

BIOMASS (LECTURE-2) (5)

* Introduction:

- an important bioresource
- refers to all organic matters generated through the process of photosynthesis
- also includes matters produced by land and water-based vegetations
- renewable and biodegradable source of energy
- which ultimate source of energy is the Sun.
- plants/vegetations capture this energy during photosynthesis

* Examples

- biomass includes agricultural and agro-industrial wastes and residues, energy plantations, farm wastes, forest products and wastes, animal waste matter, aquatic biomass etc.
- Indian context: animal wastes and cattle dung have been considered as separate category and not as a part of biomass.

* Biomass synthesis in nature (Figures: 1-3)

- biomass is composed of cellulose, hemicellulose, lignin and extractives
- organic matters that form the part of biomass are produced by reaction between CO_2 in the air, water and sunlight during photosynthesis;
- less than 1% of the available sunlight is stored as chemical energy by the plants
- when the carbon, hydrogen and oxygen bonds i.e. C-C , H-C , C=O ... are broken by digestion, combustion, or decomposition, stored chemical energy

- when the carbon-hydrogen, carbon-oxygen, carbon-hydrogen and oxygen bonds are broken during digestion, combustion or decomposition, the stored chemical energy gets released.

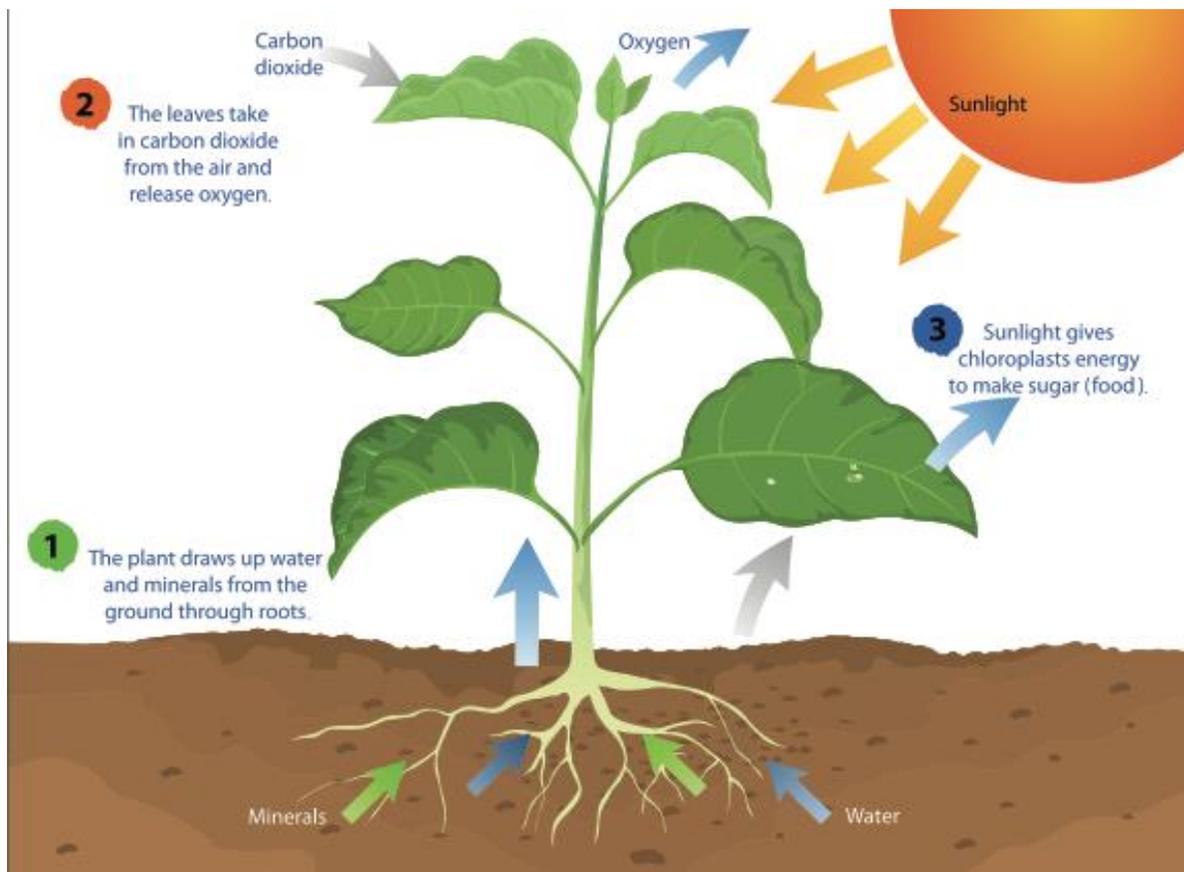
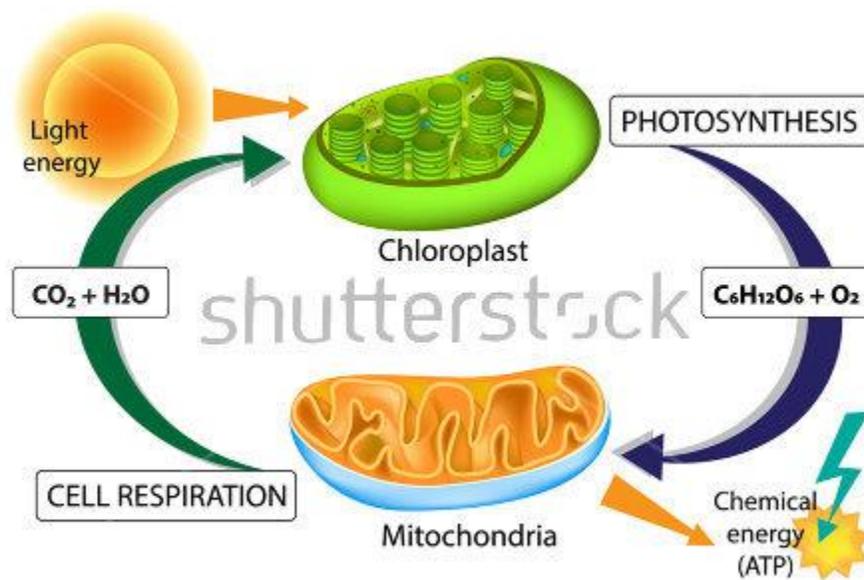


Figure-1



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Figure-2

Example of a photosynthesis Flow chart

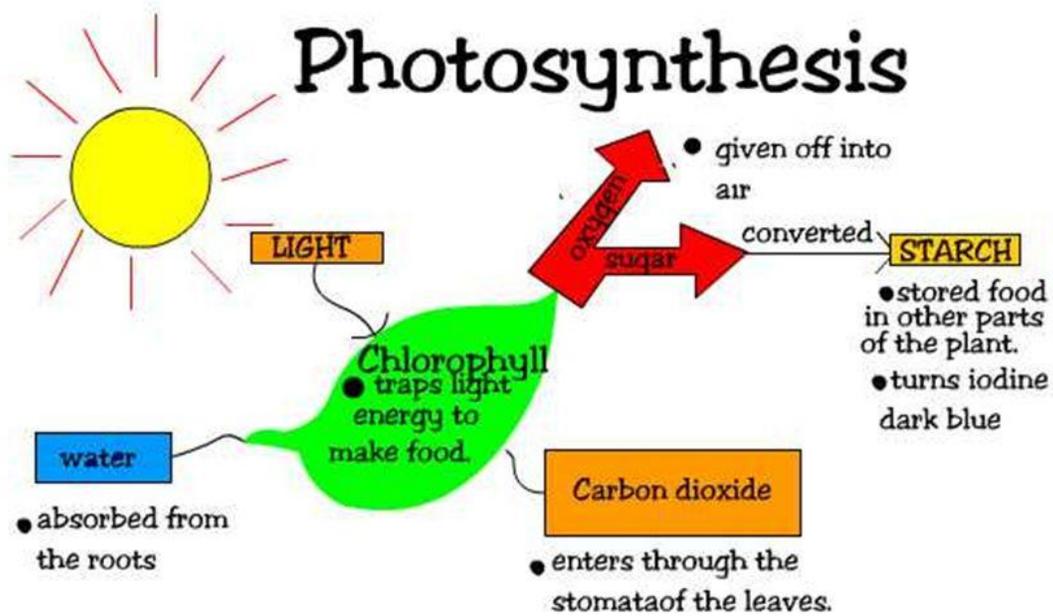


Figure-3

* Significance

- continuous depletion of fossil fuels, rising prices of petroleum, increasing demand for energy and environmental concerns are the critical reasons due to which there ^{is} emphasis on alternate renewable bioresources, like "biomass"
- biodegradability, environmental friendliness and sustainability are the important features which have made the 'biomass', a primary candidate
- it is the most abundant renewable alternate energy source evenly distributed in the world.
- fossil fuels can be substituted by 'biomass' in power plants
- biomass can be interpreted as 'stored solar energy'
- it is benign in terms of 'carbon sequestration'.
- it is non-toxic and carbon neutral source
- it has low amount of ash, nitrogen and sulfur contents which have made the biomass more attractive from the view point ^{of} environment.

* World's Energy Scenario and Biomass

- due to the population growth and industrial development, demand for energy is increasing day by day.
- bioresources like biomass, is highly significant for meeting the challenges along with other alternate sources, such as wind, solar, tidal and geothermal energies
- fast growing economies of China and India accounts for over half of the increase

- the demand China is believed to be the largest market whereas consumption in OECD (organization of economic cooperation and development) countries is slow as reported by British Petroleum Energy Outlook, 2018,
- by the year 2040, it is believed that the demand for energy would be 18 billion tonnes of oil equivalent (toe). (Figure-4).
- Figure-5 shows that ~~new~~ renewable and nuclear powers are the rapidly-expanding sources of energy
- renewable energy sources are rising by an average of 2.8%, natural gas 2.1%, nuclear generation 1.5% per year, whereas coal contribution drops from 40% to 31% per year over a period of 2015 to 2040.
- for a country like India, the use and exploitation of renewable resources (including bioresources) has become more challenging
- biomass occupies a unique place among the various alternate renewable energy sources
- India has a high renewable target of 175 GW by 2022 and 275 GW by 2026-27.
- India has decided to achieve 40 GW from solar roof tops by 2022 (WEC, 2018).
- rest 135 GW of energy would be generated through other sources, where biomass plays significant role.

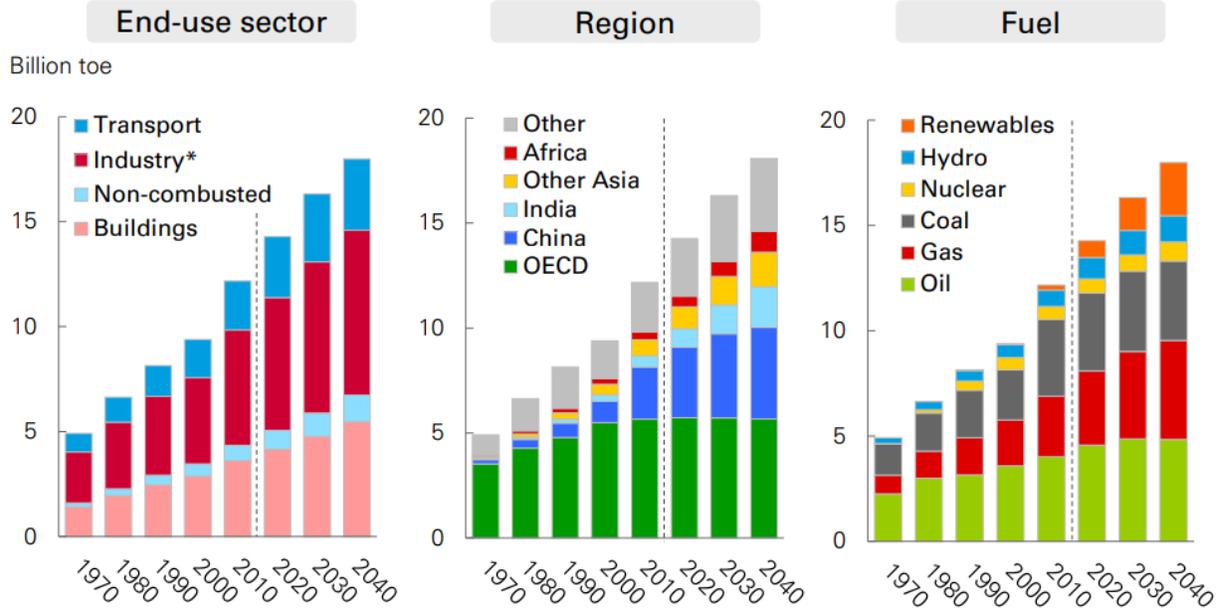


Fig. 4: Global energy demand through three different lenses: sector, region and fuels.
 Source: (BP Energy outlook, 2018).

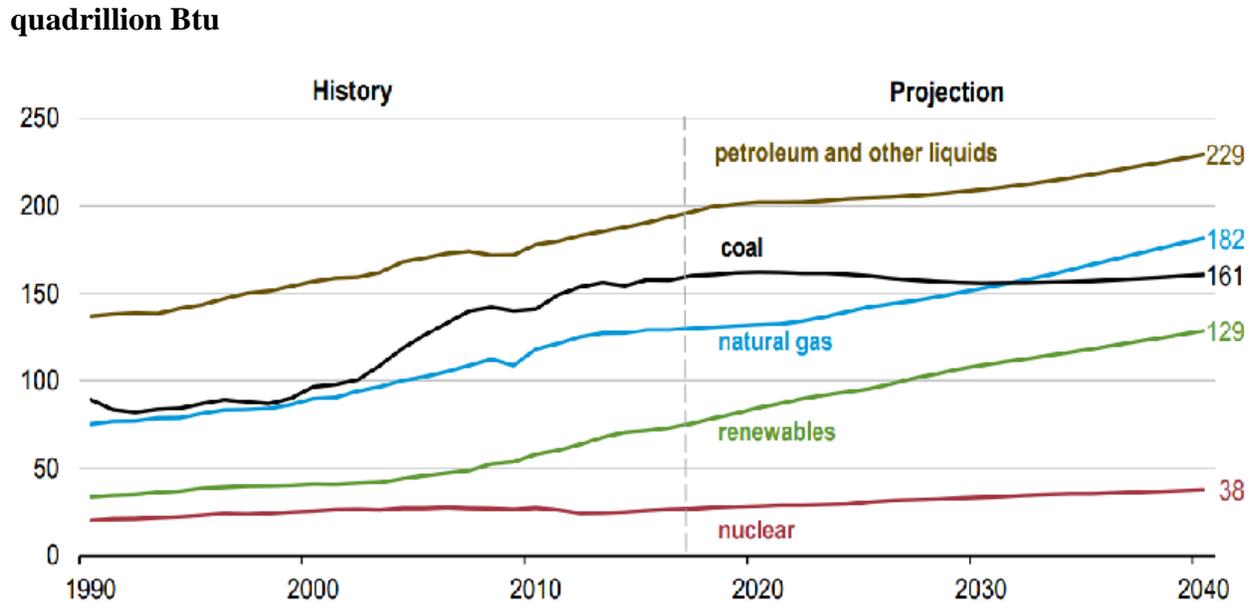


Fig. 5: World energy consumption by different types of energy sources, 1990-2040.
 Source: (International Energy Outlook, 2018)

* Physico-Chemical Properties of Biomass Materials

- highly significant from the stand point of conversion technologies
- effect the cost of conversion
- conversion of biomass to energy and other products (chemicals) are effected by the characteristics of biomass
- the properties of interest are: moisture content, heating values, fixed carbon, volatile matter, ash, residue content, alkali metal content, and cellulose/lignin ratio and elemental composition (ultimate analysis)

⇒ Moisture Content ✓

- it is ^{the} quantity of moisture water present in the slot within dead cells and and within cell wall of biomass
- consists of intrinsic and extrinsic moisture
- intrinsic moisture is not effected by weather condition where as the extrinsic is effected
- higher the moisture content, lower is the heating values
- affects the behavior of biomass during any thermal conversion process
- the quality of pyrolysis products/by products is effected by the moisture content

- feedstock with low moisture content required in thermo-chemical conversion
- feed stock with high moisture content can effectively be processed in biochemical conversion
- feedstock with moisture content < 10% is preferred in biofuel production.

⇒ Heating Values

- expression ^{of} heat or energy released in air when ^{burnt}
- measured in terms of the heat content per unit mass or volume.
- may be expressed in two forms: gross heating value or higher heating value, and the net heating value or the lower heating value
- higher heating value is the total energy content released on burning of unit amount / volume of biomass in air.
- higher heating value also includes the latent heat contained by water vapor, therefore shows the maximum amount of energy which may be potentially recovered from the biomass
- practically, the latent heat of water vapor, cannot be used effectively, the lower heating value is the appropriate measurement for use of available energy in biomass or in any other fuel.
- some correlations w.r.t. higher heating values are given in Table-1 & Table-2

⇒ Fixed Carbon and Volatile Matter

- fixed carbon content is the mass remaining after the release of volatiles excluding the ash and moisture contents.

Ash content in biomass affects both the handling and processing costs, and the overall conversion cost. Depending on the amount of ash content, the available energy of the fuel is reduced proportionately. In thermochemical conversion, the chemical composition of ash can create operational problems due to slag formation.

volatile matter is that portion of the solid fuel which gets released as a gas (including moisture) by heating (to 950°C for 7 min).

- proximate analysis of biomass is based upon the determination of volatile matter content, ash, moisture and the fixed carbon (obtained by difference)
- proximate analysis is an essential part of the standard laboratory test of solid fuels
- ultimate analysis or elemental analysis is the analysis of C, H, O and S together with the ash contents
- volatile matter and fixed carbon contents provide a measure of the ease with which the biomass can be ignited and subsequently gasified, or oxidized.
- proximate, ultimate analyses and heating values of biomass shown in Table III H/C and O/C ratios are highly significant with respect to its quality when compared with various types of coal.

- the ratios are illustrated by the Van-Krevelen diagram as shown in Figure - 5.

- higher proportion of oxygen and hydrogen reduces the energy value of a fuel due to lower energy contained in carbon-oxygen and carbon-hydrogen bonds as compared to carbon-carbon bonds.

Ash Content: It is the inorganic residue that remains after combustion of the fuel in air at specific temperature. It is the measure of non-combustible materials which may contain the oxides of silicon, aluminium, iron, magnesium, potassium, calcium etc. Ash content acts as a heat sink as moisture does, and lowers the combustion efficiency of biomass (or any fuel) *

Table-I: Correlations for HHV based on Proximate Analysis

S. No.	Correlation	Reference
1	$\text{HHV (MJ/kg)} = 0.196 (\text{FC}) + 14.119$	Demirbas (1997)
2	$\text{HHV (kJ/kg)} = 354.3\text{FC} + 170.8\text{VM}$	Cordero et al. (2001)
3	$\text{HHV (MJ/kg)} = 0.3536\text{FC} + 0.1559\text{VM} - 0.0078\text{Ash}$	Parikh et al. (2005)
4	$\text{HHV (MJ/kg)} = 0.1905\text{VM} + 0.2521\text{FC}$	Yin (2011)

Table-II: Correlations for HHV based on Ultimate Analysis

S. No.	Correlations	References
1	$\text{HHV (MJ/kg)} = 0.4373\text{C} - 1.6701$	Tillman (1978)
2	$\text{HHV (MJ/kg)} = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{-Ash}$	Channiwala and Parikh (2002)
3	$\text{HHV (kJ/kg)} = 3.55\text{C}^2 - 232\text{C} - 2230\text{H} + 51.2\text{C} \times \text{H} + 131\text{N} + 20600$	Friedl et al. (2005)
4	$\text{HHV} = 0.2949\text{C} + 0.8250\text{H}$	Yin (2011)

Table-III: Proximate, Ultimate Analyses and Heating Value of few Biomasses

Biomass	Proximate analysis				Ultimate analysis ^{daf}					References
	M	VM ^{db}	FC ^{db}	A ^{db}	C	H	N	S	O	
Woody Biomass										
Pine chips	7.6	72.4	21.6	6	52.8	6.1	0.5	0.09	40.5	Masia (2007)
Poplar	6.8	85.6	12.3	2.1	51.6	6.1	0.6	0.02	41.7	Miles et al. (1995)
Sawdust	34.9	84.6	14.3	1.1	49.8	6	0.5	0.02	43.7	Tillman (2000)
Willow	10.1	82.5	15.9	1.6	49.8	6.1	0.6	0.06	43.4	Moilanen (2006)
Grasses and Herbs										
Herbaceous, Agricultural Biomass	12	75.2	19.1	5.7	49.9	6.2	1.2	0.15	42.6	Vassilev (2010)
Switch grass	11.9	80.4	14.5	5.1	49.7	6.1	0.7	0.11	43.4	Miles et al. (1995)
Sorghastrum grass	11.3	81.6	14.2	4.2	49.4	6.3	0.3	0.05	44	Miles et al. (1995)
Straws										
Rice straw	76	64.3	15.6	20.1	5.1	5.7	1.0	0.16	43	Miles et al. (1995), Thy et al. (2006)
Wheat straw	10.1	74.8	18.1	7.1	49.4	6.1	0.7	0.17	43.6	Vassilev (2010)
Aquatic Biomass										
Marine Macroalgae	10.7	50.5	25.9	23.6	43.2	6.2	2.2	2.6	45.8	Tite (2006), Ross et al. (2008)
Duckweed	14	78	8.8	26	30	4.3	2.1	0.8	21	Duan (2013), Muradov et al. (2012)
<i>C. demersum</i>	8±1.21	76±1.46	10.08±0.84	13.92±0.68	35.58	5.89	3.26	0.22	41.13	Rather (2017)
<i>P. lucens</i>	8±0.46	64.51±1.34	23.65±1.43	11.85±2.13	38.61	6.05	2.4	-	41.09	
<i>A. cristata</i>	8±1.34	61.91±0.67	27.81±1.45	10.28±1.88	40.06	6.08	2.41	-	41.17	
Water hyacinth	9.54	77	0.85	21.8	34.98	6.46	0.76	1.4	-	Singh (2015)
Typha latifolia	-	71.9	18	10.2	43.45	5.98	2.49	0.52	30.89	Ciria et al. (2005)

db: Dry basis, **daf:** Dry, ash-free basis, **C:** *Ceratophyllum*, **P:** *Potamogeton*, **A:** *Azolla*
Source: M.A. Rather, Ph.D. Thesis, 2017. Dept. of Chem. Eng., NIT Srinagar.

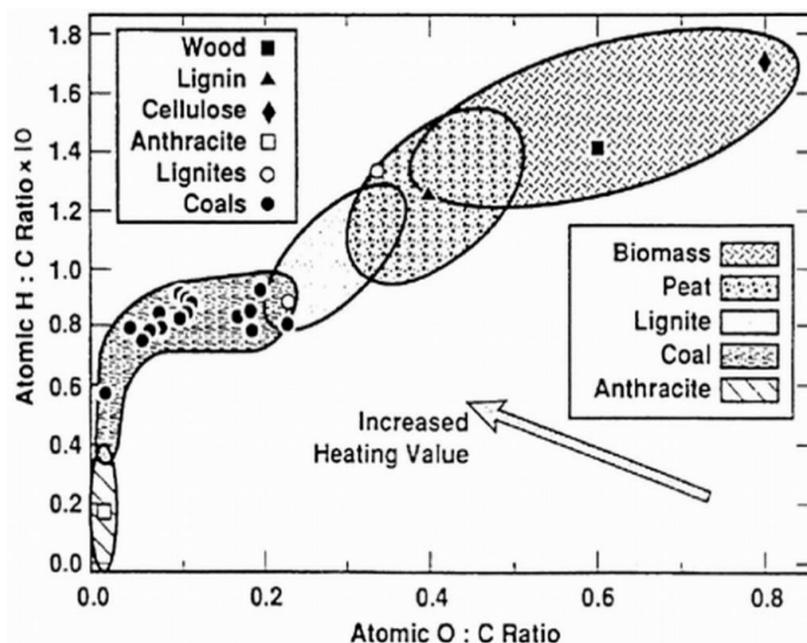


Figure-6: Van Krevelen diagram (Loo, and Koppejan, 2007).

⇒ Alkali Metal Content

- alkali metal contents present in biomass, i.e. Na, K, Mg, P and Ca is very significant for thermochemical conversion
- when alkali metals react with silica present in the ash, sticky mobile phase is formed which leads to the blockages of airways in the power plants

⇒ Cellulose/Lignin Ratio

- the ratio is important from the stand point of energy conversion technology
- since the biodegradability of cellulose is higher than the lignin, overall conversion of carbon-containing plant material as cellulose is greater than plants with higher proportion of lignin
- in biochemical processing, presence of larger amount of cellulose is the determining factor in selection
- higher heating value of biomass increases with lignin, content is the determining factor in selection for as fuel for power plants.

- CO_2 (methane)

- CH_4 (methane)

- H_2 (hydrogen)

... no other products

... remains properties of biomass ...

... conversion

... (2) ...

INTRODUCTION

1.1 BIOMASS

Biomass represents all organic material that stems from plant kingdom (including algae, trees and crops). It is produced by green plants converting sunlight into plant nutrients, water and atmospheric gases through photosynthesis and includes all land and water-based vegetations. They also include municipal organic wastes, organic wastes from industries and excretal matter from all life forms- humans and animals.

Carbohydrates that form the building blocks of biomass are produced by reaction between CO₂ in the air, water and sunlight, via photosynthesis. Typically photosynthesis converts less than 1% of the available sunlight to stored, chemical energy (Mc-Kendry, 2002). The solar energy driving photosynthesis is stored in the chemical bonds of the structural components of biomass.

When the bonds between adjacent carbon, hydrogen and oxygen molecules are broken by digestion, combustion, or decomposition, stored chemical energy gets released (Mc-Kendry, 2002).

Biomass is the fourth largest and the most abundant renewable energy resource in the world leaving aside solar energy. Fossil fuels like coal, petroleum crude and natural gas are depleting day by day, leaving large carbon prints on their usage.

Biomass appears to be an attractive feedstock for three main reasons: firstly it is a renewable resource of energy that may be sustainably developed in future, secondly it has formidable positive environmental properties due to reduced green house gas (GHG) emissions and thirdly it appears to have significant economic potential due to fossil fuel price increase in the future (Saxena et al., 2009). It is also a sustainable feedstock for chemicals and energy generation. Biomass feedstocks are more evenly distributed in the world. As an energy source that is highly productive, renewable, carbon neutral, and easy to store and transport; biomass has drawn worldwide attention (Ladanai, 2009).

1.2 WORLD'S ENERGY SCENARIO

World's energy demand is significantly increasing due to the huge population growth and industrial development. Just in one generation, the population has increased by 2 billion, developing countries being the major contributors. The 21st century is witnessing major challenges with respect to energy and environment (Kannan and Vakeesan, 2016). Alternative energy sources which include biomass, wind, and solar, geothermal and hydro electric power are highly significant for meeting the demand of energy (Tekin et al., 2014).

The growth in the world energy demand comes from fast-growing emerging economies, with China and India accounting for over half of the increase. Energy demand within the OECD barely grows as presented in the following Fig.1.1. China is believed to be the largest growth market for energy, although it is likely to be overtaken by India towards the end of the Outlook.

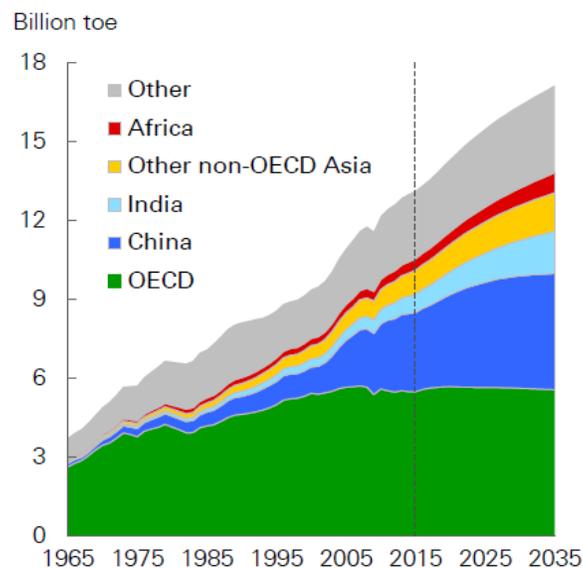


Fig. 1.1: World energy consumption by region.

Source: BP Energy Outlook 2017

The Outlook for energy use worldwide demonstrated in the Fig.1.2 continues to show increasing trend over the next three decades. There is sharp rise in countries outside the Organization for Economic Cooperation and Development (OECD), particularly in Asia. Non-OECD Asia, including China and India, account for more than half of the world's total increase in energy consumption over the years 2012 to 2040. By 2040, energy use in non-OECD Asia exceeds that of the entire OECD by 40 quadrillion British thermal units (Btu).

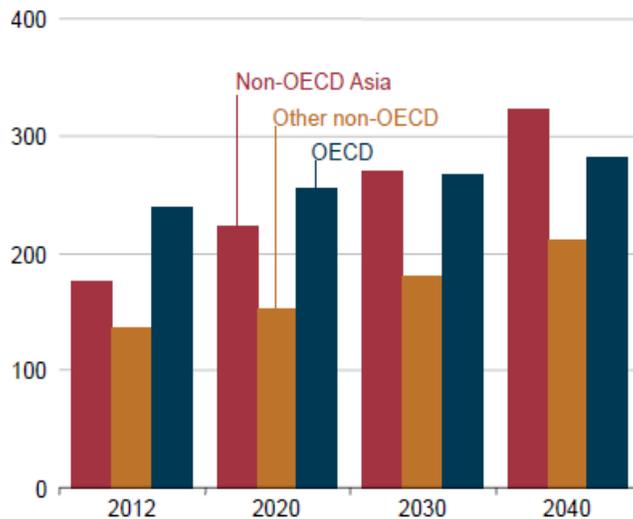


Fig.1.2: World energy consumption by country grouping, 2012–40 (quadrillion Btu)

Source: U.S. Energy Information Administration, International Energy Outlook 2016

The Fig.1.3 shows that the fuel mix is set to continue with renewables, together with nuclear and hydroelectric power, expected to account for half of the growth in energy supplies over the next 20 years. It is evident from this that renewable energy is the fastest growing source of energy (7.1% p.a.), with its share in primary energy increasing to 10% by 2035, up from 3% in 2015.

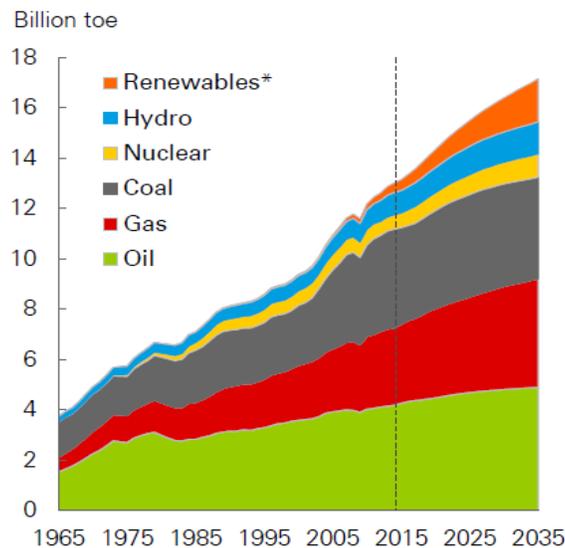


Fig.1.3: Primary energy consumption by fuel.

Source: BP Energy Outlook 2017

As projected in the following Fig. 1.4, renewables are the world’s fastest-growing energy source. Renewables include biomass, biofuels, and wind, solar, geothermal and hydroelectric

energy. Their consumption increases by an average 2.6%/year between 2012 and 2040. Nuclear power is the world's second fastest-growing energy source, with consumption increasing by 2.3%/year over that period.

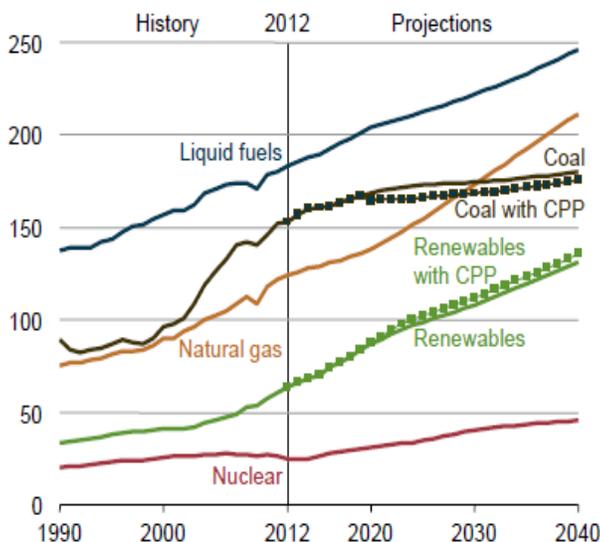


Fig.1.4: World energy consumption by types of source, 2012–40 (quadrillion Btu).

Source: U.S. Energy Information Administration, International Energy Outlook 2016.

Biomass has always been a major source of energy for mankind; it accounts for 10–14% of worldwide energy demand. However, by 2050, it is projected that the world wide supply of oil reserves would be exhausted and nearly half of the global energy demand would be supplanted by biomass (McKendry, 2002b; Saxena et al. 2009).

1.3 BIOMASS CHARACTERISTICS

The building blocks of biomass are cellulose, hemicellulose, lignin and small amount of other extractives. Cellulose and hemicellulose are together referred to as holocellulose. The lignin fraction consists of non-sugar type macromolecules. Cellulose, hemicellulose and lignin, have the rough formulae $CH_{1.67}O_{0.83}$, $CH_{1.64}O_{0.78}$ and $C_{10}H_{11}O_{3.5}$ respectively (Pavlovic et al., 2013).

Cellulose is a glucose polymer, consisting of linear chains of (1, 4)-D-glucopyranose units in which the units are linked 1–4 in the β -configuration with an average molecular weight of around 100,000 (Demirbas, 2009). Fig. 1.5 shows the molecular chain structure of cellulose.

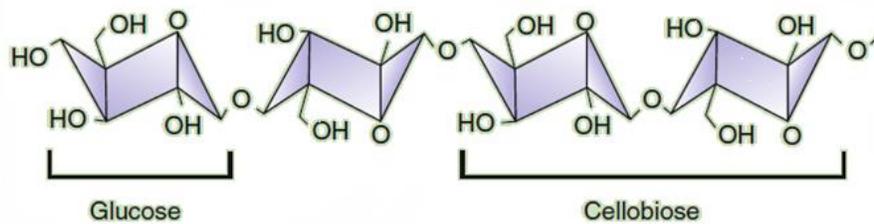


Fig.1.5: Molecular chain structure of cellulose (Chen, 2014).

Hemicellulose is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methyl glucuronic and galaturonic acids with an average molecular weight of $< 30,000$ Daltons (Mc-Kendry, 2002). In contrast to cellulose, hemicellulose is a heterogeneous branched polysaccharide that binds tightly but non-covalently to the surface of each cellulose micro fibril. Hemicellulose differs from cellulose in consisting primarily of xylose and other five-carbon monosaccharides.

Among the most important sugar components of hemicellulose is the xylose. In hardwood xylan, the backbone chain consists of xylose units which are linked by β -(1, 4)-glycosidic bonds and branched by α -(1, 2)-glycosidic bonds with 4-Omethylglucuronic acid groups (Hashem et al., 2007). In addition, O-acetyl groups some time replace the OH groups in position C2 and C3 (Fig.1.6). For soft wood xylan, the acetyl groups are fewer in the backbone chain. However, soft wood xylan has additional branches consisting of arabinofuranose units linked by α -(1, 3)-glycosidic bonds to the backbone (Chen, 2014). In Fig.1.6 it has been schematically illustrated.

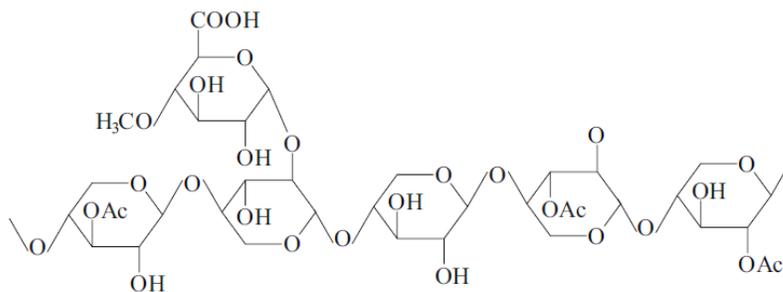
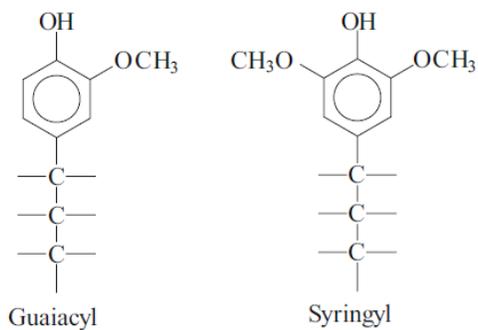
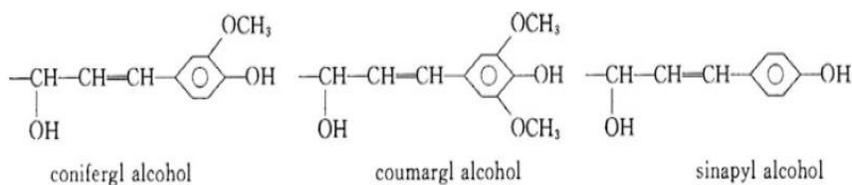


Fig.1.6: Schematic illustration of xylans (Chen, 2014).

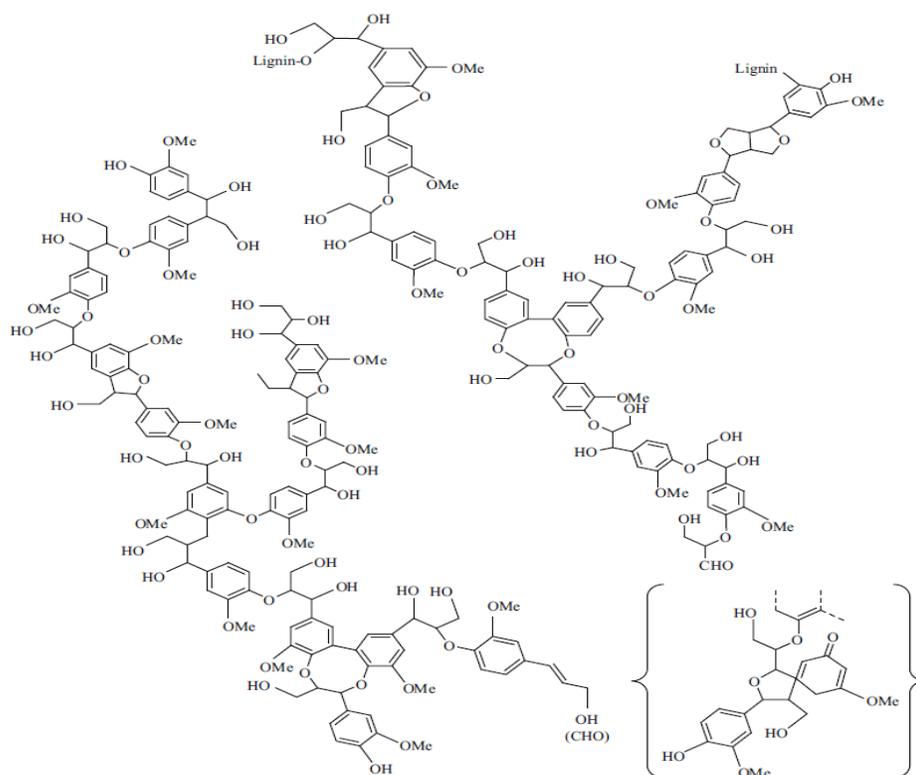
Fig. 1.7(a) shows the basic structural unit of lignin, Fig. 1.7(b) the schematic illustration of building units of lignin and Fig. 1.7(c) the structural model of lignin.



(a)



(b)



(c)

Fig.1.7: Basic structural unit of lignin (a), schematic illustration of building units of lignin (b) and structural model of lignin (c) (Chen, 2014).

Lignin is a group of amorphous, high molecular-weight, chemically related compounds. The building blocks of lignin are believed to be a three carbon chain attached to rings of six

carbon atoms, called phenyl-propanes. These may have zero, one or two methoxyl groups attached to the rings, giving rise to three structures, termed I, II and III, respectively. The proportions of each structure depend on the source of the polymer i.e. structure I is found in plants such as grasses; structure II in the wood of conifers; while structure III is found in deciduous wood.

Cellulose is generally the largest fraction, representing about 40–50% of the biomass by weight; the hemicelluloses portion represents 20–40% of the material by weight (McKendry, 2002).

1.4 **PROPERTIES OF BIOMASS AS AN ENERGY SOURCE**

The conversion of biomass to energy is affected by its physicochemical properties. These properties not only determine the conversion process, but in general, also influence the cost evaluation of the conversion technology. The properties of interest are moisture content, heating value (HV), fixed carbon (FC), volatile matters (VM), ash/residue content, alkali metal content and cellulose/lignin ratio. These properties are summarized in the following subsections:

1.4.1 **Moisture Content**

Moisture content has effect on conversion efficiency and heating value of biomass. It is stored in spaces within the dead cells and within the cell walls. When the fuel is dried, the stored moisture equilibrates with the ambient relative humidity. Moisture content of aquatic weeds freshly collected is generally over 90 % (Little, 1967), whereas in wood species (fresh) it has been found to vary in the range of 41.27 to 70.20% (Demirbas, 2004).

Moisture contents of some typical biomass after ambient drying have been reflected in Table-1.1.

Table-1.1: Proximate and Ultimate Analysis of some Common Biomass Feed Stocks (wt. %)

Biomass	Proximate analysis				Ultimate analysis ^{daf}					References
	M	VM ^{db}	FC ^{db}	A ^{db}	C	H	N	S	O	
Woody Biomass										
Pine chips	7.6	72.4	21.6	6	52.8	6.1	0.5	0.09	40.5	Masia (2007)
Poplar	6.8	85.6	12.3	2.1	51.6	6.1	0.6	0.02	41.7	Miles et al. (1995)
Sawdust	34.9	84.6	14.3	1.1	49.8	6	0.5	0.02	43.7	Tillman (2000)
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Sorghastrum grass	11.3	81.6	14.2	4.2	49.4	6.3	0.3	0.05	44	Miles et al. (1995)
Straws										
Rice straw	76	64.3	15.6	20.1	5.1	5.7	1.0	0.16	43	Miles et al. (1995), Thy et al. (2006)
Wheat straw	10.1	74.8	18.1	7.1	49.4	6.1	0.7	0.17	43.6	Vassilev (2010)
Aquatic Biomass										
Marine Macroalgae	10.7	50.5	25.9	23.6	43.2	6.2	2.2	2.6	45.8	Tite (2006), Ross et al. (2008)
Duckweed	14	78	8.8	26	30	4.3	2.1	0.8	21	Duan (2013), Muradov et al. (2012)
Water hyacinth	9.54	77	0.85	21.8	34.98	6.46	0.76	1.4	-	Singh (2015)
Typha latifolia	-	71.9	18	10.2	43.45	5.98	2.49	0.52	30.89	Ciria et al. (2005)

db: Dry basis daf: Dry, ash-free basis.

In biochemical conversion plants, like anaerobic digestion plants the feedstock with only high moisture content can be effectively processed whereas thermochemical conversion processes require a biomass with low moisture content. Water in biomass is not a combustible material and has a negative impact on the overall energy balance. However, some moisture content is required in the gasification process of the biomass for the production of hydrogen which is increased with moisture. For gasification, decreasing the moisture content beyond 30% gives only marginal improvements in overall efficiency (Juneja et al., 2013).

The moisture present in biomass comprises intrinsic moisture and extrinsic moisture. Intrinsic moisture content of the material is not influenced by the weather whereas the extrinsic moisture is influenced by the prevailing weather conditions. Moisture in biomass decreases its heating value. The presence of water in biomass influences its behavior during pyrolysis and affects the physical properties and the quality of the pyrolysis products.

1.4.2 Proportions of Fixed Carbon and Volatile Matter

For solid fuels chemical energy is stored in two forms, fixed carbon and volatiles. The fixed carbon content (FC) is the mass remaining after the releases of volatiles excluding the ash and moisture contents. Whereas the volatiles content, or volatile matter (VM) of a solid fuel is that portion driven-off as a gas (including moisture) by heating (to 950 °C for 7 min). Proximate analysis of a fuel is based upon the determination of VM content, ash, moisture and the FC (determined by difference). Standard laboratory tests are used to determine the proximate analysis of the fuel. Table-1.1 gives the proximate analyses of some typical biomass sources. Elemental analysis of a fuel, presented as C, N, H, O and S together with the ash content is termed as the ultimate analysis of a fuel. Table-1.1 gives the ultimate analysis data for some biomass materials.

The significance of the VM and FC contents is that they provide a measure of the ease with which the biomass can be ignited and subsequently gasified, or oxidized, depending on how the biomass is to be utilized as an energy source.

The significance of the O/C and H/C ratios on the HV of solid fuels can be illustrated using a Van Krevelen diagram shown in Fig. 1.8 (Van Loo & Koppejan, 2007). Comparison of biofuels with fossil fuels, such as coal, shows clearly that the higher proportion of oxygen and hydrogen, compared with carbon, reduces the energy value of a fuel, due to the lower energy contained in carbon–oxygen and carbon–hydrogen bonds, than in carbon–carbon bonds.

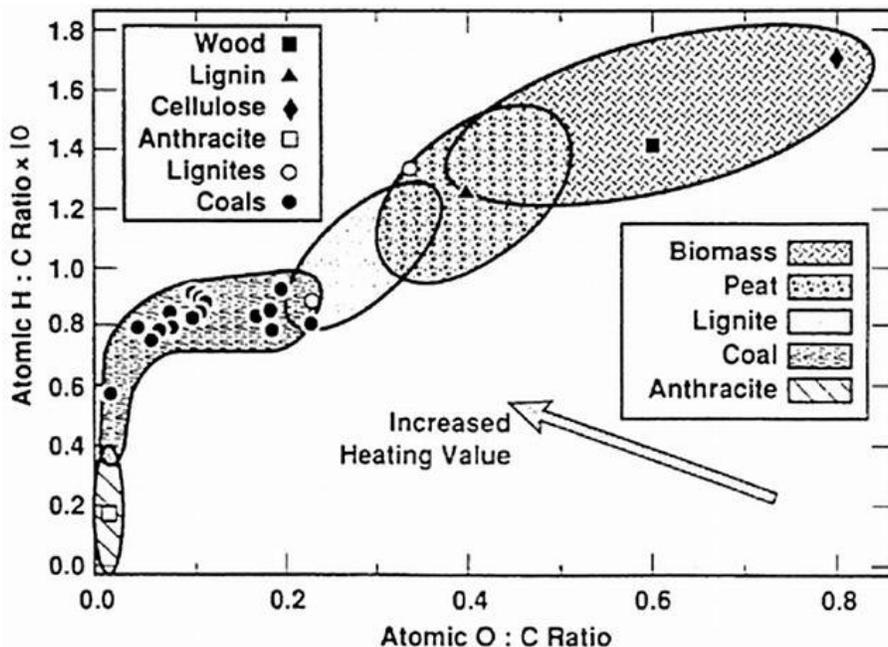


Fig.1.8: Van Krevelen diagram (Van Loo & Koppejan, 2007).

1.4.3 Heating Value

The heating value (HV) of a material is an expression of the energy content, or heat value, released when burnt in air. The HV is usually measured in terms of the energy content per unit mass, or volume. The HV of a fuel can be expressed in two forms, the gross HV (GHV), or higher heating value (HHV) and the net HV (NHV), or lower heating value (LHV). The HHV is the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapour and, therefore, represents the maximum amount of energy potentially recoverable from a given biomass source. In practical terms, the latent heat contained in the water vapour cannot be used effectively and, therefore, the LHV is the appropriate value for the subsequent use of the energy available in biomass.

Based on proximate analysis many correlations have been developed from time to time by various researchers relating HHV in terms of FC and VM of the biomass as detailed below in Table-1.2:

Table-1.2: Correlations for HHV based on Proximate Analysis

S. No.	Correlation	Reference
1	$\text{HHV (MJ/kg)} = 0.196 (\text{FC}) + 14.119$	Demirbas (1997)
2	$\text{HHV (kJ/kg)} = 354.3\text{FC} + 170.8\text{VM}$	Cordero et al. (2001)
3	$\text{HHV (MJ/kg)} = 0.3536\text{FC} + 0.1559\text{VM} - 0.0078\text{Ash}$	Parikh et al. (2005)
4	$\text{HHV (MJ/kg)} = 0.1905\text{VM} + 0.2521\text{FC}$	Yin (2011)

Based on ultimate analysis too, a number of correlations have been developed for HHV as function of elemental carbon, hydrogen, oxygen, sulfur and nitrogen. Only a few of these are given below in Table-1.3:

Table 1.3: Correlations for HHV based on Ultimate Analysis

S. No.	Correlations	References
1	$\text{HHV (MJ/kg)} = 0.4373\text{C} - 1.6701$	Tillman (1978)
2	$\text{HHV (MJ/kg)} = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{-Ash}$	Channiwala and Parikh (2002)
3	$\text{HHV (kJ/kg)} = 3.55\text{C}^2 - 232\text{C} - 2230\text{H} + 51.2\text{C} \times \text{H} + 131\text{N} + 20600$	Friedl et al. (2005)
4	$\text{HHV} = 0.2949\text{C} + 0.8250\text{H}$	Yin (2011)

In the present study, the correlation given by Parikh et al. (2005) has been used for calculation of HHV.

1.4.4 Ash/Residue Content

The chemical breakdown of a biomass fuel by either thermochemical or bio-chemical processes produces a solid residue. When produced by combustion in air, this solid residue is called ‘ash’. Ash acts as a heat sink in the same way as moisture, lowering the combustion efficiency. Soluble ionic compounds in ash can have a catalytic effect on the pyrolysis and combustion of the fuel. The composition of mineral matter can vary between and within each biomass sample (Demirbas, 1997). The ash content of biomass affects both the handling and processing costs of

the overall biomass energy conversion cost. During biochemical conversion, the percentage of solid residue will be greater than the ash content formed during combustion of the same material. For biochemical conversion process, the solid residue represents the quantity of non-biodegradable carbon present in the biomass. This residue will be greater than the ash content because it represents the recalcitrant carbon which cannot be degraded further biologically but which could be burnt during thermochemical conversion. Depending on the magnitude of the ash content, the available energy of the fuel is reduced proportionately. In a thermochemical conversion process, the chemical composition of the ash can present significant operational problems. This is especially true for combustion processes, where the ash can react to form a 'slag', a liquid phase formed at elevated temperatures, which can reduce plant throughput and result in increased operating costs.

1.4.5 Alkali Metal Content

The alkali metal content of biomass i.e. Na, K, Mg, P and Ca is especially important for any thermochemical conversion processes. The reaction of alkali metals with silica present in the ash produces a sticky mobile liquid phase which can lead to blockages of airways in the furnace in power plants.

1.4.6 Cellulose/Lignin Ratio

The proportions of cellulose and lignin in biomass are important in energy conversion processes. The biodegradability of cellulose is greater than that of lignin. Hence the overall conversion of the carbon-containing plant material present as cellulose is greater than that for plants with a higher proportion of lignin. It is a determining factor while selecting biomass plant species for biochemical processing. HHV of biomass fuels increases with increasing lignin contents (McKendry, 2002; Demirbas, 2009).

1. PHYSICOCHEMICAL AND THERMOCHEMICAL ANALYSIS

1.1 Proximate Analysis

The proximate analysis of feedstock, hydrochar (HC) and biocrude oil (BO) are carried out for determining the mass percentage of water or moisture (M), volatile matter (VM), ash (A) and fixed carbon (FC) contents. The analysis of M, VM, A and FC of feed stock are performed by proximate analyzer as per ASTM standard procedures: E871-82 (2013), D1102- 84(2013) and E872 - 82(2013), respectively. Moisture is determined at the temperature of 103 ± 1 °C for 2h or until constant weight is obtained. Ash is found at a temperature of 580 °C for 30 min and volatile matter is estimated at a temperature of 950 °C for 7 min. Fixed carbon is calculated by subtracting the summation of the percentages of moisture, ash and volatile matter from 100.

1.2 Ultimate Analysis

The ultimate analysis determines the elemental mass percentage of carbon, hydrogen, oxygen, nitrogen, sulfur and ash in a fuel. It is carried out using a CHNS/O elemental analyzer as per procedure given in ASTM D5373-08. The analyzer operates on the principle of the dynamics of flash combustion of the sample. The sample is weighed in a tin or silver capsule and introduced into the combustion chamber of the reactor, where with the proper amount of oxygen and combustion catalysts, the sample is combusted. The sample and the tin capsule react with oxygen and combust at temperatures of 1700-1800 °C and the sample is broken down into components: N₂, CO₂, H₂O and SO₂. High performance copper wires absorb the excess oxygen which is unused in the sample.

The flue gases pass through the gas chromatographic (GC) separation column which is kept at a constant temperature with a variation of ± 0.1 °C. During normal system operation, helium carrier gas circulates within the analytical circuit which consists either of a combustion reactor for CHNS or a pyrolysis reactor for oxygen. The carrier gas brings the combustion (for oxygen analysis: pyrolysis) gases to a gas chromatographic separation column and thermal conductivity detector (TCD) for CHNS/O analysis. The TCD generates a signal which is proportional to the amount of the element in the sample. The instrument software compares the elemental peak of the gases with known standard material (after calibration) and generates a report for each element on the weight basis.

In the case of solid samples the amount of elemental oxygen is determined by finding the difference of total percentage of C, H, N, and S from 100.

In the case of liquid oil samples, oxygen is determined separately. Helium carrier gas circulates through the analytical circuit, which consists of a pyrolysis reactor filled with a special nickelized carbon wool contact material heated to 1080 °C, a trap for acidic gases formed during the pyrolysis, a GC column which separates the gas mixture, and a TCD. Samples are dropped automatically into the pyrolysis reactor. They break down with the release of oxygen which reacts with the nickel carbon wool to form CO and N₂. The software compares the elemental peak to a known standard material (sulfanilamide) and generates a report for each element on a weight basis after calibration.

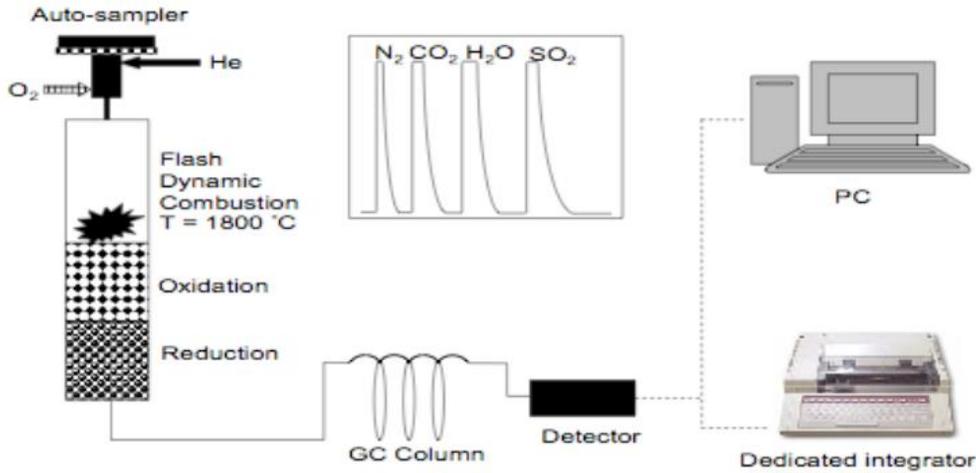


Figure-1: CHNS analysis general schematic diagram (Courtesy: Euro Vector via Alessandro Manzoni, 1, 27050 Redavalle PV, Italy).

Tests are conducted in triplicate and reported as the average of all the results. C, H, N and S are determined by chemical analysis and expressed on a moisture free basis. Ash is determined in proximate analysis and calculated on moisture free basis. Then % O is found by the Equation:

$$\% O = 100 - (\%C + \%H + \%N + \%S + \%Ash) \quad (1)$$

1.3 Heating Value

Calorific value in the form of higher heating value (HHV) may be evaluated by using any of the equations given in the literature with proper justification. Many people use the Equation (2):

$$HHV \left(\frac{MJ}{kg} \right) = 0.3491C + 1.1783 H + 0.1005S - 0.1034 O - 0.0151N - 0.021A \quad (2)$$

as applied by Channiwala & Parikh (2002), where C, H, O, N, S and A represent elemental carbon, hydrogen, oxygen, nitrogen, sulfur and ash contents of the material, respectively and expressed as mass percentage on dry basis.

1.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are determined as a function of increasing temperature (with constant heating rate), or as a function of time. TGA is commonly used to determine selected characteristics of materials that exhibit mass loss taking place due to various thermal phenomena.

TGA may be performed for the raw feed under isothermal/non-isothermal conditions in the presence/absence of oxygen at various heating rates. Activation energy (E_a) and pre-exponential factor (A) may be calculated by using the iso-conversional method (Park et al., 2009; Biagini et al., 2010; Gasparovic, 2010; Wongsiriamnuay and Tippayawong, 2010a, 2010b; Chandrasekaran, 2012). The effect of temperature on the kinetics of the reaction is determined by using Arrhenius Equation (3):

$$k(T) = A \exp \left(- \frac{E_a}{RT} \right) \quad (3)$$

Where, A , E_a , R and k are the pre-exponential factor, the activation energy, the universal gas constant and the kinetic constant, respectively. Temperature ranges in which breakdown of cellulose, hemicellulose, lignin and char takes place in thermal process may be identified and compared on the similar line as done by Gangavati et al. (2005) and Safi et al. (2004).

The experiments are carried out in a thermogravimetric analyzer (TGA)/ differential thermal analysis (DTA) apparatus. The instrument supported on a vibration resistant structure is highly sensitive to weight and temperature changes of biomass sample during burning. All necessary calibrations in temperature, weight and sample platform are carried out for the instrument prior to testing. In experiment, alumina crucible is used to hold about 10 mg of sample spread at the bottom. Pyrolysis experiments are carried out under oxidative/inert high purity nitrogen gas atmosphere with a specific flow rate at atmospheric pressure. Isothermal/Non-isothermal experiments are performed at various temperatures under different heating rates. Continuous records of weight loss and corresponding temperatures with time are obtained. General schematic diagram of the apparatus is shown in Figure 2. Experiments may be repeated in order to get reproducible results.

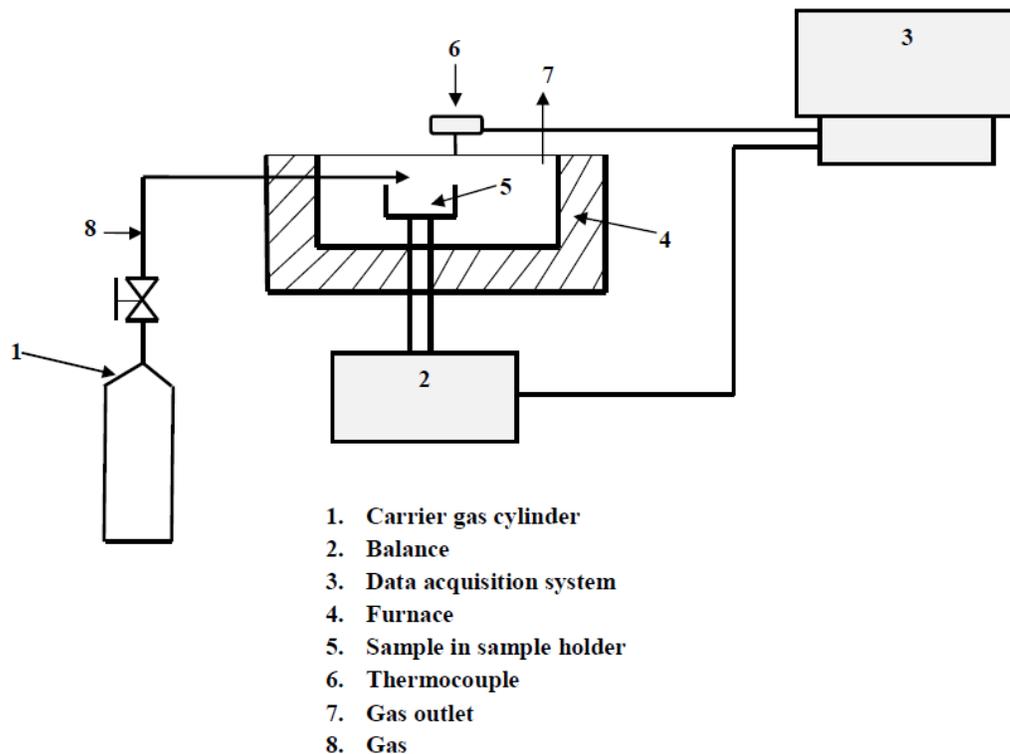


Figure-2: Schematic diagram of TGA apparatus for pyrolysis.

2. ANALYSIS OF HOLOCELLULOSE AND LIGNIN

2.1 Holocellulose

Holocellulose comprises both the true cellulose and hemicelluloses of wood and is the lignin-free total carbohydrate fraction of extractive-free wood. The procedure used for the isolation and determination of holocellulose may be adopted from Technical Association of the Pulp and

Paper Industry Standard T 9m-54 (TAPPI, 1954). Holocellulose is taken as the residual matter after successive pre-extraction of wood meal with ethanol-benzene, ethanol, and hot water to remove extraneous substances, followed by a succession of chlorination and extraction with monoethanolamine (MEA) to remove lignin. Two grams of air-dry wood meal, whose moisture content is known, is weighed to the nearest 0.1 mg. The sample is rendered extractive- and moisture-free. The fritted glass crucible containing the extractive-free sample is placed in the chlorination apparatus. The crucible is surrounded and its contents are moistened with ice water. The sample is chlorinated for 5 minutes with moderate suction by passing chlorine gas through the inlet tube jacket fitted over the top of the crucible. The ice water is then withdrawn from around the crucible, and the chlorinated sample covered with 25 ml of ethanol for 1 min to remove excess chlorine and hydrochloric acid. The sample is submitted to two 2-minute treatments, each with a 3% solution (v/v) of ethanolic MEA maintained at 75 to 80 °C. The excess MEA is removed by washing the sample twice, each with 25 ml of ethanol and twice with just sufficient distilled ice water to cover the sample. The solvent and the washing solution are removed with suction. The sample is thoroughly stirred with a glass stirring rod upon addition of each solvent and washing solution. After the second water wash, the crucible is again surrounded with ice water and the chlorination and extraction are repeated until the sample becomes essentially white and shows no color change upon addition of the hot MEA solution. The chlorination period for each successive treatment may be 5 min for the first treatment; 4 min for the second, 3 min for the third, and 2 min for the subsequent treatments. After the final chlorination and extraction treatment, the holocellulose preparation is washed twice again, each with 25 ml of ethanol, and three times, each with 25 milliliters of ethyl ether. The crucible is wiped clean with an ether dampened cellulose tissue and placed in a weighing bottle in an oven at 35 °C for at least 2 h to remove ether. The yield of holocellulose is determined as the percent of the weight of the original moisture-free sample.

2.2 Lignin

Acid-insoluble lignin is determined by TAPPI standard T 222 om-02 (TAPPI, 2002). The procedure is briefly stated in the following paragraph:

1.0 ± 0.1 g test specimen is weighed out. To the test specimens in 100-mL beakers, 15.0 mL of cold (10 to 15°C) sulfuric acid (72%) is added. Beaker is kept in a bath at 2 ± 1 °C during dispersion of the material. After the specimen is dispersed, the beaker is covered with a watch glass and kept in a bath at 20 ± 1°C for 2 h. The material is frequently stirred during this time to ensure complete solution. About 300 to 400 mL of water is added to a flask and the material is transferred from the beaker to the flask. Then the solution is rinsed and diluted with water to 3 % concentration of sulfuric acid, to a total volume of 575 mL for wood. The solution is boiled for 4 h, maintaining constant volume either by using a reflux condenser or by frequent addition of hot water. The insoluble material (lignin) is allowed to settle, keeping the flask in an inclined position. Without stirring up the precipitate, the supernatant solution is decanted in a filtering crucible. Then the lignin is transferred quantitatively to the filter, using hot water and a rod with rubber policeman. Lignin is washed with hot water, until free of acid. Crucible is dried with lignin in an oven at 105 ± 3°C to a constant weight, and then cooled in desiccators and weighed. Lignin content in the test specimen is calculated by the Equation (4) as given on the next page:

$$\text{Lignin , \%} = \frac{W_L \times 100}{W_s} \quad (4)$$

Where, W_L is the weight of lignin, and W_s is the oven-dry weight of test sample.

3. SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDS)

Morphology and surface composition are tested by SEM coupled with EDS. Small quantities of the samples are sprinkled onto a double-sided carbon tape mounted on a SEM stub. Samples are initially dried so as to be free from moisture. SEM/EDS analysis provides insight into the particle morphology, external surface structure and external elemental distribution. Schematic diagram has been shown by the Figure-3.

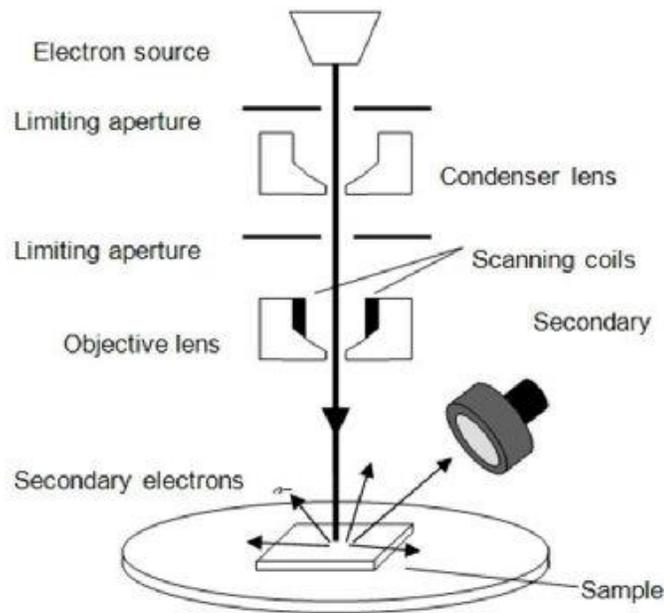


Figure-3: Schematic diagram of SEM (Kalantar-Zadeh, 2007).

4. FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

FT-IR is a technique used to obtain an infrared spectrum of emission or absorption of a solid, liquid or gas. Identification of various functional groups in the raw material and the derived biofuels, viz. HC and BO oil is carried out by FT-IR (Anastasakis and Ross, 2011, Duan et al. 2013).

The FT-IR spectroscopy characterizes the functional group and fingerprint region of very small quantities of samples. The infrared spectra are obtained by using FT-IR spectrometer. The spectra may be taken in various wave-length regions as desired at the given room temperature. Software support may be further used for obtaining the spectra and advanced data analysis.

5. ANALYSIS OF HYDROCHAR AND BIOCRUDE

The mathematical formulae used by Danso-Boateng et al. (2015) given below may be adopted for calculation of yield (Y), energy densification (E_d), and energy yield (E_y) of hydrochar and biocrude:

$$Y \text{ (wt. \%)} = \frac{\text{mass of dry hydrochar or biocrude}}{\text{mass of dry feedstock}} \times 100 \quad (5)$$

$$E_d = \frac{\text{HHV char}}{\text{HHV freestock}} \times 100 \quad (6)$$

$$E_y(\%) = E_d \times Y \quad (7)$$

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