plot and thus we take the help of the DTG curve to understand the decomposition behavior of the different component present in the given field sample. So, if you see here this particular DTG curve shows different decomposition pattern of component present in the sample in the form of different step that is basically this indicates the drying and the evaporation step. This particular part indicates the devolatilization step followed by the further decomposition of the remaining sample in the pan.

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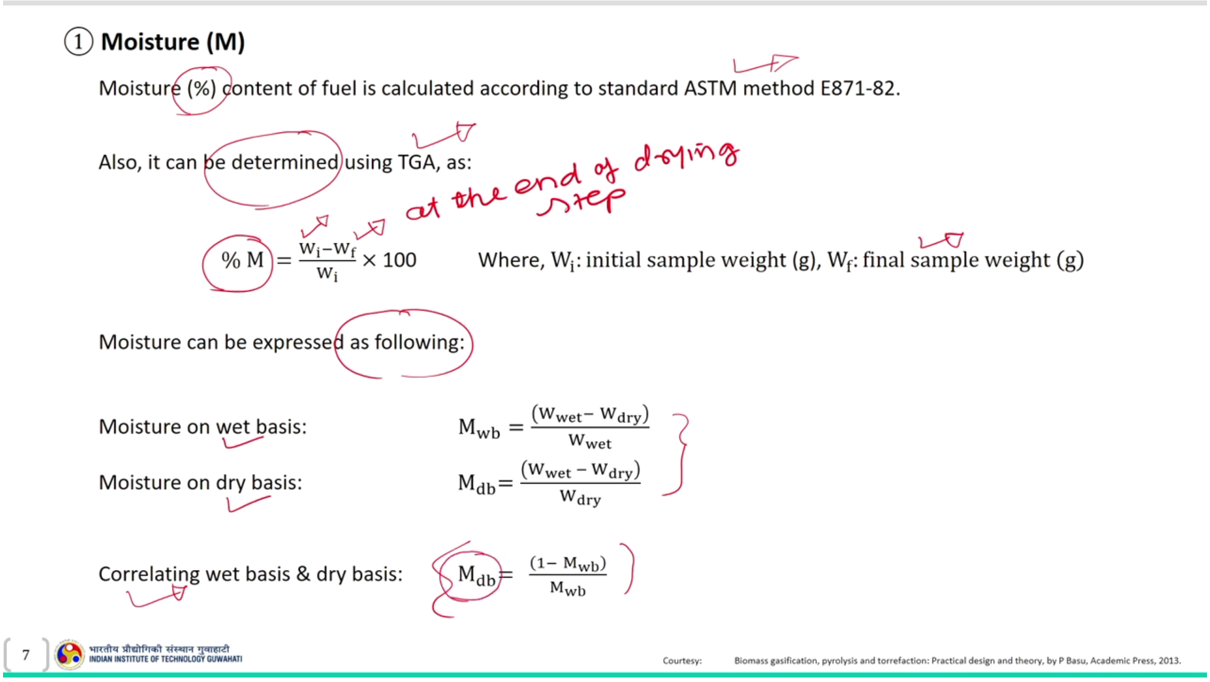

① **Moisture (M)**

Moisture (%) content of fuel is calculated according to standard ASTM method E871-82.

Also, it can be determined using TGA, as:

at the end of drying step

$$\% M = \frac{W_i - W_f}{W_i} \times 100$$

Where, W_i: initial sample weight (g), W_f: final sample weight (g)

Moisture can be expressed as following:

Moisture on wet basis: $M_{wb} = \frac{(W_{wet} - W_{dry})}{W_{wet}}$

Moisture on dry basis: $M_{db} = \frac{(W_{wet} - W_{dry})}{W_{dry}}$

Correlating wet basis & dry basis: $M_{db} = \frac{(1 - M_{wb})}{M_{wb}}$

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

After understanding about the thermogravimetric analysis technique, let us discuss about the moisture content and how to estimate this moisture content in the given sample. Percentage moisture content of a fuel can be calculated according to the standard ASTM method and it can also be determined using the TGA analysis. So, if we remember the previous graph, so once we know the initial weight of the sample and the final weight of the sample at the end of drying step, then we can easily calculate the percentage moisture content of a fuel. So, to better understand this concept I will just go back to the previous slide.

So, as we know w_i is the initial weight of the sample and w_f is the final weight of the sample that means final weight of the sample at the end of drying step and this w_i is the initial weight of the sample. Once we know these two values we can easily calculate the percentage moisture present in the fuel which corresponds to this particular line here on the y axis. So, this particular weight difference indicates the percentage moisture present in the given fuel sample. Similarly, this moisture it can be expressed as following that is on the wet basis and dry basis. And it can be estimated using this following expression and this moisture on the wet basis and dry basis can also be correlated using this equation.

So, once we know the moisture on the wet basis then we can calculate the moisture on the dry basis using this correlation.

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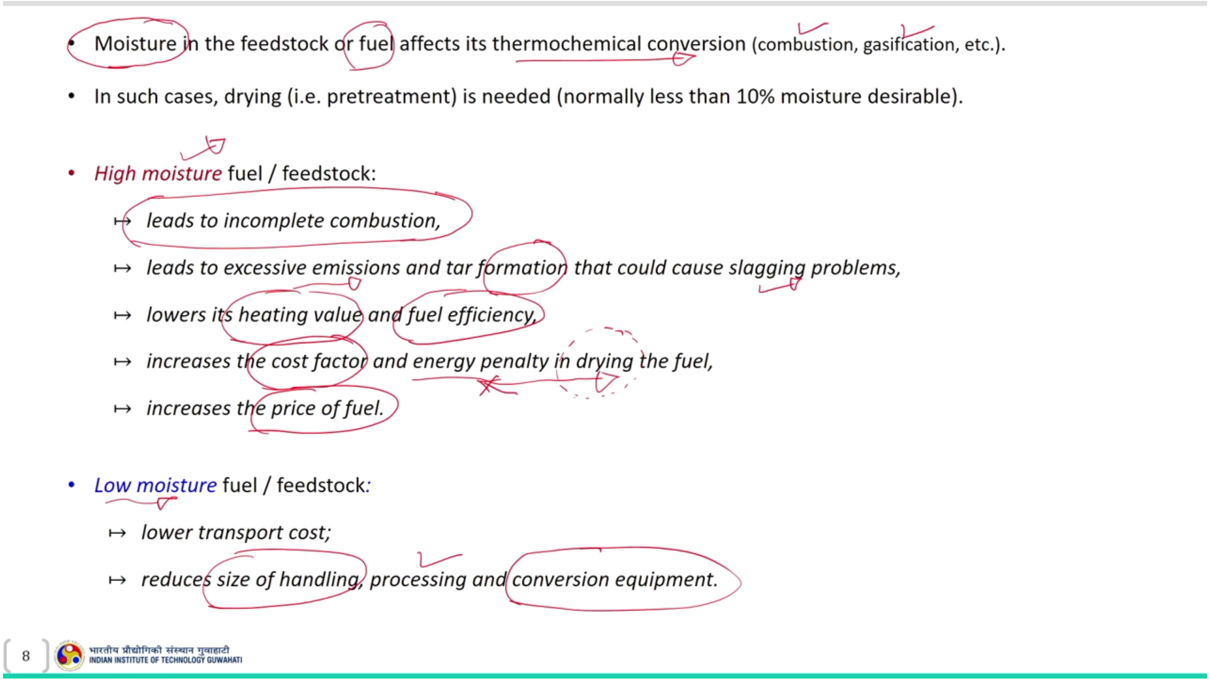

- Moisture in the feedstock or fuel affects its thermochemical conversion (combustion, gasification, etc.).
- In such cases, drying (i.e. pretreatment) is needed (normally less than 10% moisture desirable).

- *High moisture* fuel / feedstock:
  - ↦ *leads to incomplete combustion,*
  - ↦ *leads to excessive emissions and tar formation that could cause slagging problems,*
  - ↦ *lowers its heating value and fuel efficiency,*
  - ↦ *increases the cost factor and energy penalty in drying the fuel,*
  - ↦ *increases the price of fuel.*

- *Low moisture* fuel / feedstock*:*
  - ↦ *lower transport cost;*
  - ↦ *reduces size of handling, processing and conversion equipment.*

The moisture is one of the most important parameter in the approximate analysis. Because the moisture in the feedstock or fuel it affects the thermochemical conversion process that is gasification and combustion because if the moisture contained in the feedstock or the fuel is relatively high that is say between 15 to 30 percent then most of the energy goes waste in removing this moisture from the incoming feed material. As a result it eventually hampers the efficiency of the thermochemical conversion process. In such cases additional operation in terms of drying is needed to remove the moisture and bring the moisture in the feed material to a desirable limit of 10%.

Because in thermochemical conversion processes the moisture content of 10% or less is desirable for the efficient conversion of the feedstock to a valuable product. However, if the moisture content in the fuel or the feedstock is high, then it leads to the incomplete combustion that is one of the problems associated with the high moisture content in the feedstock. It also leads to excessive emissions and tar formation that could cause slagging problem in the gasifier or we can say in the boiler. It also lowers its heating value because if the moisture content is high in the feedstock or in the given fuel then it may lower its heating value as well as the fuel efficiency and increases the cost factor and energy penalty in drying the fuel. Because this additional operation need to be carried out to take away the excessive moisture from the feedstock material.

And that may lead to the energy penalty of the fuel and that may eventually results in increasing the price of a fuel. If the moisture content is low then it reduces the size of handling processing and conversion equipment. That is the reason as I mentioned earlier, moisture content is one of the most important parameter that need to be taken into consideration while designing a specific energy conversion process or system.

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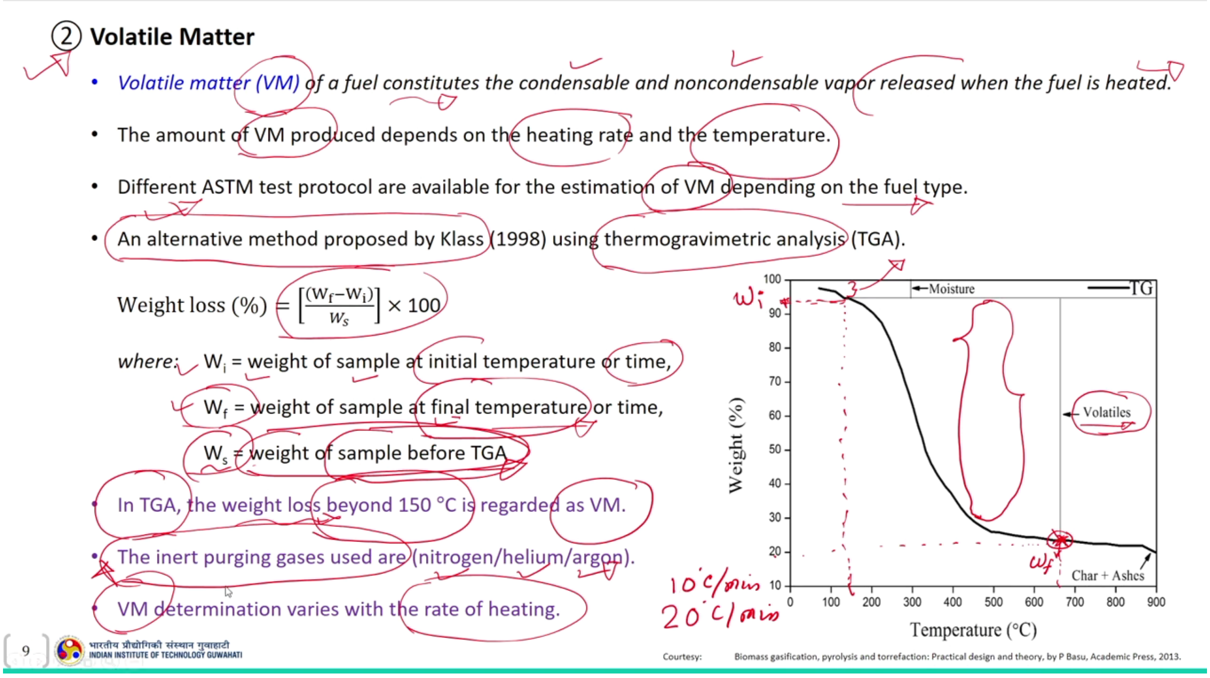

② **Volatile Matter**

- *Volatile matter (VM) of a fuel constitutes the condensable and noncondensable vapor released when the fuel is heated.*
- The amount of VM produced depends on the heating rate and the temperature.
- Different ASTM test protocol are available for the estimation of VM depending on the fuel type.
- An alternative method proposed by Klass (1998) using thermogravimetric analysis (TGA).

$$\text{Weight loss (\%)} = \left[\frac{(W_f - W_i)}{W_s}\right] \times 100$$

where: W_i = weight of sample at initial temperature or time,

W_f = weight of sample at final temperature or time,

W_s = weight of sample before TGA

- In TGA, the weight loss beyond 150 °C is regarded as VM.
- The inert purging gases used are (nitrogen/helium/argon).
- VM determination varies with the rate of heating.

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

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So, the next in the list of approximate analysis is the volatile matter. Volatile matter of a fuel constitutes the condensable and non-condensable vapours released when the fuel is heated and the amount of volatile matter produced is depends on the heating rate and the temperature.

Different standard ASTM protocols are available for the estimation of the volatile matter depending on the fuel type and alternative technique as proposed by class. That is thermogravimetric analysis can also be used to estimate the volatile matter present in the given fuel. The volatile matter content can be estimated using this following expression where we required weight of the sample at initial temperature, weight of the sample at final temperature and weight of the sample before TGA. So, as discussed earlier in TGA the weight loss or the devolatilization of the sample starts between 150 to 200 °C. So, this particular point on the TGA curve can be considered as weight of the sample at the initial temperature and the devolatilization step ends at around 600 to 650 °C.

So, this particular point on the graph considered as the weight of the sample at a final temperature and once we know these two quantities, we can easily calculate the volatile matter which is present in the sample. For that we need to know only the weight of the sample before TGA. Once we know all these terms we can easily calculate the volatiles which are present in the given sample. And, while doing this analysis the inert purging gases used for the estimation of the volatile matters are Nitrogen, Helium and Argon. And, the estimation of the volatile matter it varies with the rate of heating.

That means, if you are carrying out the TGA analysis at say for example 10 °C/min if somebody is carrying out at 20 °C/min, so there will be some variation in the volatile matter estimation. Because with the change in the rate of heating there will be a variation in the volatile matter estimation using this TGA technique.

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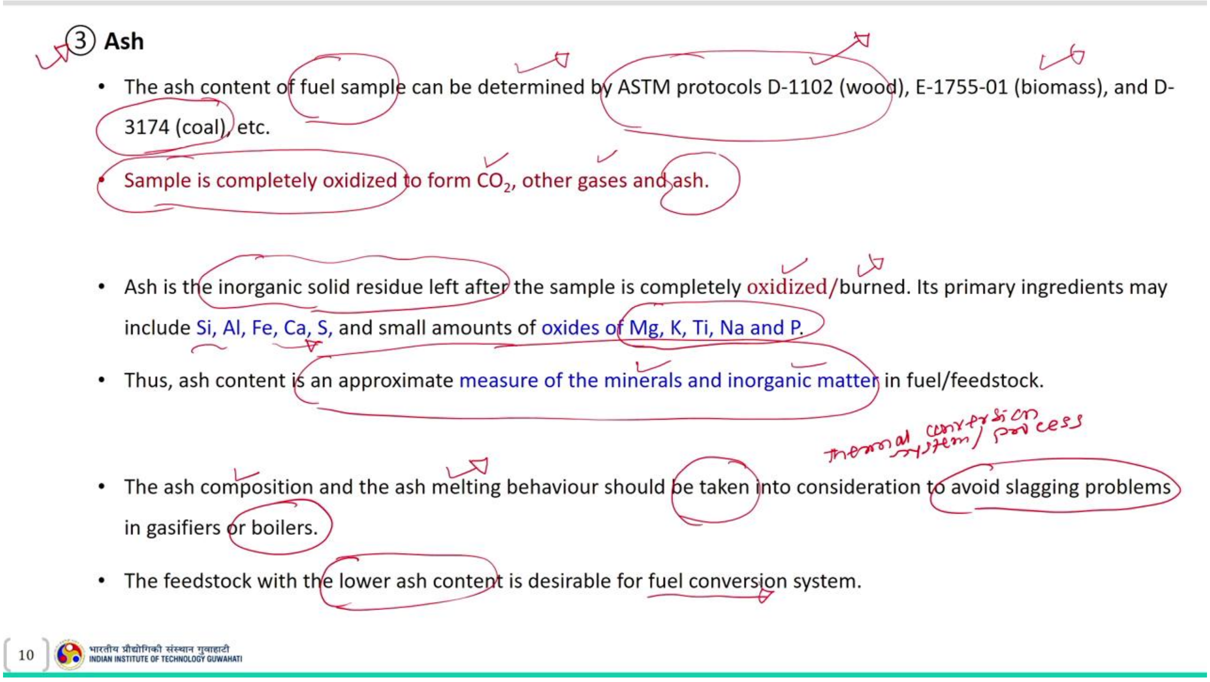

③ **Ash**

- The ash content of fuel sample can be determined by ASTM protocols D-1102 (wood), E-1755-01 (biomass), and D-3174 (coal), etc.
- Sample is completely oxidized to form CO_2, other gases and ash.

- Ash is the inorganic solid residue left after the sample is completely oxidized/burned. Its primary ingredients may include Si, Al, Fe, Ca, S, and small amounts of oxides of Mg, K, Ti, Na and P.
- Thus, ash content is an approximate measure of the minerals and inorganic matter in fuel/feedstock.

thermal conversion system/process

- The ash composition and the ash melting behaviour should be taken into consideration to avoid slagging problems in gasifiers or boilers.
- The feedstock with the lower ash content is desirable for fuel conversion system.

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And next in the proximity analysis is the ash. The ash content of a fuel sample, it can be determined by standard ASTM protocol. This protocol is for the wood sample, this is for biomass and this protocol is for the coal sample.

So, in case of estimation of the ash the sample is completely oxidized to form CO_2 and other gases and the leftover material in the pan or the crucible is termed as a ash. Ash is a inorganic solid residue that is left after the sample is completely oxidized or we can say burned and its primary ingredients may include following elements and small amount of oxides of this particular element. Thus ash content is an approximate measure of the minerals and inorganic matter which are present in the fuel and the feedstock.

The ash composition and the ash melting behavior should be taken into consideration while designing thermal conversion system or process to avoid the slagging problem in the gasifier or boiler. Therefore, the feedstock with lower ash content is desirable for the fuel conversion system.

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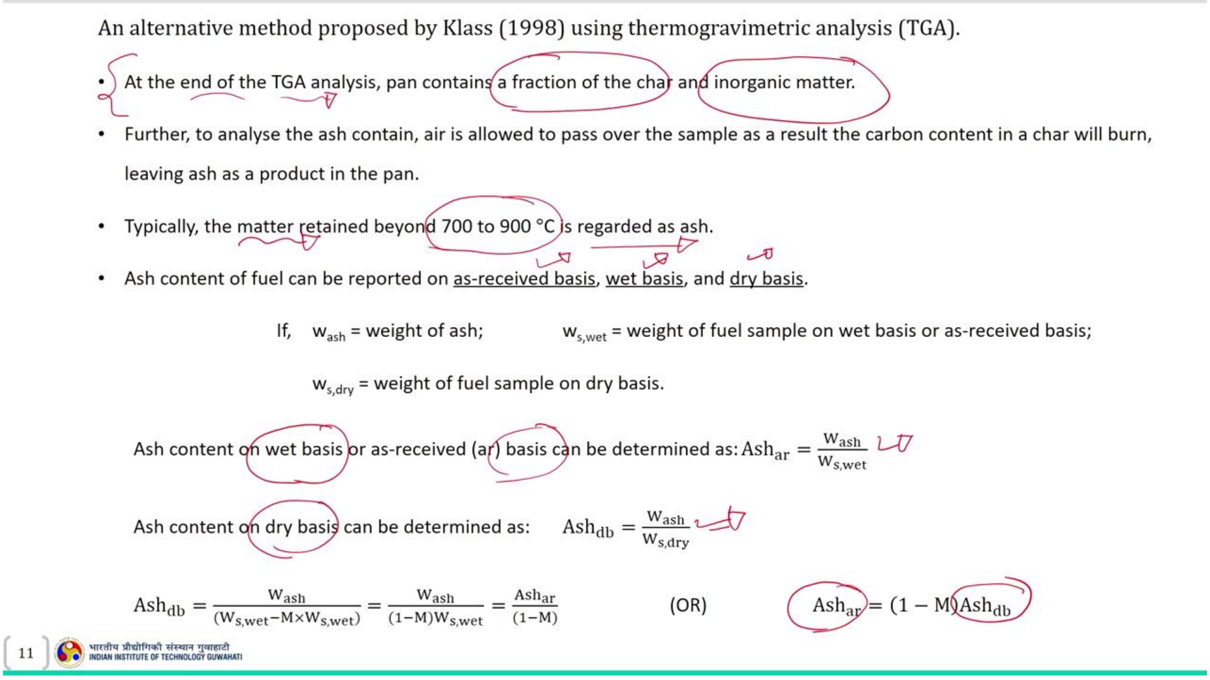

An alternative method proposed by Klass (1998) using thermogravimetric analysis (TGA).

- At the end of the TGA analysis, pan contains a fraction of the char and inorganic matter.
- Further, to analyse the ash contain, air is allowed to pass over the sample as a result the carbon content in a char will burn, leaving ash as a product in the pan.
- Typically, the matter retained beyond 700 to 900 °C is regarded as ash.
- Ash content of fuel can be reported on as-received basis, wet basis, and dry basis.

If, w_{ash} = weight of ash; $w_{s,wet}$ = weight of fuel sample on wet basis or as-received basis;

$w_{s,dry}$ = weight of fuel sample on dry basis.

Ash content on wet basis or as-received (ar) basis can be determined as: $\mathrm{Ash_{ar}} = \frac{W_{ash}}{W_{s,wet}}$

Ash content on dry basis can be determined as: $\mathrm{Ash_{db}} = \frac{W_{ash}}{W_{s,dry}}$

$$\mathrm{Ash_{db}} = \frac{W_{ash}}{(W_{s,wet} - M \times W_{s,wet})} = \frac{W_{ash}}{(1-M)W_{s,wet}} = \frac{\mathrm{Ash_{ar}}}{(1-M)} \quad \text{(OR)} \quad \mathrm{Ash_{ar}} = (1-M)\mathrm{Ash_{db}}$$

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Similarly, an alternative to ASTM method that is thermogravimetric method can also be used to estimate the ash content in the given sample. Because if you remember, the TGA curve at the end of the TGA analysis pan contains the fraction char and inorganic matter. I will just show you the graph once again. So, if you see this graph so at the end of the TGA analysis the pan contains char and ash. And this particular step is also called as an end of the devolatilization step.

Hence to analyze the ash content in the given sample the purging gas needs to be switched from nitrogen to oxygen or air. And oxygen or air is allowed to flow over a sample. As a result the carbon content in the char will burned leaving the ash in the pan. And the final ash content is regarded as the inorganic matter present in the biomass or the given fuel sample. Typically the matter retained beyond 700 to 900 °C in the TGA analysis is regarded as ash.

And ash content can also be reported on as received basis, dry basis and the wet basis. Ash content on wet basis or as received basis can be determined using this expression as well as on dry basis can be determined using the following equation. And once we know the ash content on dry basis then ash content on the as received basis can be calculated using this correlation.

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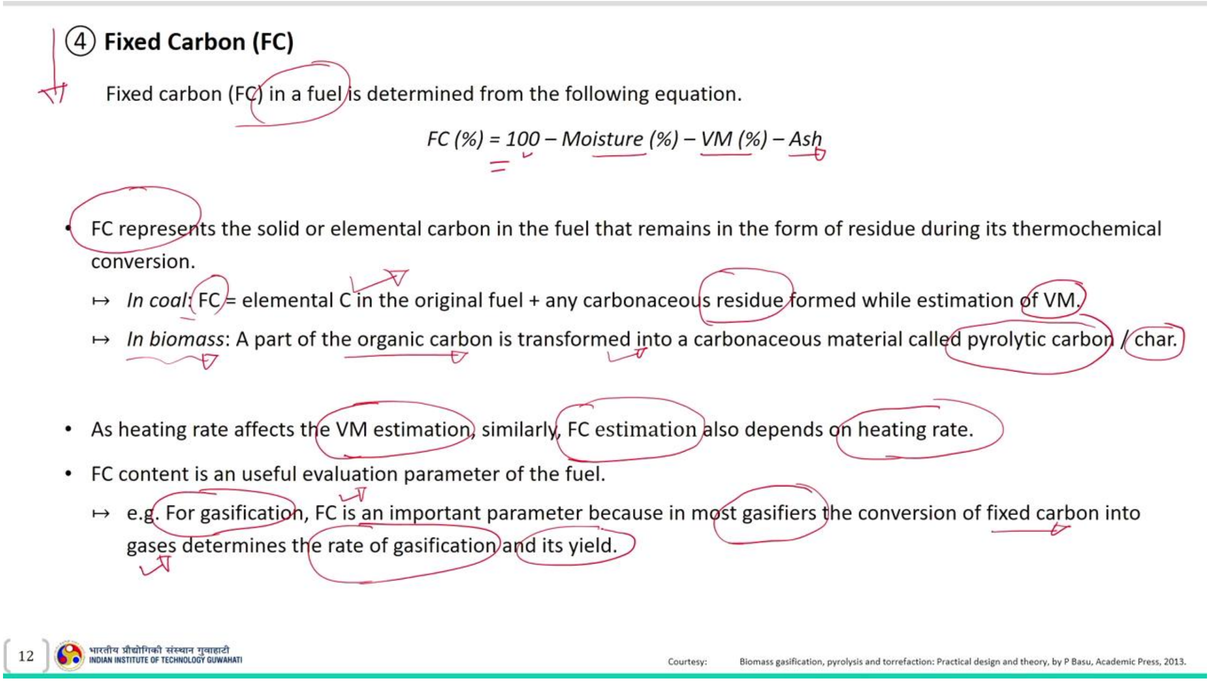

④ **Fixed Carbon (FC)**

Fixed carbon (FC) in a fuel is determined from the following equation.

FC (%) = 100 – Moisture (%) – VM (%) – Ash

- FC represents the solid or elemental carbon in the fuel that remains in the form of residue during its thermochemical conversion.
    - ↦ *In coal:* FC = elemental C in the original fuel + any carbonaceous residue formed while estimation of VM.
    - ↦ *In biomass*: A part of the organic carbon is transformed into a carbonaceous material called pyrolytic carbon / char.
- As heating rate affects the VM estimation, similarly, FC estimation also depends on heating rate.
- FC content is an useful evaluation parameter of the fuel.
    - ↦ e.g. For gasification, FC is an important parameter because in most gasifiers the conversion of fixed carbon into gases determines the rate of gasification and its yield.

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

So, next in the approximate analysis list is the fixed carbon content. Fixed carbon in a fuel is determined from the following equation and it is 100 minus moisture percentage, volatile matter percentage and ash content in the given fuel sample.

And this fixed carbon represents the solid or elemental carbon in the fuel that remains in the form of residue during its thermochemical conversion. So, in coal fixed carbon includes elemental carbon in the original fuel plus carbonaceous residue form while estimation of the volatile matter and in biomass it includes part of the organic carbon that is transformed into carbonaceous material called pyrolytic carbon or char.

As the heating rate affects the estimation of the volatile matter, similarly the estimation of the fixed carbon content also depends on the heating rate of a given sample. And the fixed carbon content is a useful evaluation parameter of the fuel.

Example, for gasification fixed carbon content is an important parameter because in most gasifiers the conversion of the fixed carbon into gases determines the rate of gasification and its yield.

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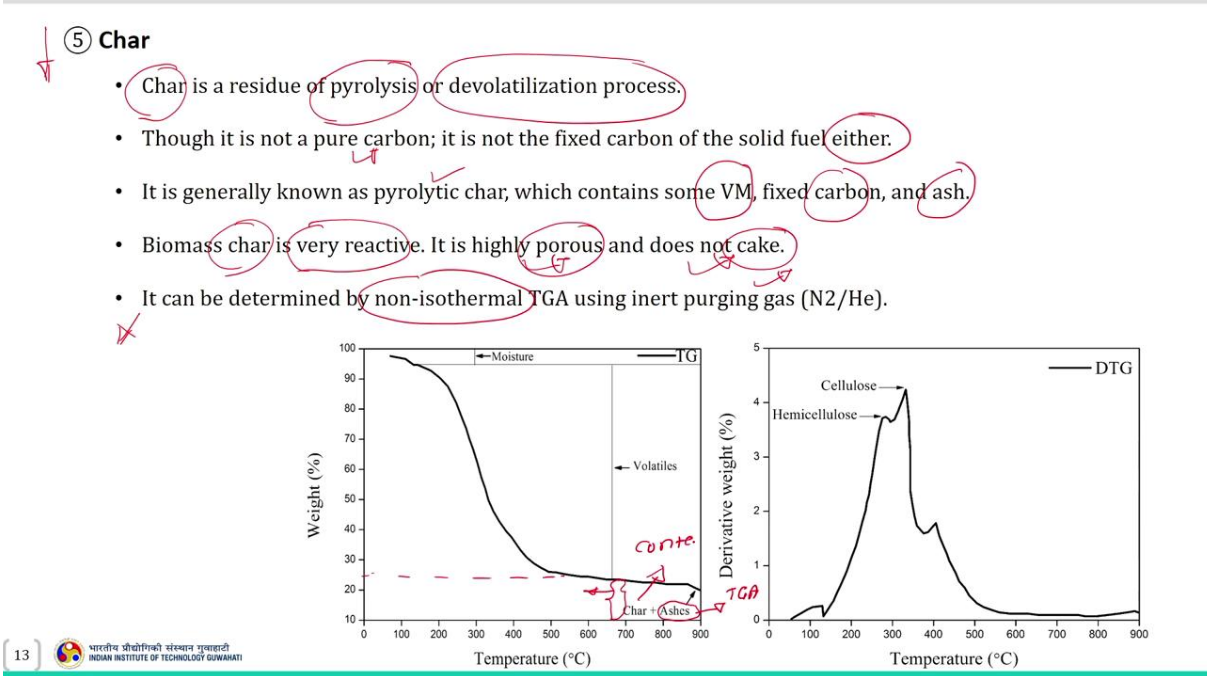

⑤ **Char**

- Char is a residue of pyrolysis or devolatilization process.
- Though it is not a pure carbon; it is not the fixed carbon of the solid fuel either.
- It is generally known as pyrolytic char, which contains some VM, fixed carbon, and ash.
- Biomass char is very reactive. It is highly porous and does not cake.
- It can be determined by non-isothermal TGA using inert purging gas (N2/He).

And next is the char. So, as just discussed recently the char is a residue of pyrolysis and devolatilization process. Though it is not pure carbon, it is not fixed carbon of solid fuel either and it is generally known as a pyrolytic char which contains some volatile matter, fixed carbon and ash. Biomass char is very reactive even it is highly porous and does not cake.

The char content can also be estimated by non-isothermal TGA technique using inert purging gas. So, if we recollect our discussion in the previous slide, as I mentioned at the end of TGA analysis, the pan contains char and ash. Once we estimate the ash content in the material, so the remaining fraction represent as the char content of the given fuel sample. And how to estimate the ash content using TGA, we have already discussed in the previous slide. So, once we know the ash content and its value, so the total weight minus ash gives the char content in the given fuel sample.

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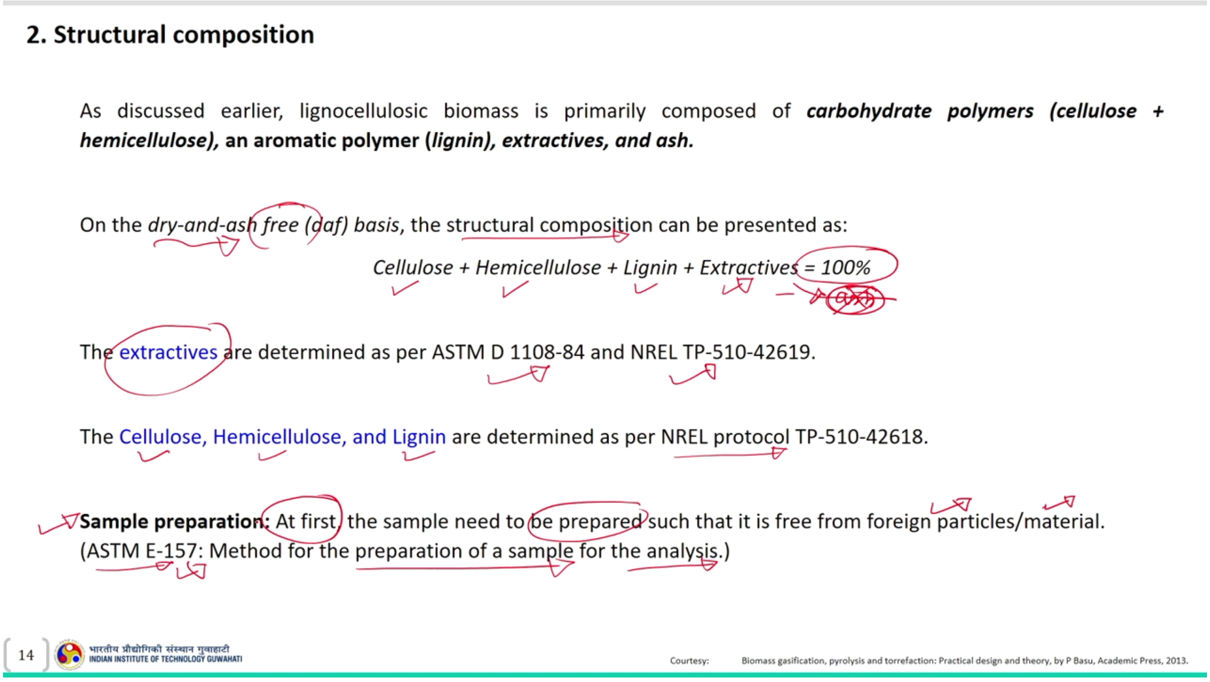

2. Structural composition

As discussed earlier, lignocellulosic biomass is primarily composed of ***carbohydrate polymers (cellulose + hemicellulose),*** **an aromatic polymer (*lignin*), *extractives, and ash.***

On the *dry-and-ash free (daf) basis*, the structural composition can be presented as:

Cellulose + Hemicellulose + Lignin + Extractives = 100%

– ~~ash~~

The extractives are determined as per ASTM D 1108-84 and NREL TP-510-42619.

The Cellulose, Hemicellulose, and Lignin are determined as per NREL protocol TP-510-42618.

Sample preparation: At first, the sample need to be prepared such that it is free from foreign particles/material. (ASTM E-157: Method for the preparation of a sample for the analysis.)

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

So, the next is the structural composition. As discussed earlier in one of the lecture in the previous module, lignocellulose biomass mainly constitutes of extractives, cell wall component and ash. The cell wall component includes the carbohydrate polymer that is cellulose and hemicellulose and aromatic polymer that is a lignin. And all these components collectively known as the structural composition of a biomass. On dry and ash free basis the structural composition can be presented as cellulose, hemicellulose, lignin plus extractives except ash. The extractives are determined as per the ASTM standard method and NRL protocol.

The cellulose, hemicellulose and lignin are determined as per the NRL protocol. Before going for the compositional analysis of the biomass, its sample preparation is one of the most important steps. So, at first the sample needs to be prepared such that it is free from foreign particles and material. And standard ASTM method is available for the preparation of sample for the compositional analysis purpose. So, this method can be followed for the preparation of the sample before going for the compositional analysis.

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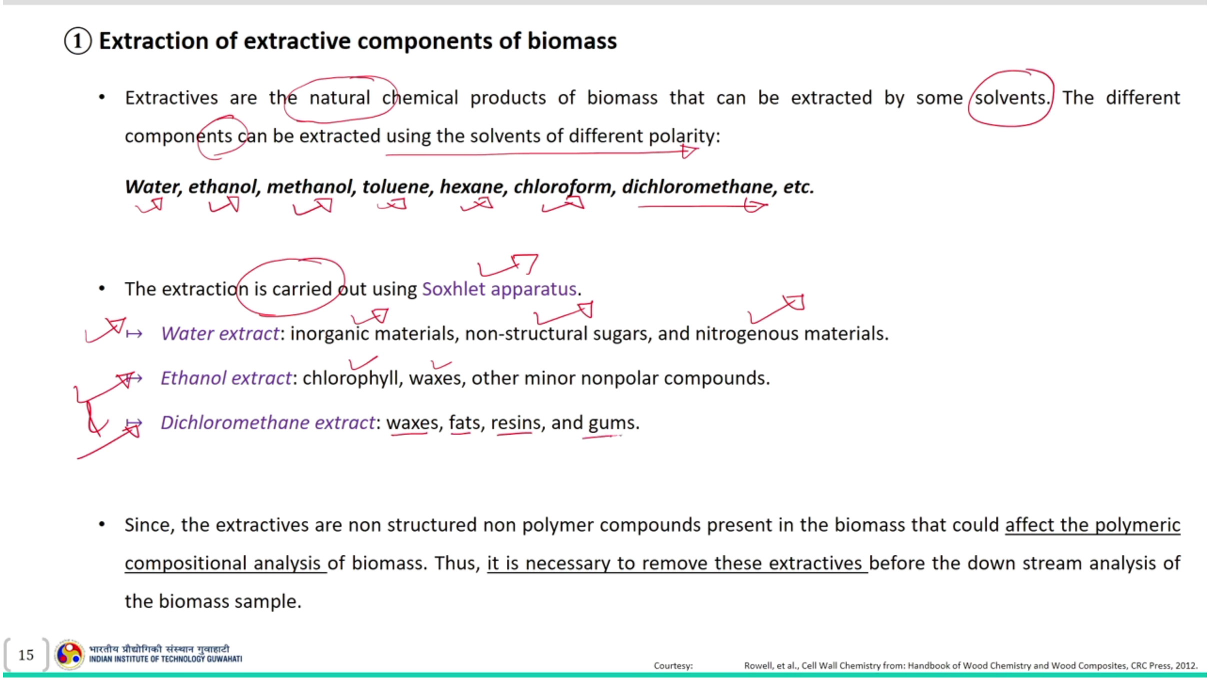

① **Extraction of extractive components of biomass**

- Extractives are the natural chemical products of biomass that can be extracted by some solvents. The different components can be extracted using the solvents of different polarity:

  Water, ethanol, methanol, toluene, hexane, chloroform, dichloromethane, etc.

- The extraction is carried out using Soxhlet apparatus.
  - ↦ *Water extract*: inorganic materials, non-structural sugars, and nitrogenous materials.
  - ↦ *Ethanol extract*: chlorophyll, waxes, other minor nonpolar compounds.
  - ↦ *Dichloromethane extract*: waxes, fats, resins, and gums.

- Since, the extractives are non structured non polymer compounds present in the biomass that could affect the polymeric compositional analysis of biomass. Thus, it is necessary to remove these extractives before the down stream analysis of the biomass sample.

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Courtesy: Rowell, et al., Cell Wall Chemistry from: Handbook of Wood Chemistry and Wood Composites, CRC Press, 2012.

So, now let us discuss about the extraction of the extractive component of biomass. So, the extractives are the natural chemical product of biomass that can be extracted by some solvents and the solvents that are used for the extraction of component of the biomass include water, ethanol, methanol, toluene, hexane, chloroform, and dichloromethane. And the different component of the biomass can be extracted using solvents of this different polarity.

The extraction is carried out using the Soxhlet apparatus and if the water is used as a solvent then the water extracts include inorganic minerals, non-structural sugars and nitrogenous materials. And the ethanolic extracts include chlorophyll, wax and other minor non-polar compounds.

And dichloromethane extracts include mostly waxes, fats, resins and gums. Since these extractives are non-structured and non-polymer compound present in the biomass that could affect the composition analysis of the biomass. And hence it is necessary to remove these extractives before the composition analysis of the biomass so that it will not interfere in the composition analysis of the biomass sample.

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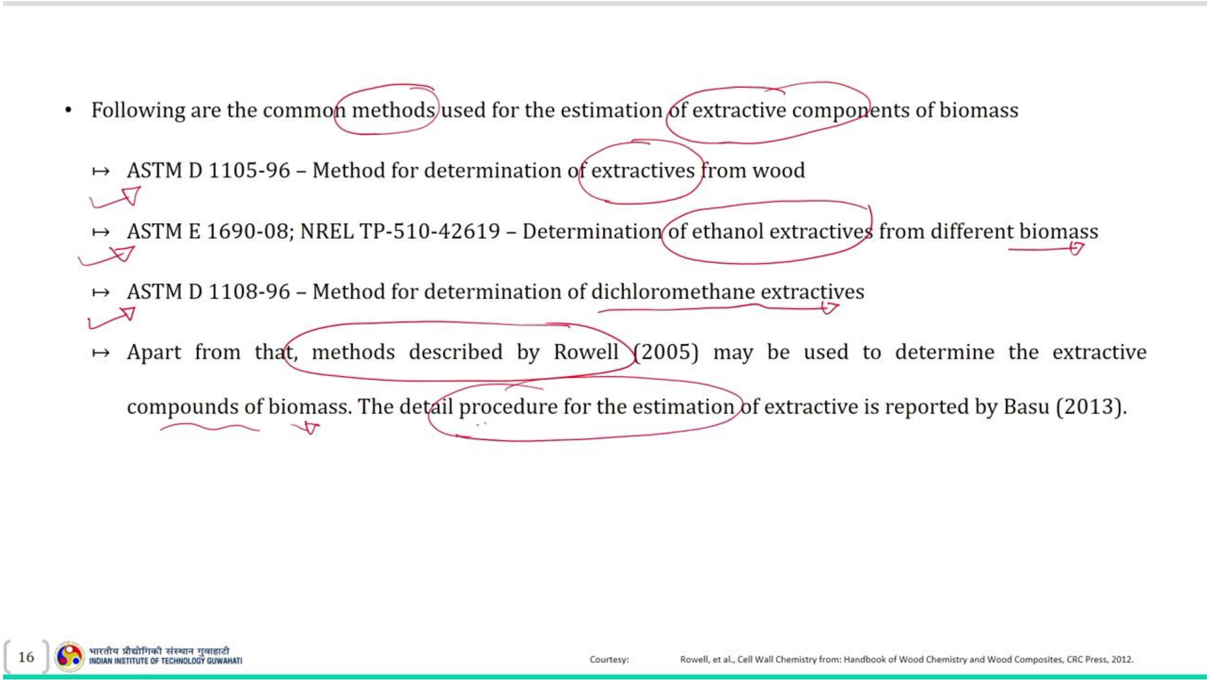

- Following are the common methods used for the estimation of extractive components of biomass
  - ↦ ASTM D 1105-96 – Method for determination of extractives from wood
  - ↦ ASTM E 1690-08; NREL TP-510-42619 – Determination of ethanol extractives from different biomass
  - ↦ ASTM D 1108-96 – Method for determination of dichloromethane extractives
  - ↦ Apart from that, methods described by Rowell (2005) may be used to determine the extractive compounds of biomass. The detail procedure for the estimation of extractive is reported by Basu (2013).

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Courtesy: Rowell, et al., Cell Wall Chemistry from: Handbook of Wood Chemistry and Wood Composites, CRC Press, 2012.

Following are the common methods used for the estimation of the extractive component of the biomass. So, this ASTM method is used for the determination of the extractives from wood.

This ASTM as well as the NRL protocol is used for the estimation of the ethanol extractives from the different biomass samples. ASTM method is used for the determination of the dichloromethane extractives. And apart from this method, the method described by Rowell may be used to determine the extractive compounds of biomass. And the detailed procedure of estimation of the extractives by the Rowell method is available in this reference.

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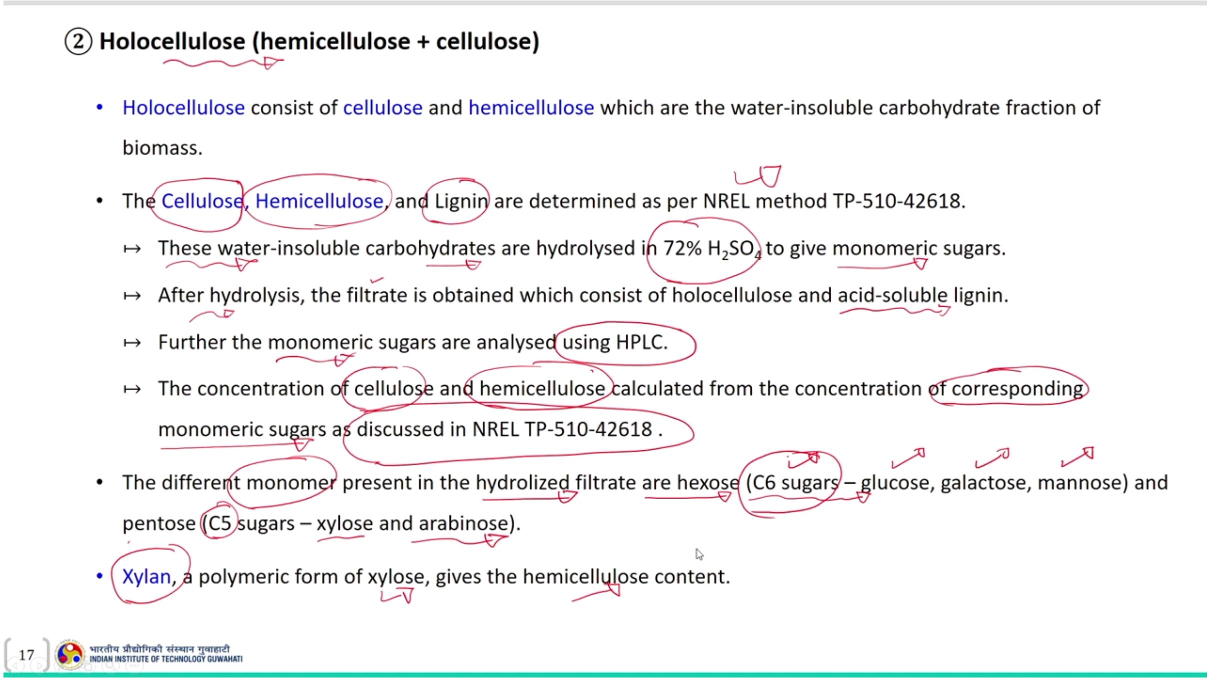

② Holocellulose (hemicellulose + cellulose)

- Holocellulose consist of cellulose and hemicellulose which are the water-insoluble carbohydrate fraction of biomass.
- The Cellulose, Hemicellulose, and Lignin are determined as per NREL method TP-510-42618.
  - ↦ These water-insoluble carbohydrates are hydrolysed in 72% H_2SO_4 to give monomeric sugars.
  - ↦ After hydrolysis, the filtrate is obtained which consist of holocellulose and acid-soluble lignin.
  - ↦ Further the monomeric sugars are analysed using HPLC.
  - ↦ The concentration of cellulose and hemicellulose calculated from the concentration of corresponding monomeric sugars as discussed in NREL TP-510-42618 .
- The different monomer present in the hydrolized filtrate are hexose (C6 sugars – glucose, galactose, mannose) and pentose (C5 sugars – xylose and arabinose).
- Xylan, a polymeric form of xylose, gives the hemicellulose content.

So, the next component in the composition analysis of the biomass is the holocellulose. Holocellulose consists of cellulose and hemicellulose which are water insoluble carbohydrate of biomass fraction. The cellulose and hemicellulose as well as the lignin are determined as per the standard NRL protocol. So, in this protocol these water insoluble carbohydrates are hydrolyzed in 72% H_2SO_4 to give mostly monomeric sugars and after hydrolysis the filtrate obtained mostly consists of the holocellulose and acid soluble lignin.

Further the monomeric sugars are analyzed using the HPLC analysis and the concentration of the cellulose and the hemicellulose in the given sample can be calculated from the concentration of corresponding monomeric sugar. And detail about such calculation is discussed in this particular protocol.

The different monomers which are present in the hydrolyzed filtrate are basically the hexose sugar that is C6 sugar consists of glucose, galactose and mannose. These are basically the C6 sugars and pentose sugar that is known as the C5 sugar A polymer form of xylose gives the hemicellulose content in the given sample and glucose C6 sugar gives the cellulose content in the given biomass sample.

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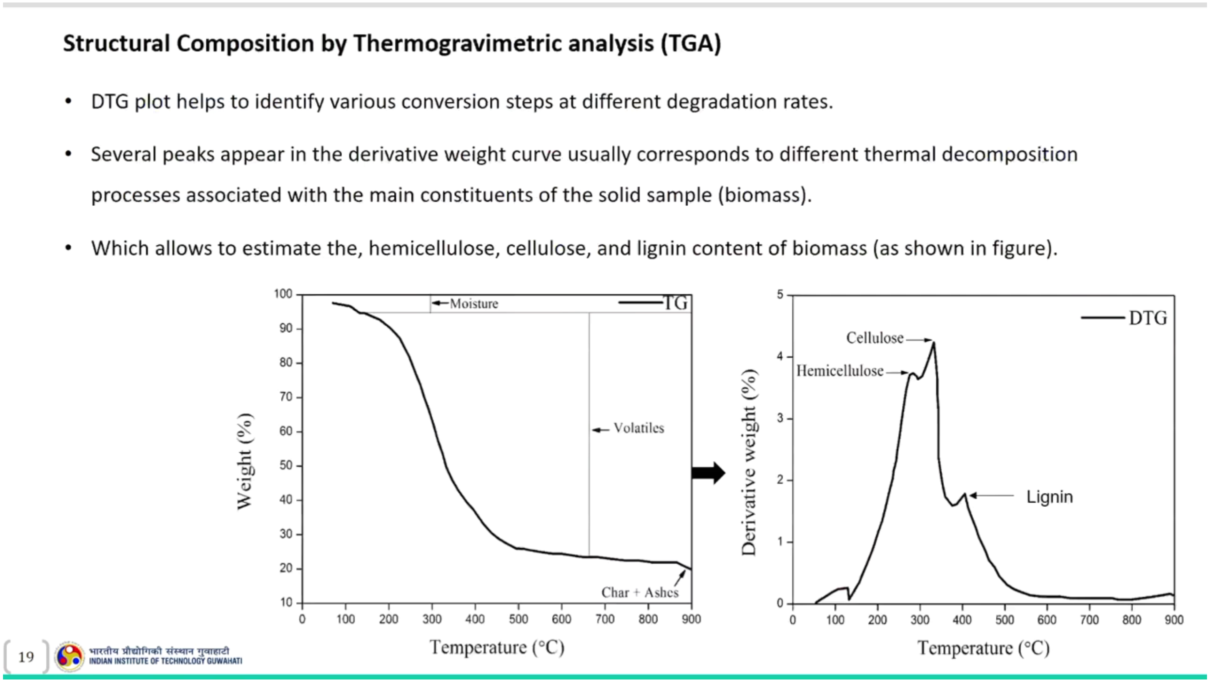

Structural Composition by Thermogravimetric analysis (TGA)

- DTG plot helps to identify various conversion steps at different degradation rates.
- Several peaks appear in the derivative weight curve usually corresponds to different thermal decomposition processes associated with the main constituents of the solid sample (biomass).
- Which allows to estimate the, hemicellulose, cellulose, and lignin content of biomass (as shown in figure).

And lastly the lignin content is determined again using the same NRL protocol. The acid hydrolyzed filtrate obtained in the holocellulose analysis method consists of some acid soluble lignin which can be estimated using the UV visible spectrophotometer. And the residue from the acid hydrolysis step consists of the acid insoluble lignin and ash.

So, the acid insoluble lignin is determined by further evaluating and subtracting the component of ash and this acid insoluble lignin as well as acid soluble lignin represents the lignin fraction in the given biomass sample. So, as we discussed about this ASTM method, so the determination of the compositional analysis of biomass by this ASTM method, it is time consuming and even expensive.

Therefore, an alternative method which is proposed by Class using thermogravimetric analysis is the preferred technique for the compositional analysis of biomass.

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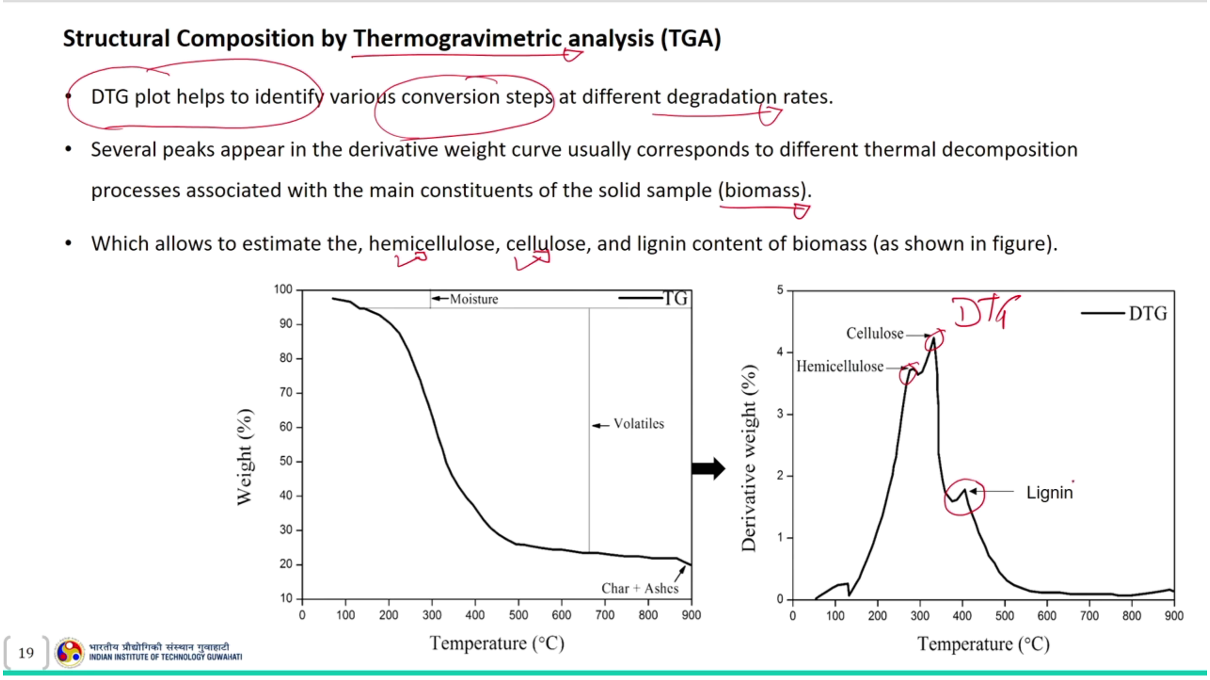

Structural Composition by Thermogravimetric analysis (TGA)

- DTG plot helps to identify various conversion steps at different degradation rates.
- Several peaks appear in the derivative weight curve usually corresponds to different thermal decomposition processes associated with the main constituents of the solid sample (biomass).
- Which allows to estimate the, hemicellulose, cellulose, and lignin content of biomass (as shown in figure).

Similarly, the structural composition of the biomass can also be estimated using the thermogravimetric analysis method. So, as we discussed in the previous slide as well, the DTG plot helps to identify various conversion steps at different degradation rate here in the specific DTG plot.

And this several peaks which appears in the derivative curve usually corresponds to different thermal decomposition processes associated with the main constituents of solid sample that is biomass and which allows us to estimate the hemicellulose, cellulose and the lignin content of the biomass sample.

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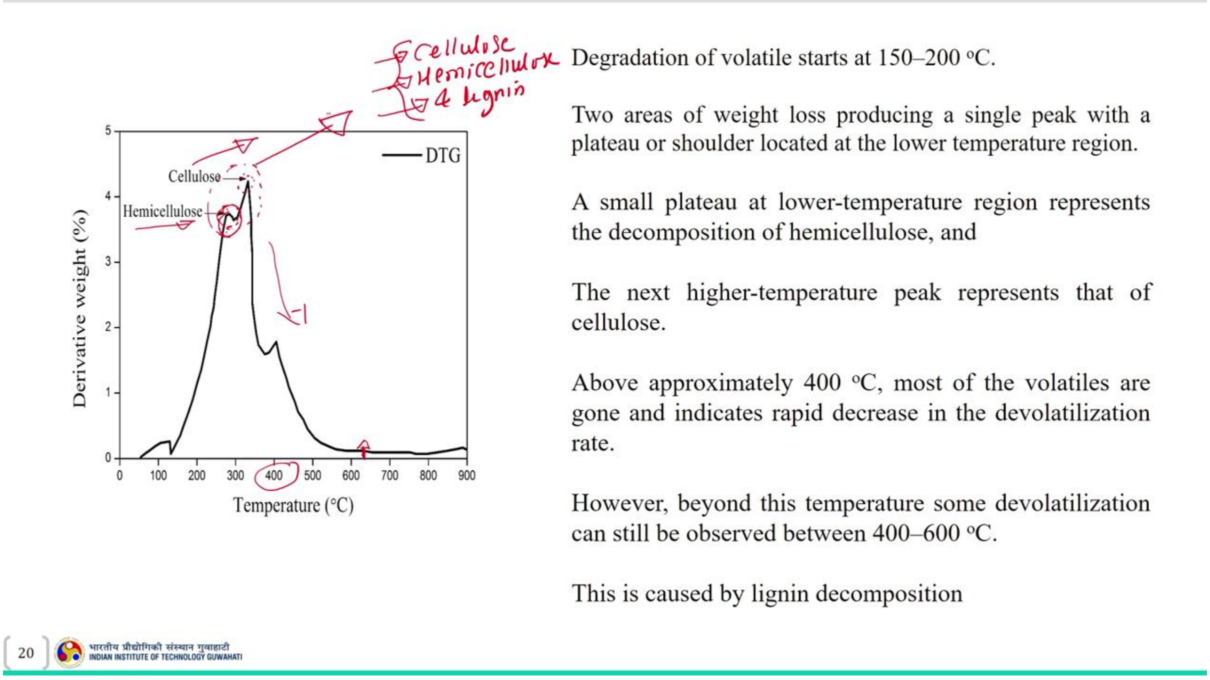

Degradation of volatile starts at 150–200 °C.

Two areas of weight loss producing a single peak with a plateau or shoulder located at the lower temperature region.

A small plateau at lower-temperature region represents the decomposition of hemicellulose, and

The next higher-temperature peak represents that of cellulose.

Above approximately 400 °C, most of the volatiles are gone and indicates rapid decrease in the devolatilization rate.

However, beyond this temperature some devolatilization can still be observed between 400–600 °C.

This is caused by lignin decomposition

So, if you see this DTG curve very carefully as we discussed earlier as well, degradation of the volatile starts at 150 to 200 °C and two areas of weight loss producing a single peak here with a plateau or shoulder located at the lower temperature region. A small plateau at a lower temperature region here basically represents the decomposition of the hemicellulose fraction in the given sample.

And the next peak which is at relatively higher temperature it represents the decomposition of the cellulose fraction in the given sample. And above approximately 400 °C see most of the volatiles are gone and indicates the rapid decrease in the de-volatilization rate of the sample.

However, beyond this particular temperature some de-volatilization still observed between 400 to say 600 or 650 °C up to this particular point and this mainly caused by the decomposition of the lignin. By this way we can estimate the cellulose, hemicellulose and lignin fraction in the given sample.

Apart from that even the standard cellulose, lignin component can be analyzed using TGA individually and the weight loss which occurs due to degradation of the cellulose, hemicellulose and lignin between the specific temperature ranges can be referred for the estimation of the cellulose, hemicellulose and lignin in a given sample. This describes the advantage of using thermogravimetric analysis technique for the proximate analysis.

With this we will end our lecture here. In the next lecture we will discuss about the liquid fuel properties.

Thank you.