CHAPTER 1

Introduction

1.1 Current energy scenario

The remarkable and rapid industrialization and urbanization has overwhelmed the global and regional energy resources. Population and economic growth have emerged as the prime anthropogenic drivers of climate change and global warming. There is a need of decoupling over-reliance on fossil-based fuels and pursuing novel approaches for addressing energy requirements focusing on reliable, green, clean, affordable, and sustainable energy (Agnihotri and Mondal, 2023a). According to the United Nations, in 2030 the world population is projected to reach 8.5 billion, and in 2050 it will increase to 9.7 billion and by 2100 it will reach new highs of 10.4 billion (Population - the United Nations). Explosive population growth will lead to energy and emission intensive scenario. Considering population growth from 7.7 billion in 2020 to 8.5 billion in 2030 and further 9.7 billion in 2050 (Fig. 1.1a), International Energy Outlook (EIA, 2021) anticipates that global energy consumption is projected to climb from 601.5 quadrillion British thermal units (quadrillion Btu) in 2020 to 705. 2 quadrillion Btu in 2030, and further to 886.3 quadrillion Btu in 2050 (Fig. 1.1b). World carbon dioxide emissions will increase from 34,343 million metric tons in 2020 to 37,414 million metric tons in 2030, and further to 42,839 million metric tons in 2050 as per the data provided by the U.S. Energy Information Administration (EIA) (Fig. 1.1c). According to the report of EIA, India's population is expected to grow from 1422.1 million in 2022 to 1670.9 million in 2050 (Fig. 1.2a), in same duration energy consumption is likely to rise from 38.3 quadrillion Btu to approximately 110.4 quadrillion Btu (Fig. 1.2b) and CO_2 emissions is

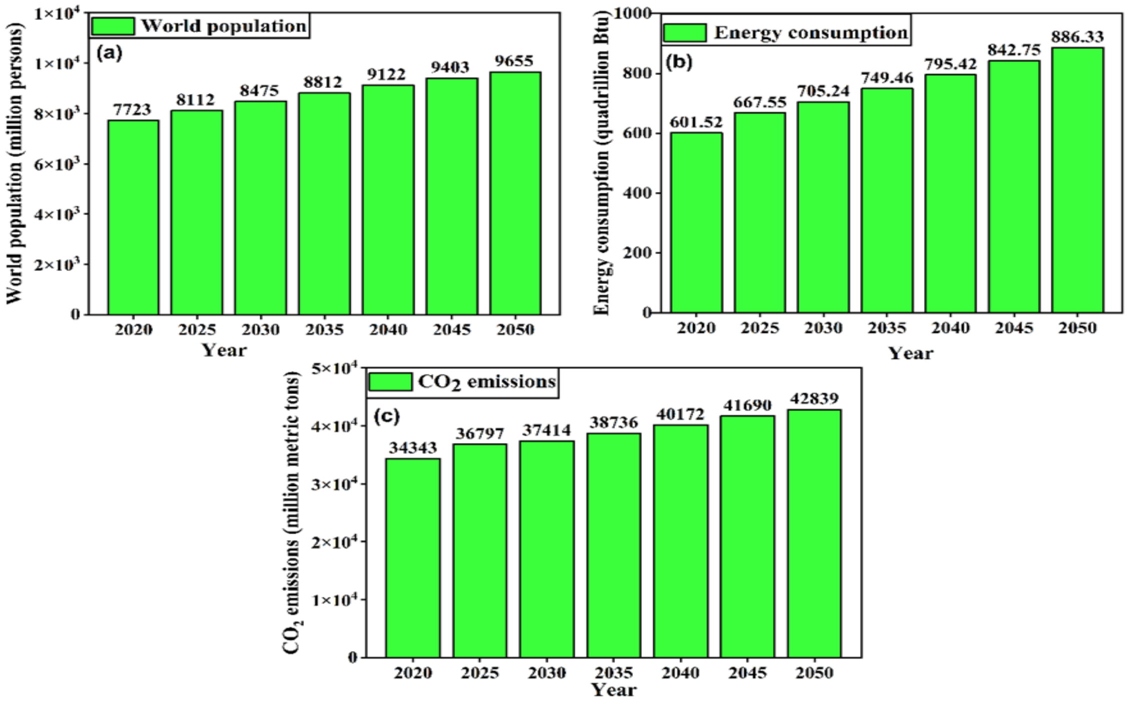

Figure 1.1. Overview of (a) World population (b) World energy consumption (c) World CO_2 emissions (EIA, 2021)

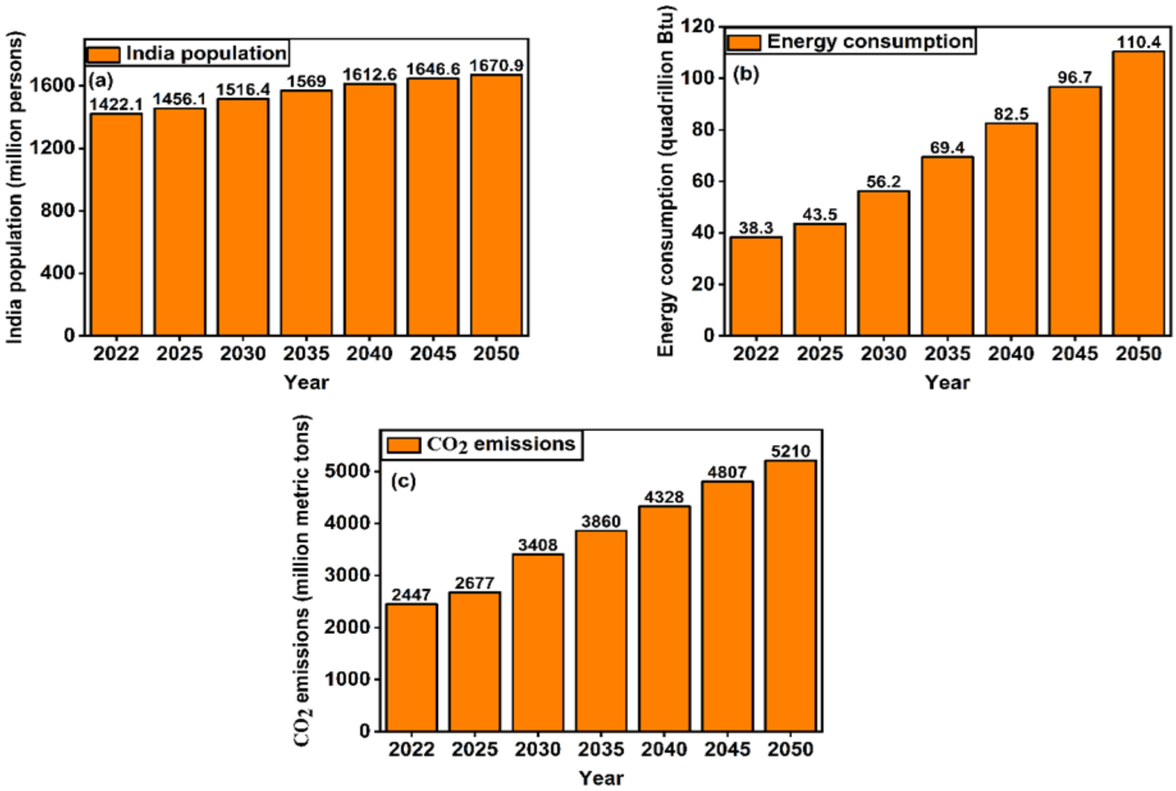

Figure 1.2. Overview of (a) India population (b) India energy consumption (c) India CO_2 emissions (EIA, 2023)

anticipated to increase to 5210 million metric tons in 2050 from 2447 million metric tons in 2022 (Fig. 1.2c).

According to the Ministry of New and Renewable Energy, the current availability of biomass in India is estimated at about 750 million metric tons per year (https://mnre.gov.in/bio-energy/current-status). International Energy Outlook (EIA, 2023) reports that in 2022, total energy consumption of the world stood at 637.8 quadrillion Btu and out of this major portion was fulfilled from conventional non-renewable sources. Currently, around 79% of the worldwide energy aspirations are being fulfilled by fossil-based energy sources like coal, oil, and natural gas (Fig. 1.3). Using fossil resources results in several negative environmental impacts such as pollution and particulate matters, greenhouse gas, CO_2, NO_X and SO_X emissions. Meanwhile, depletion of fossil fuel has also been identified as a significant future challenge as they are present only in limited quantity and are non-renewable in nature and cannot be replenished because they originated from fossilized remains of dead plants and animals by exposure to pressure and heat in Earth's crust over millions of years. Therefore, it is need of the hour to ensure environmental conscious energy sources as well as ensuring that the needs of the future are taken care of.

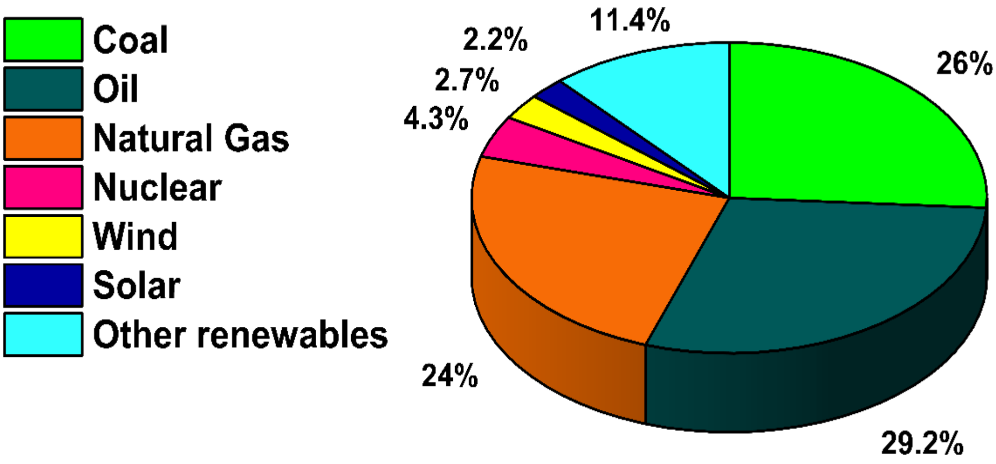

Figure 1.3. Primary energy use by fuel, world 2022 (EIA, 2023)

A green energy pathway is absolutely essential towards achieving rapid shift towards sustainability in a de-fossilized and de-carbonized way. Renewable sources of energy offer numerous opportunities associated with them such as energy security, safe energy access for present and upcoming generations, economic and social development, mitigation of climatic changes, reduction in adverse environmental and ecological impacts at global, regional, and, local levels for human beings and flora and fauna.

Renewable energy is defined as the energy derived from natural sources that get replenished constantly. There are plentiful sources of renewable energy all around us like solar energy, hydropower, biomass, wind and ocean energy and geothermal energy. Biomass is one of the most promising renewable alternatives of fossil resources as it takes in CO_2 as it grows and releases this CO_2 when used for energy, resulting in a carbon-neutral cycle that does not increase the atmospheric concentration of greenhouse gases. In addition to it, biomass contains lesser amounts of nitrogen and sulphur, which results in lesser NO_X and SO_X emissions. Also, it is widely available all around the globe. Utilization of waste biomass for energy generation is capable of strengthening waste-to-wealth approach as it will serve the dual purpose of energy generation and waste management simultaneously (Agnihotri et al., 2022).

1.2 Biomass: a renewable source of energy

Biomass is organic, non-fossil material of biological origin which means it is organic matter that originates from plants and animals. In context of energy, it is often used to refer to material originating from plants. Biomass is carbon based and consists of a mixture of carbon, hydrogen, oxygen, often nitrogen and also small quantities of other elements. Biomass is a renewable material, it gets replenished either through natural processes, or it can be produced as a by-product of human activities like organic wastes.

Biomass resources which are available on a renewable basis and are utilised either directly as a fuel or converted to some other form or energy product are commonly known as “feedstocks.” Common biomass feedstocks are dedicated energy crops, agro-industrial waste, forestry residues, agricultural crop residues, wood processing residues, sawdust, algae, municipal waste, de-oiled cakes, and wet waste (crop wastes, purpose-grown grasses, forest residues, industrial wastes, woody energy crops, algae, urban wood waste, sorted municipal solid waste, and food waste).

1.2.1 Properties of biomass

The properties of biomass are influenced by several factors like climatic conditions under which they are grown, its inherent composition and geographical location etc. The physicochemical properties of biomass are determined by proximate analysis, ultimate analysis and higher heating value (HHV) and composition analysis. Proximate analysis is used to evaluate the moisture content, volatile matters, ash content, and fixed carbon content of the biomass. Ultimate analysis provides elemental (Carbon, hydrogen, nitrogen, sulfur and oxygen) analysis. Compositional analysis gives information about hemicellulose, cellulose and lignin in the lignocellulosic biomass.

1.2.1.1 Proximate analysis

Moisture content: This can be defined as the moisture percentage of any biomass sample under examination when it is heated just above the water’s boiling point (105°C). Water gets evaporated from biomass by the heat provided at this temperature, which decreases the initial weight of the biomass. When further changing in biomass weight stops, the difference between the initial weight and the final weight expresses the moisture content. It is expressed in terms of weight percentage (wt.%) of biomass material.

Volatile matter content: The condensable vapors and non-gaseous condensables (excluding water vapor) which liberate from biomass upon heating is known as volatile matter of the biomass. Biomass feedstocks with higher volatile matter content produce higher amount of bio-oil in pyrolysis.

Ash content: When the biomass is subjected to incineration, its moisture gets evaporated, and the volatile matter content gets burnt out, the remaining matter is known as the ash of the biomass. Ash content is made up of inorganic materials like calcium, sodium, alumina, potassium, and silica etc. High ash content creates problems in thermochemical processes like pyrolysis, gasification, and combustion. High amount of ash tends to decrease the fusion point, which may lead to fouling and slagging because the ash has alkaline nature.

Fixed carbon: It is combustible remaining solid residue after the biomass is burnt at a temperature of 750°C for 7 min. Fixed carbon content is determined after removing the moisture content, ash content, and volatile matter from the biomass.

1.2.1.2 Ultimate analysis

Ultimate analysis is employed to analyse the elemental composition of the biomass. An elemental analyzer or CHNS analyzer is used for carrying out ultimate analysis. It gives amount of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) present in the biomass. Oxygen (O) is generally determined by subtracting summation of C, H, N, and S wt.% from 100.

1.2.1.3 Heating value

Energy content is commonly measured as heating value (or calorific value). There are two ways of measuring heating value, lower heating value (LHV) and higher heating value (HHV). The HHV is defined as the total amount of heat available within biomass including the latent heat of vaporization of water in the fuel and the reaction products.

Whereas, the latent heat of vaporization of water is excluded for calculation of LHV. Therefore, HHV is the sum of LHV and the latent heat of vaporization of water**.**

In Table1.1 proximate analysis, ultimate analysis and HHV analysis of several biomass is presented.

Table 1.1. Proximate, ultimate and HHV analysis of various biomass

Analysis/ Biomass	**Soybean Stalk**	**Coconut fiber**	**Sal sawdust**	**Walnut shell**	**Wheat straw**	**Teak sawdust**
Proximate analysis (wt.%)						
Moisture content	2.5	-	8.88	10.6	4.41	3.87
Ash content	4.5	2.9	1.14	10.5	6.77	3.53
Volatile matter	75.9	79.61	76.03	63	81	78.17
Fixed carbon*	17.8	17.5	14.09	15.9	8.13	14.43
Ultimate analysis (wt.%)						
Carbon	43.08	46.54	49.83	41.7	42.4	49.17
Hydrogen	6.36	6.88	6.01	5	6.01	5.93
Nitrogen	0.85	0.36	0.58	0.4	0.5	1.03
Oxygen*	44.51	43.13	43.56	41.7	41.1	43.87
HHV (MJkg-1)	17.59	17.7	18.02	17.4	16.1	17.73

* By difference

(Reference: Agnihotri and Mondal, 2023b)

1.2.2 Composition of biomass

Biomass is composed of hemicellulose, cellulose and lignin. cellulose and hemicellulose are carbohydrate polymers and lignin is an aromatic-rich polymer. In pyrolysis hemicellulose and cellulosic portions of biomass contribute the bio-oil production yield whereas lignin is responsible for production of solid bio-char. In general lignocellulosic biomass consists of 15-40 wt.% hemicellulose , 25–50 wt.% cellulose, 10-40 wt.% lignin. Besides these major components extractives such as proteins, resins, pectin, gums and fats along with minute fractions of inorganic matter like Na, Mn, K, Mg, Si, Al, Zn, etc. are also found in biomass (Kan et al., 2016). Composition of some lignocellulosic biomass materials is summarized in Table 1.2.

Table 1.2. Lignocellulosic composition of various biomass

Biomass	**Cellulose (wt.%)**	**Hemicellulose (wt.%)**	**Lignin (wt.%)**	**References**
Oak	40.4	35.9	24.1	Isikgor and Becer, 2015
Douglas fir	44.0	11.0	27.0	Isikgor and Becer, 2015
Eucalyptus	54.1	18.4	21.5	Isikgor and Becer, 2015
Spruce	45.5	22.9	27.9	Isikgor and Becer, 2015
Oilseed rape	27.3	20.5	14.2	Petersson et al., 2007
Cotton stalk	31	11	30	Menon and Rao, 2012
Barley hull	34	36	19	Menon and Rao, 2012
Corn Cobs	33.7	31.9	6.1	Isikgor and Becer, 2015
Switchgrass	35	25	15	Isikgor and Becer, 2015
Poplar	50.8	26.2	15.5	Isikgor and Becer, 2015
Pine	42	24	20	Isikgor and Becer, 2015

1.2.2.1 Hemicellulose

Hemicellulose is made up of a random and amorphous structure, and many heteropolymers like glucuronoxylan, xylan, galactomannan, glucomannan, arabinoxylan and xyloglucan are its main constituents. Softwood hemicelluloses mainly contain glucomannans whereas hemicelluloses of hardwood have xylans as their major constituent. The hemicellulose heteropolymers are composed of distict 5- and 6-carbon monosaccharide units: pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose) and acetylated sugars. Hemicellulose provides strength to plant cell wall through complex matrix of bond by linking cellulose fibres with microfibrils and cross-linking with lignin (Agbor et al., 2011). Hemicellulose is the second most abundant polymer in biomass after cellulose.

1.2.2.2 Cellulose

Cellulose is major component of any lignocellulosic biomass. Disaccharide cellobiose is repeating unit in the cellulose and in it exists a robust crystalline structure. The generic formula of a cellulose molecule is $(C_6H_{12}O_5)_n$. It is made up of a skeletal linear polysaccharide, and β-1,4- glycosidic linkages join its glucose-based monomer units. The glucose units of cellulose are tightly bound with intermolecular and intramolecular network of hydrogen bonding in its structure. Transformation of cellulose into fuel is of prime importance as around half of the organic carbon exists in cellulose form in the biosphere. Cellulose is the most abundant fraction of biomass (Nishiyama et al., 2003).

1.2.1.3 Lignin

Lignin is a heterogeneous, highly crosslinked polymer. It is aromatic, hydrophobic and rigid. It is a cross-linked amorphous resin which acts as a binder for hemicellulose and cellulose. It commonly exists at the exterior of the fibres and bonded with hemicellulose by co-valent bond and provide rigid nature to the plant cell wall and holds polysaccharide fibers together. Because of co-valent bond depolymerisation of lignin becomes difficult (Isikgor and Becer, 2015).

1.3 Pathways for conversion of biomass into bio-energy

The energy derived from biomass feedstocks is known as bio-energy. Mainly, there are two pathways for the conversion of biomass into energy or high-value added products, namely, thermochemical conversion and biochemical conversion methods. In Fig. 1.4, an overview of main conversion routes of biomass into bio-energy are illustrated. Selection of conversion process depends up on numerous factors like characteristics and quantity of biomass feedstock, end -use demands, location, economics, and environmental standards.

1.3.1 Biochemical conversion processes

Biochemical conversion of biomass produces liquid or gaseous fuels like bio-ethanol and bio-gas with the help of microorganisms, enzymes, and bacteria. Main biochemical conversion processes are anaerobic digestion, and fermentation. Biochemical conversion processes proceed at lower temperatures and lower reaction rates and can offer high selectivity towards specific products and are highly sensitive to contamination.

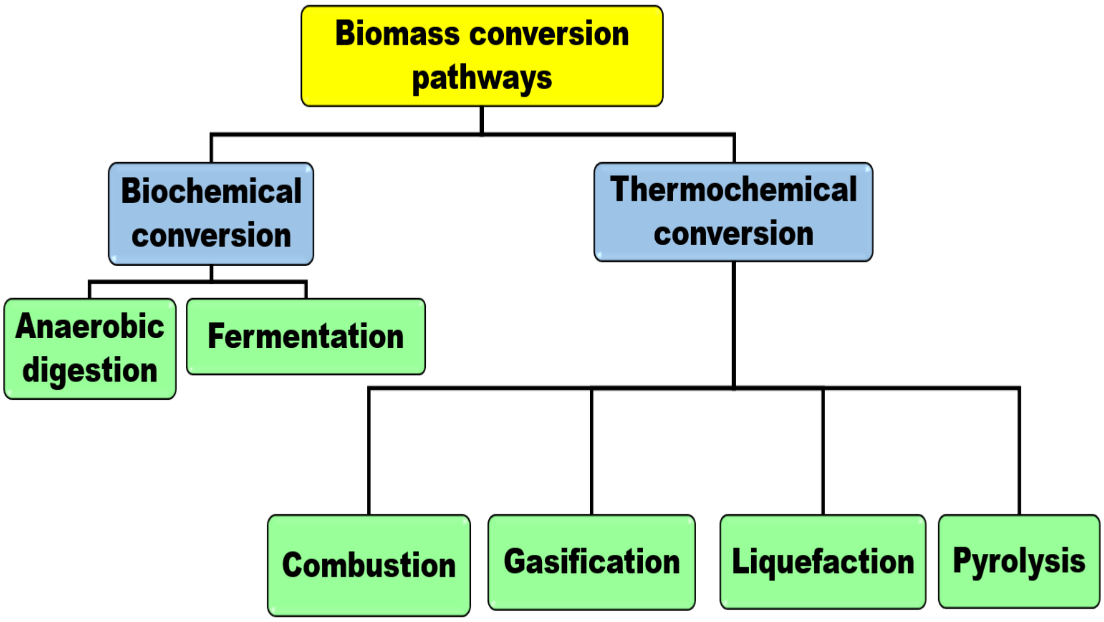

Figure 1.4. Pathways for conversion of biomass into bio-energy

1.3.1.1 Anaerobic digestion

The anaerobic digestion process occurs in an anaerobic environment and produces biogas containing mostly methane and carbon dioxide, which may be accompanied by impurities such as moisture, hydrogen sulfide, particulate matter, ammonia and siloxane. Anaerobic digestion takes place in four steps hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In the hydrolysis stage both insoluble organic matter and high molecular weight compounds like lipids, proteins, and polysaccharides reduce into amino and fatty acids. Second is acidogenesis stage in which components formed during hydrolysis break and acidogenic bacteria produce carbon dioxide, volatile fatty acids, ammonia, hydrogen sulfide , and other by-products. The third stage is acetogenesis in which acetic acid, hydrogen and carbon dioxide are produced as a result of digestion of alcohols and the higher organic acids and alcohols. Methanogenesis is the final step where methane gas is formed by two methanogenic bacterial groups, first one breaks down acetate into methane and carbon dioxide; and the second one uses hydrogen and carbon dioxide to produce methane (Nguyen et al., 2020).

1.3.1.2 Fermentation

Fermentation is carried out by microorganisms in the absence of oxygen. Biomass gets fragmented into smaller particles and further starch gets converted into sugar and then finally into alcohol with the help of enzymes. Sugar is converted into acid, alcohol, or gaseous mixture of carbon monoxide and hydrogen sulfide. Fermentation of starch and sugar containing materials into ethanol is common but fermentation of cellulose is complicated. The efficiency of fermentation process for lignocellulosic material is very low due to slow rate of specific growth of micro-organisms (Hu et al., 2005). Fermentation like any other bio-chemical process is a slow and highly environment sensitive process, with possibility of contamination from foreign substances and microorganisms.

1.3.2 Thermochemical conversion processes

In the thermochemical conversion processes biomass is converted into energy using heat and chemical reactions. Combustion, pyrolysis, gasification and liquefaction are four main process alternatives for thermochemical conversion of biomass as depicted in Fig. 1.4. Biomass is transformed into liquid fuels (like bio-oil and hydrocarbons), solids (such as bio-char or hydro-char) and gaseous products (like syngas) via thermochemical processes depending up on the conditions of reaction including temperature, pressure, heating rate and residence time. The selection of conversion type can be influenced by the nature and quantity of biomass feedstock, the preferred type of energy, for example; end use conditions and environmental principles etc.

1.3.2.1 Combustion

Combustion is a high temperature thermochemical conversion process for solid wastes in which, under oxidizing environment combustible constituents of organic fractions get transformed into energy (Yao et al., 2023). Generally, it requires temperature in the range of 800-1000 °C. This process can significantly contribute in volume reduction of the wastes but it also gives rise to substantial pollution. It creates the waste management problem at site. In addition, the direct combustion of biomass has low efficiency, as well as the burning of biomass forms airborne fly ash and emits SO_X, NO_X and CO_2 which can cause major health hazards (Bridgwater, 2003).

1.3.2.2 Gasification

Gasification is a thermochemical process carried out at extreme high temperature (> 700

°C) and it requires a gasification medium such as air, controlled supply of oxygen (oxygen deficient environment), CO_2 or steam or a mixture of these components. Gasification of biomass is transformation of carbon containing materials into gaseous products or synthesis gas (which is a mixture of CO (carbon monoxide) and H_2 (hydrogen) along with small fractions of CH_4 (methane), H_2O (water), N_2 (nitrogen) and CO_2 (carbon dioxide). It is important to reduce moisture content of feedstock by drying or pre-heating as moisture content leads to energy losses (Peres et al., 2013). Devolatilization is the first step of gasification in which char and vapors are produced, next steps include cracking and reforming of volatiles and char gasification. Using steam in gasification increases reforming reactions and char gasification resulting in enhanced production of H_2, CO, and CO_2. Composition and production of gases is influenced by several factors such as gasification medium, feedstock properties, operating conditions and type of reactor employed for gasification (Ahmad et al., 2016).

1.3.2.3 Liquefaction

Liquefaction is a thermochemical process for conversion of biomass into liquid fuel often called as bio-oil. This process requires some suitable solvent such as water, 200-400 °C temperature and 5-25 MPa pressure (Behrendt et al., 2008). Biomass liquefaction can broadly be categorised in three groups (1) Hydrothermal liquefaction; (2) Liquefaction with solvents, and (3) Liquefaction with solvent and catalysts. Biomass with high moisture content can be handled by liquefaction as it occurs in some liquid medium like water but this process is highly complicated due to high pressure and solvent requirements. A highly reactive environment is created due to high pressure, temperature and, solvent and bio-oil, aqueous dissolved chemicals, some gases and solid residue formation takes place due to decomposition and repolymerization reactions during liquefaction. Nature of biomass, solvent type, biomass-to-solvent ratio, temperature, residence time and catalyst remarkably influence quality and yield of liquefaction products (Dimitriadis and Bezergianni 2017).

1.3.2.4 Pyrolysis

The word pyrolysis is derived from two Greek words, *pyro* and *lysis* which means fire and separating or splitting, respectively. Pyrolysis is a thermochemical process which involves the decomposition of materials thermally at high temperature in an inert atmosphere. Generally, it is carried out at 400-900 ℃ and is an endothermic process. Pyrolysis of biomass is a thermochemical route for transforming it into bio-fuels including pyrolysis liquid called as bio-oil, solid bio-char and gaseous products at high temperature and in absence of oxygen. During pyrolysis, biomass decomposes thermally and releases condensable and non-condensable vapors along with solid-phase biochar. Upon condensation, condensable vapors produce bio-oil. Pyrolysis bio-oil is known by many other names like bio-crude, bio-fuel oil, wood oil, pyroligneous tar, wood liquid, wood distillate, pyroligneous acid, and liquid smoke (Agnihotri and Mondal, 2022).

Three products are always produced, but the proportions can be varied over a wide range by adjustment of the process parameters including temperature, sweeping gas flow rate, particle size of feedstock, and pyrolysis time etc. Pyrolysis of lignocellulosic biomass takes place in three major stages (1) evaporation of moisture, (2) primary biomass degradation, (3) secondary reactions including repolymerization and cracking.

Bio-oil is a dark brown coloured multi-component mixture of various compounds resulting due to depolymerization and fragmentation of cellulose, hemicellulose, and lignin. It consists of a large number of compounds like hydrocarbons, carbonyl compounds (ketones, acids and aldehydes), sugar compounds like furans, lignin compounds like phenols and aromatics. Bio-oil can be employed as a transportation fuel after upgrading. Further, bio-oil can serve as a raw material for production of valuable chemicals like phenols which is mainly produced from petrochemical sources (Yogalakshmi et al., 2022). Bio-oil can also be utilized as a starting material for additives used in pharmaceutical and fertilizer industry.

Bio-char is the solid product obtained by pyrolysis of lignocellulosic biomass and is a carbon rich material. The properties of bio-char depend upon feedstock characteristics and process parameters applied during pyrolysis process. Bio-char finds its wide application in filtration and adsorption of toxics present in wastewater due to high specific surface area and highly porous structure. Bio-char is also used as a substrate for producing activated carbon, electrochemical energy storage, soil amendments, fermentation detoxication, organic fertilizer due to it nutrient retention ability and composting etc (Yogalakshmi et al., 2022).

Pyrolytic-gases are mainly a mixture of H_2, CO, CO_2, and Hydrocarbon gases (C1-C4). High temperature favours formation of more H_2 rich or synthetic gas production during pyrolysis of lignocellulosic biomass. Degradation of C-H and aromatic groups results in H_2 gas production, cleavage of carbonyl and carboxyl functional groups lead to the formation of CO_2 and CO is produced due to breaking of C-O-C and C=O bonds. Lignin degradation at high temperature favours CH_4 production whereas low temperature favours production of CO and CO_2. Use of catalysts like CaO, Ni/Fe, Ni/Al, K_2CO_3 and Na_2CO_3 enhance H_2 gas production. Some unwanted substances like tar, dust, H_2S and steam are present in gases, therefore some treatment is necessary to control them. Pyrolytic gaseous products find application in heat/electricity generation, bio-fuels and sometimes as a carrier gas for pyrolysis.

1.3.2.4.1 Catalytic pyrolysis

Often, bio-oil is the main targeted product of pyrolysis, but it has several drawbacks like high oxygen and water content, high acidity and viscosity which create limitations of pyrolysis-to-energy chain. Catalytic pyrolysis is a promising route to yield pyrolytic products with a higher quality. Catalysts are used in pyrolysis to improve yield and quality of the end products as compared to that is obtained by thermal pyrolysis. When catalysts are added to the pyrolysis system, they give rise to the chemical reactions like hydrocracking, cracking, decarboxylation, hydrodeoxygenation and hydrogenation. In literature, numerous catalysts such as zeolites, zeolite-based catalysts, metal oxides, molecular sieves, inorganics and composites of these materials have been reported to be used. Use of commercial catalysts for pyrolysis makes it costly. Therefore, some renewable and low-cost catalyst for pyrolysis is required.