

# CHAPTER 1

## Introduction

### 1.1 Energy scenario

Energy availability is directly or indirectly related to the growth, economical development and social prosperity of the nation. According to the statistics provided by the United Nations, the population of the world was 7.2 billion in the year 2013 and it is expected to increase by 33% in the year 2050 (Tripathi et al., 2016). With such high rate of increase in the population, demand in every aspect (food, shelter, energy, etc.) is becoming higher continuously. Energy plays a very crucial role in every sector such as transportation, agriculture, industry, power generation and many others. The global consumption of fuel has increased from 84319.17 Twh in 1980 to 161471.36 Twh in 2018 as shown in Fig. 1.1 and at the same time the change in energy demand has also increased from 49 Mtoe in 2015 to 328 Mtoe in 2018 as shown in Fig. 1.2.

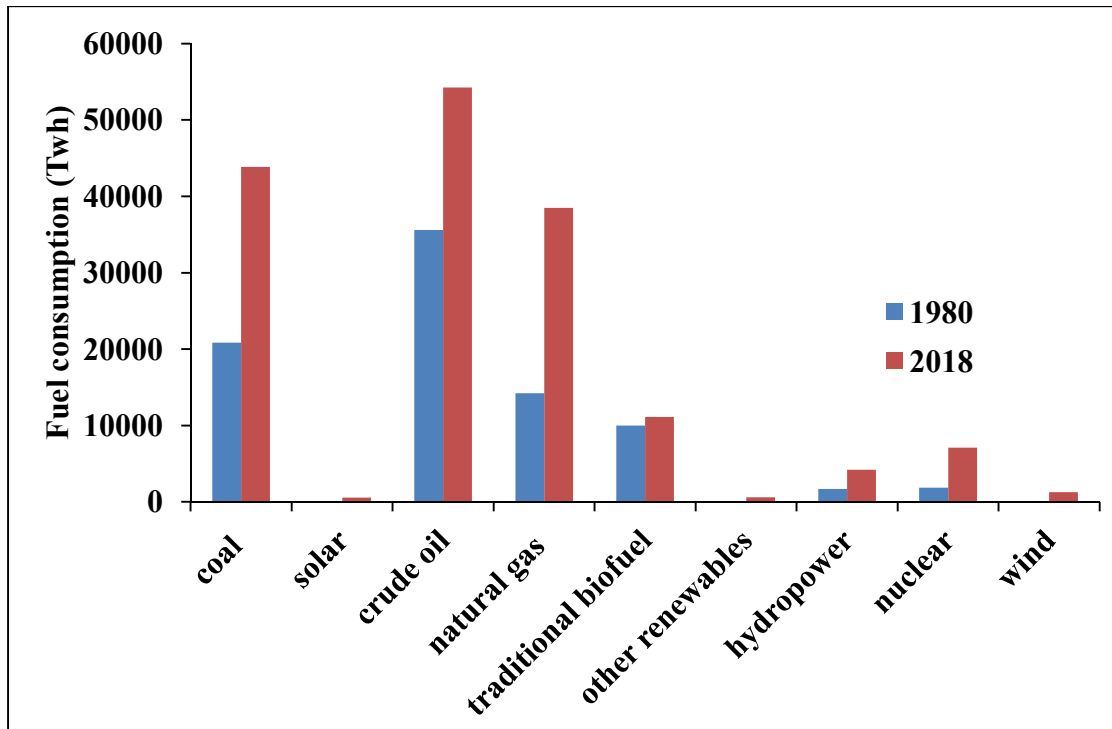


Fig. 1.1 Fuel consumption from 1980 to 2018 (Data source: <https://ourworldindata.org/energy-production-consumption>)

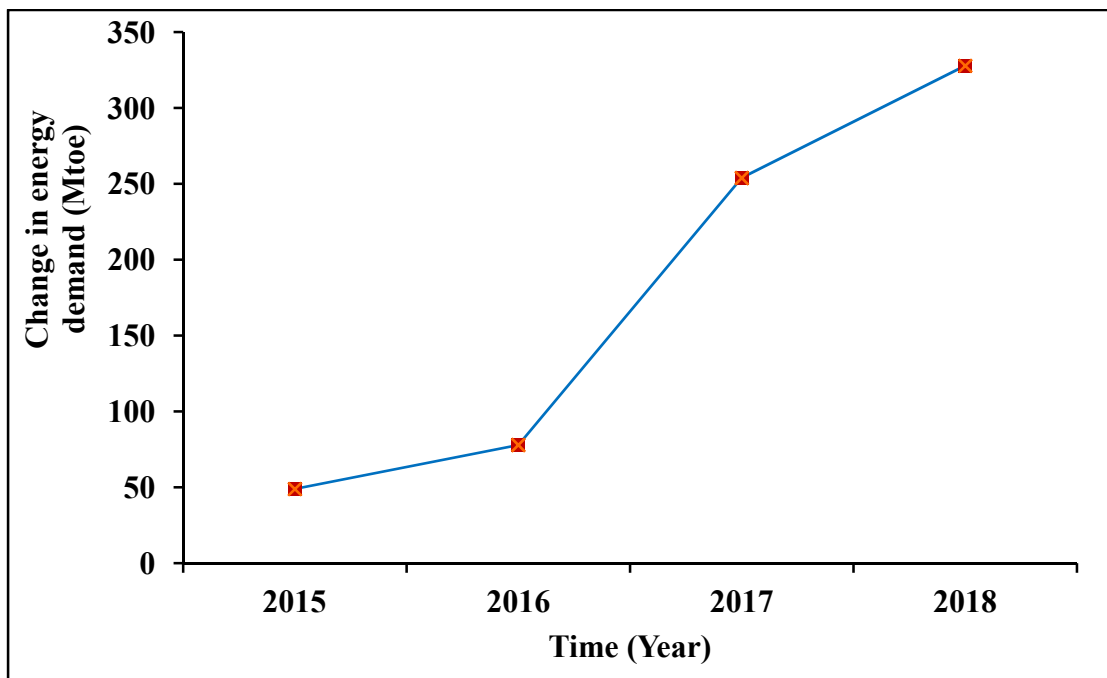


Fig. 1.2 Energy overview of annual change in global energy demand (Data source: <https://www.iea.org/reports/global-energy-co2-status-report-2019>)

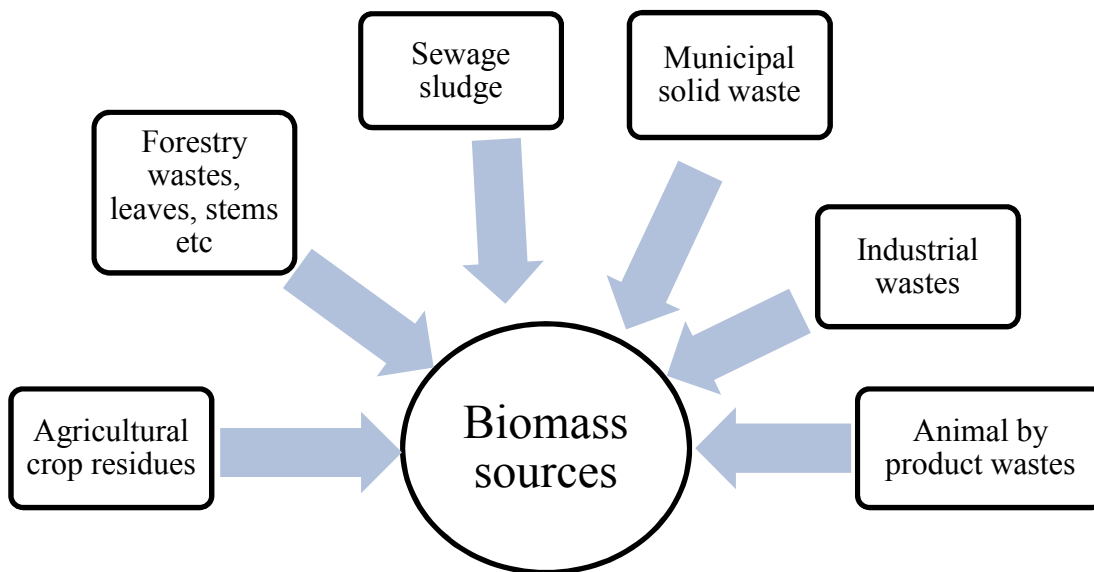
In present scenario, around 90 % of the energy consumption in developing countries is fulfilled by fossil fuels (coal, petroleum and natural gas). It has been reviewed that 70% of petroleum necessities of India are met out through imports and it is expected to increase in coming future (Singh et al., 2014). Approximately, India shares only 0.4 % of the world's reserves of crude oil. According to the data provided by World Energy Outlook, by 2030, 94 % of India's crude oil demand would be fulfilled through imports (Data source: <https://www.iea.org/topics/world-energy-outlook>; Karmakar et al., 2012). The technological developments, on the other hand, are responsible for depleting the limited fossil fuel reserves (Isahak et al., 2012) and have also increased the release of toxic gases to the environment causing global warming. It is anticipated that energy requirement is going to be doubled by the year 2050 (Anahas et al., 2018) and the present conventional energy sources are insufficient to meet the future world energy demand. The growing demand for energy and environmental concerns have shifted the alertness of researchers to find out a substitute renewable, sustainable, environmental friendly and cleaner energy source for the coming generation. Although various renewable energy resources are available such as wind energy, solar energy, hydrothermal etc. but they have certain limitations which include intermittent source of energy, costly, time and location specific etc. Among the available resources, biomass has gathered much attention in recent time since it is available in plenty throughout the year, less or negligible market importance, clean and sustainable. Other advantages of biomass include carbon neutral, low sulphur and nitrogen content (Mahinpey et al., 2009) resulting in less SO<sub>x</sub> and NO<sub>x</sub> emission as compared to fossil fuels.

## 1.2 Biomass

Biomass is a complex bio-residue organic or non-organic solid products obtained from living or dead organisms and are available naturally. It is a renewable source of energy that contains complex mixture of carbon, nitrogen, hydrogen and oxygen. Along with these, various other wastes such as waste paper, animal manure, industrial wastes, sludge etc. are considered as biomass because these wastes also contain mixture of organic and non-organic compounds that can be processed to get bio-energy.

### 1.2.1 Sources and types of biomass

Biomass can be categorised in different ways depending upon certain parameters like organic, inorganic, primary biomass, secondary biomass, etc. Different forms of biomass are available in India and they are classified based on their availability in the environment. The different sources of biomass include food crops, vegetables, energy crops, lignocellulosic wastes, manures, algae, municipal solid wastes, etc. Classification of different types of biomass is presented in Fig.1.3.



**Fig.1.3 Sources of biomass**

Huge amount of agricultural residue are produced everywhere which can be a potential source for energy generation. These residues include the by-products collected after harvesting the agricultural crops and it can be primary or secondary. Wheat straw, sugar cane tops etc. are the primary residues whereas rice husk, bagasse, etc. are example of secondary residues. Primary residues are mostly used as animal fodder and are less available for bio-energy generation as compared to secondary residues. Forestry wastes are other sources of biomass which basically comprise of woody biomass. This type of biomass includes stem, branches, leaves, bark, etc. from different trees like pine, oak, redwood, etc. Agricultural residues and woody biomass are widely used for bio-energy generation in different parts of the world. However, along with these, municipal solid wastes and energy crops are also sources of biomass. Municipal solid wastes include the kitchen wastes, office wastes, animal and human wastes, paper, plastics, etc. and the energy crops are the starch producing species like root crops, cassava, etc.

### **1.2.2 Characteristics of biomass**

The entire pathway i.e. starting from collection to conversion of biomass to useful products depends upon its type and physicochemical properties. These physical and chemical properties play a vital role for the design and development of different processes that convert the biomass to biofuel. The properties of the biomass vary depending upon the location, climatic condition, inherent composition etc. Since mostly agricultural and woody biomass is being used for the production of bio-energy, thus considering this, physicochemical properties of biomass are summarized below.

Physicochemical properties of biomass describe the proximate analysis (moisture content, ash content volatile matter and fixed carbon), ultimate analysis (carbon, hydrogen, nitrogen, sulphur and oxygen), heating value and compositional analysis.

**Moisture content (MC)** is the amount of water (internal and external) present in the biomass sample and it is expressed as the percentage by weight. The presence of MC in the biomass affects the handling, storage, transportation, and the biomass conversion efficiency thus for better yield of products amount of MC should be less.

**Ash content (AC)** is one of the most important properties of biomass. It is the amount of residue left over after complete combustion of biomass. Ash contains an enormous amount of inorganic elements, such as sodium, potassium, calcium, alumina, silica, and iron, which describes its behavior of forming deposits in the boiler or gasifiers.

**Volatile matter (VM)** is the amount of gases and vapours except MC that is liberated when biomass is heated at high temperature in absence of air. It is the additive of condensable vapors and non-condensable gases. Higher amount of VM signifies higher amount of liquid and gaseous biofuel. Generally in biomass it varies from 60 to 80 % by weight.

**Fixed carbon (FC)** is the amount of solid combustible residue left after eliminating the MC, AC, and VM. Generally in biomass it varies from 15 to 20 % by weight.

The **ultimate analysis** gives more widespread results as compared to the proximate analysis. It determines the amount of carbon, hydrogen, nitrogen, and sulfur content in the biomass. This analysis is performed using CHNS analyzer on a dry basis. The amount of carbon and hydrogen in biomass wastes generally varies from 40 to 50 wt. % and 4 to 6 wt. %, respectively.

**Heating value** of biomass refers to the energy content, that is, the amount of energy stored in the unit mass of biomass and it is expressed as MJ/kg. Basically, there are two types of heating value. One is lower heating value (LHV) and the other is high heating value (HHV). LHV is the amount of heat stored in the biomass excluding the latent heat of vaporization of water, whereas HHV is additive of LHV and latent heat of

vaporization of water. Table 1.1 presents the proximate analysis, ultimate analysis, and HHV of some biomass wastes.

### **Compositional analysis**

Lignocellulosic biomass comprises mainly three components, i.e. hemicellulose, cellulose, and lignin. The quantity of each component can be determined by using Van Soest's method, National Renewable Energy Protocol method, or Technical Association of the Pulp and Paper Industry method. The amount of the three components varies depending upon the nature and part of the biomass being considered. Accurate component analysis of biomass is essential as it determines the conversion efficiency based on the conversion methods.

Hemicellulose is the short and heterogeneous branched chain of polymers (pentose and hexose), which surrounds the cellulose and also links the cellulose with lignin. Unlike cellulose, it has a lower degree of polymerization and is amorphous in nature.

Cellulose is a natural polymer and repeating units of six carbon ring D-glucose. The three hydroxyl groups in each unit are linked with one another forming intramolecular and intermolecular hydrogen bonds. These bonds provide cellulose, a crystalline structure, and the stability (mechanical and chemical) (Saini et al., 2015). The acetal bonds link the C-1 of one pyranose ring to C-4 of the succeeding ring forming a long chain. The degradation temperature of cellulose is around 240 – 360 °C and it mainly produces liquid products after conversion.

Lignin is the aromatic, most complex, and high molecular weight polymer with cross linking of phenolic groups (Lebo et al., 2000). It is the amorphous cross-link resin that serves as a binder for the fibrous cellulose and hemicellulose components. It is located mainly on the exterior of the microfibrils and also covalently bonded to hemicellulose and impart rigidity to cell wall. As it is covalently bonded, it is not easily depolymerise.

**Table 1.1 Proximate, Ultimate and HHV of different biomass wastes from literature**

<b>Biomass waste</b>	<b>Proximate analysis, Wt. %</b>				<b>Ultimate analysis, Wt. %</b>					<b>HHV (MJ/kg)</b>	<b>Reference</b>
	<b>MC</b>	<b>VM</b>	<b>FC</b>	<b>AC</b>	<b>C</b>	<b>H</b>	<b>N</b>	<b>S</b>	<b>O</b>		
Wheat straw	8.5	63	23.50	5.5-13.5	53.90	7	3	-	36.10	17.10	Demirbas and Demirbas (1997); Vassilev et al. (2012)
Corn cob	9.7	80.6	18.2	1.2-2.8	43.6	5.8	0.7	1.3	48.6	16.9	Azeez et al. (2010); Savova et al. (2001)
Sugarcane bagasse	8.5	84.0	1.64	4.5-9.0	45.13	6.05	0.3	-	42.77	18.17	Al Arni et al. (2010)
Banana waste	7.8	78.2	15.6	11.4	43.5	6.2	0.86	0.95	42.3	17.1	Sellin et al. (2016)
Barley straw	6.9	78.5	4.8	5-9.8	41.4	6.2	0.63	0.01	51.7	15.7	Naik et al. (2010)
Almond shell	8.7	79.7	4.9	2.3	54.7	7.5	0.3	0.3	37.4	20.2	Caballero et al. (1997)
Flax straw	7.9	80.3	8.8	3.0	43.10	6.20	0.68	0.09	49.90	17.0	Naik et al. (2010)
Rice husk	-	81.6	-	18.4	36.9	5.0	0.4	-	37.9	15.29	Raveendran et al. (1995)
Hazelnut shell	9.0	69.3	28.3	4.3	52.30	6.50	5.20	9.2	26.8	19.3	Demirbas and Demirbas (1997); Haykiri-Acma and Yaman (2010)
Babool seeds	12.5	69.1	11.0	7.3	54.1	6.12	5.23	-	34.53	-	Garg et al. (2016)

(MC-Moisture content, VM-Volatile matter, AC-Ash content, FC-Fixed carbon)



Apart from these three components, biomass also contains some extractives and inorganic elements. Inorganic elements (Na, K, Mn, Mg, Cl, Al, Zn, Si, etc.) are basically present in the AC whereas extractives include proteins, fats, resins, gums, pectins, etc. that can be extracted using polar and nonpolar solvents. Table 1.2 presents the compositional analysis of some of the biomass wastes.

**Table 1.2 Lignocellulosic compositions of different biomass residues**

<b>Agricultural waste</b>	<b>Hemicellulose (wt. %)</b>	<b>Cellulose (wt. %)</b>	<b>Lignin (wt. %)</b>
Rice husks	12.0-29.3	28.7-35.6	15.4-20.0
Rice straw	23.0-25.9	29.2-34.7	17.0-19.0
Wheat straw	23.0-30.0	35.0-39.0	12.0-16.0
Corn cob	31.9-36.0	33.7-41.2	6.1-15.9
Corn stalk	16.8-35.0	35.0-39.6	7.0-18.4
Sugarcane bagasse	28.0-32.0	25.0-45.0	15.0-25.0

(References: Cai et al., 2017; Demirbas and Demirbas, 1997)

### **1.2.3 Biomass: an alternative source of energy**

Among the available energy sources, biomass ranks fourth after coal, petroleum, and natural gas that alone provide 14 – 15 % of the world’s energy requirement including 38 – 43 % to the developing nations (Ertas and Alma, 2010). Other benefits of biomass cover carbon neutral, low sulfur, and nitrogen content that account for lesser SO<sub>x</sub> and NO<sub>x</sub> productions as compared to fossil fuels. Thus depending upon the type of waste the

production of biofuels from these biomasses has been divided into four different generations.

**First generation:** Different food and oil crops, such as sorghum, wheat, rice, and corn, are utilized directly as feedstock for biofuel generation. The starch present in the biomass is basically used for the production of biofuel. The major drawback with this generation is the fight between fuels versus food as it increases the food prices.

**Second generation:** To overcome the drawbacks of first-generation biofuels, lignocellulosic wastes, such as organic wastes, wood, crop residues, sugarcane bagasse, forest residues etc. were used for the generation of biofuels using different techniques. The advantage of this generation fuel is that it utilizes the lignocellulose present in the biomass for biofuel production.

**Third generation:** In this generation, engineered energy sources, such as algae, are utilized as feedstock for biofuel production. Algae have no relation with the food or other crops and can be easily cultivated in lagoons or in open ponds with less expense.

**Fourth generation:** In the fourth generation, increased production of biofuel takes place by using metabolically engineered species (engineered algae, bacteria, and other microbes) and plants with low lignin content along with CO<sub>2</sub> capture and storage technique. Some of the species contain high lipid contents that can be degraded to polymeric hydrocarbons or other petroleum products. Biomass materials, which have absorbed CO<sub>2</sub> while growing, are converted into fuel using the same processes as second-generation biofuels and the production rate is high. The research is at initial stage and requires high investment.

These biomass can be converted to valuable products via different conversion techniques as described in the next section.

### **1.3 Bio-energy conversion pathways**

The speedy development in the country in every sector has increased the use of conventional energy sources and created pressure regarding the depletion of fossil fuel reserves. In addition to it, the use of these fuels also releases toxic gases (SO<sub>x</sub>, NO<sub>x</sub>, etc.) to the environment, which leads to the change in the environmental conditions and ultimately to the global warming. Therefore, from the last few decades, there has been an increasing interest in the treating biomass as valuable resource rather than a reject. Biomass has adequate potential and availability to be converted into valuable products, such as bio-oil, biogas, biochar, chemicals, or fertilizers. In addition, it will also put a curtain on biomass disposal or land filling, lessen the environmental problems, and will provide wealth and employment.

At present irrespective of various technologies, biochemical and thermochemical conversion processes have gathered much attention in fruitful utilization of biomass wastes into bio-energy generation. Depending upon the type, extent, and properties of biomass, any of the technologies can be used. In general, biochemical conversion processes need microbes and bacteria for the biomass degradation, thus biomass with lesser amount of lignin is preferred. For thermochemical processes, lesser amount of MC is preferred as it reduces the use of extra energy for drying.

#### **1.3.1 Biochemical conversion**

Biochemical conversion of agricultural biomass waste to bioenergy is an environment-friendly and sustainable technique. It involves the use of different microbes and bacteria that helps in decomposition of biomass waste to bio-energy. Anaerobic digestion (AD) and fermentation are the two important biochemical processes.

### **1.3.1.1 Anaerobic digestion**

AD is a biochemical process that is performed in oxygen-free environment with the help of different microorganisms that degrade the organic components into biogas. Biogas is a mixture of carbon dioxide and methane produced from biodegradable material by the enzymatic action of microorganisms under anaerobic condition and also traces of other gases, such as H<sub>2</sub>S are also produced. There are basically four steps in AD process: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The AD is a widely used technology for wastes with high MC (80 - 90 %). Different types of substrates, such as animal manure, fruit and vegetable waste, municipal solid waste, agricultural residues, microalgae and industrial waste water, can be used as substrate for biogas production. AD requires an adequate amount of carbon and nitrogen content to balance the C/N ratio for process stability. Biogas yield and composition vary according to the substrate and inoculum used. The main constituents of biogas are CH<sub>4</sub> (50 – 70 %) and CO<sub>2</sub> (30 – 50 %) with other trace gases (Bala et al., 2019). Biogas produced can be used in spark engines or in turbines. Further, it can also be upgraded to natural gas with the removal of CO<sub>2</sub>. The left-over solid digestate can be used as soil conditioner as it has important nutrients.

### **1.3.1.2 Fermentation**

Fermentation is another biological process that operates in the absence of oxygen and involves the use of microorganisms to convert sugar to alcohol, acid, or mixture of gases (CO and H<sub>2</sub>S). The biomass is converted to smaller particles and then starch is converted to sugar and then to alcohol with the help of enzymes. A variety of substrates, such as starch biomass, lignocellulosic biomass, and algal biomass, is converted into fermentable sugar. However, fermentation of biomass wastes is difficult as it has complex long-chain polymeric molecules and requires acid or enzymatic hydrolysis before the sugar is

fermented to alcohol. Fermentation is prolonged time-consuming process, with probability of contamination of other foreign microorganisms. Although, it is a promising approach but high cost is preventing its movement from laboratory to commercial world. Generally, butanol and ethanol are produced by fermentation process. Biobutanol has higher HHV, lower volatility, less ignition problems, and viscosity than bioethanol (Ibrahim et al., 2018). Although biochemical processes are capable in producing bio-energy but they have certain disadvantages as well. These processes are tedious or time consuming and also they have lesser efficiency.

### **1.3.2. Thermochemical conversion**

These processes mainly comprise pyrolysis, gasification, and combustion that require high temperature for the treatment of agricultural wastes into various useful products, such as bio-oil, syngas and biochar. Fig. 1.4 depicts different thermochemical techniques.

#### **1.3.2.1. Combustion**

Combustion is among the oldest and simplest thermo-chemical technique for the utilization of biomass. It is entirely an oxidative operation that is carried out in the temperature range of 800 – 1000 °C. This thermal degradation process involves the conversion of chemical energy of biomass to heat and power along with carbon dioxide and water. The energy produced can be utilized in steam turbines, boilers, furnaces, etc. The substrates for this process are similar as used in pyrolysis and gasification processes. For any biomass to be combusted, the MC should be below 50 wt. %. The net bioenergy conversion of biomass combustion is up to 40 %. However, its efficiency can be upgraded by co-firing the biomass with coal. Certain challenges for the process are high amount of CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub> and particulate matter emission along with the handling of ash.

### **1.3.2.2 Gasification**

Gasification is another thermochemical process that is performed in the partial oxidative (air, oxygen, or carbon dioxide) atmosphere at certain high-temperature range from 800 °C to 1000 °C. Since it is a partial oxidation process, the chemical energy of the carbon gets converted to other combustible fuel gas which has certain high efficiency as compared to raw biomass. The substrates for the gasification are similar to that are used in pyrolysis process, such as agricultural wastes, woody biomass, and energy crops. The main end product of the gasification process is syngas (CO + H<sub>2</sub>) around 85 % along with some amount of tar with approximately 5 wt. % and biochar around 10 wt. % (Bridgwater, 2004; Ram and Mondal, 2018). Some amount of CH<sub>4</sub> and other hydrocarbons are also produced. The gases produced have ample amount of calorific value and can be used as fuel for engines or turbines. Syngas produced can be used in the Fisher-Tropsh synthesis for the production of valuable liquid hydrocarbon mixtures (methanol, ethanol, etc.). The process parameters are temperature, heating rate, particle size, biomass feed rate, equivalence ratio, etc. Gasification can be performed in two different modes; fixed and fluidized bed. Fixed bed process produces gases with lower calorific value (4-6 MJ/Nm<sup>3</sup>). Today, fluidized bed gasification process is mostly preferred since it provides uniform temperature distribution in the gasification zone.

### **1.3.2.3 Liquefaction**

It is another thermochemical technique to convert biomass to mainly bio-oil at moderate temperature range of 200 – 400 °C and pressure 20 – 200 bar. The process can be operated in both batch or continuous systems however continuous systems necessitate the feeding system that can be operated under pressure and also include lock and hopper arrangements for larger particles. The product stream of this process has high energy content and

distinctive characteristic of better heat recovery as compare to other processes. The produced bio-oil obtained through this process cannot be used directly as liquid fuel and requires further hydrotreatment for commercial utilization. However, complicated reaction mechanism is not required in the up gradation process as the bio-oil obtained through liquefaction has less moisture and oxygen content. Biochar collected can be directly used as a fertilizer.

#### **1.4 Pyrolysis**

The expression “pyrolysis” is derived from Greek where ‘pyro’ refer to fire and and “lysis” refer to breaking, respectively. It is the thermal depolymerization of biomass in an inert atmosphere in continuous supply of heat. It is an endothermic process and is generally performed in the temperature range of 300 - 900 °C. The sources of substrate for biomass pyrolysis are agricultural wastes (corn stover, corn cob, rice husk, wheat straw, etc.), woody biomass (redwood, pine, beech, teak, etc.), energy crops (bamboo, sorghum, etc.), and also municipal solid wastes. The rapid heating of biomass produces vapors that are the mixtures of various hydrocarbons and some part of it can be condensed to give an organic liquid called bio-oil. Bio-oil is a brown colored viscous complex mixture of large number of organic compounds with some amount of water content. It has the HHV in the range of 20 - 30 MJ/kg and is also a source of valuable chemical compounds. The non-condensable gas that leaves the system is a mixture of valuable gases (CO, H<sub>2</sub>, CH<sub>4</sub>, etc.). These gases have good combustion properties and can be used as gaseous fuel. The remaining left-over residue is the carbon-rich compound called biochar. Biochar is a multifunctional material that can be used as solid fuel, adsorbent, sensor, fertilizer, etc.

However, the conversion of biomass to these valuable products occurs after complex reaction mechanism described below.

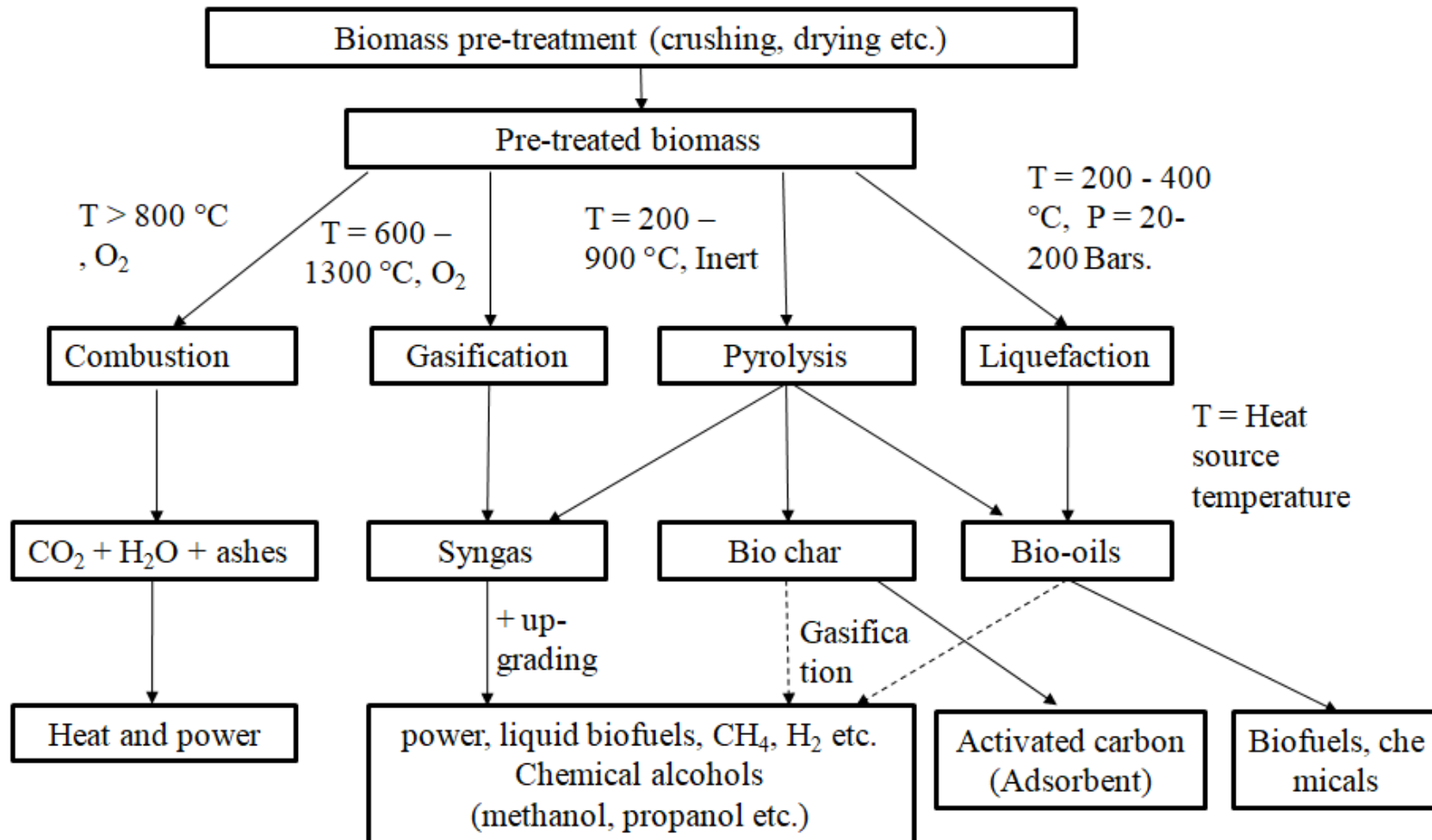


Fig. 1.4 Different routes for thermochemical conversion



### 1.4.1 General reaction mechanism for biomass pyrolysis

Biomass pyrolysis is a complex process because of the dissimilarity in decomposition of the biomass components with varying reaction mechanisms and reaction rates. During biomass pyrolysis, multiple reactions take place both in parallel as well as in series, including dehydration, depolymerisation, isomerization, aromatisation, decarboxylation, and charring (Vamvuka, 2011; Lange 2007; Collard and Blin, 2014). Basically there are three stages in the pyrolysis of biomass. The first stage is the evaporation of MC from the biomass. This stage occurs in the temperature range of around 100 – 110 °C. Thereafter in the second stage, devolatilization occurs through complex reaction mechanisms such as depolymerization, cracking and fragmentation that leads to the formation of condensable and non-condensable vapours or gases. Finally in the third stage, the charring occurs that involves the recondensation and repolymerization to form carbon rich stable solid product (biochar).

After the first stage i.e. after the removal of MC from the biomass sample, the degradation of lignocellulosic components takes place at different ranges of temperature. Among the lignocellulosic components, hemicellulose degrades first, i.e. in the temperature range of around 200 – 315 °C because of its lower thermal stability and amorphous nature. Cellulose is crystalline in nature having long polymer of glucose units that degrades to lower monomer units from 315 to 400 °C. Lignin is a heavily cross-linked stable, complex polyaromatic molecule that degrades over a wide range of temperature approximately from 180 to 900 °C (Collard and Blin, 2014). In the second stage, when the devolatilization occurs numerous heavy organic compounds such as cresol, phenol, guaiacol, levoglucosan, furfural, levomannosan, etc. are released, which can be recovered as bio-oil through condensation (Wang et al., 2013; Wang et al., 2011; Branca et al., 2013). In the final stage of charring, the volatiles liberated in the

devolatilization stage either recondenses or repolymerizes to be a part of the biochar or after further cracking they are converted to non-condensable gases (mainly H<sub>2</sub> and CO, with trace CO<sub>2</sub> and CH<sub>4</sub>) and lighter organic compounds (e.g. formic acid, formaldehyde, hydroxyacetone acetic acid, acetaldehyde etc.) that can also be condensed as bio-oil. Therefore, pyrolysis of biomass leads to the formation of solid biochar, liquid bio-oil, and pyrolytic gases via the three stages reaction discussed above.

### **1.4.2 Types of pyrolysis**

Depending upon the operating conditions such as temperature, heating rate, inert flow rate, particle size, residence time etc. pyrolysis can be categorized as slow, intermediate, fast and flash pyrolysis. Each type of pyrolysis has its own main product, advantages and certain limitations. Product distribution in the pyrolysis process primarily depends upon the compositional analysis of biomass and on the interaction among them.

#### **1.4.2.1 Slow pyrolysis**

Slow pyrolysis is a conventional type of pyrolysis which is operated at lower temperature (300–500 °C), slower heating rate (0.1 to 0.8 °C/s) and has longer residence time (5-30 min or more). Slow pyrolysis mainly favors the production of biochar but bio-oil and pyrolytic gases are also formed in small quantities (Demirbas and Arin, 2002). A typical slow pyrolysis produces 20-50 wt. % bio-oil, 25-35 wt. % biochar and 20-50 wt. % pyrolytic gases (Brownsort, 2009). The processing time can be of several hours to ensure sufficient time for the volatiles to recombine with the biochar to maximize its yield. Longer vapor residence time along with lower heating rate furnish a suitable environment and adequate time for the completion of secondary reactions. This eventually results into the creation of solid biochar.

### **1.4.2.2 Fast pyrolysis**

This type of pyrolysis is carried out in the temperature range of 450 – 850 °C, at the heating rate of 10 – 200 °C/s with a small vapour residence time varying from 1 – 10 s. This type of pyrolysis is performed mainly to collect bio-oil as the main product; however biochar and pyrolytic gases are also produced in small amounts. Around 60–75 wt. % of bio-oil, 15 – 25 wt. % of biochar and 10 – 20 wt. % of pyrolytic gases are obtained from fast pyrolysis (Bridgwater, 2003). The low vapour residence time inside the reactor reduces the exposure time of the volatiles with the biochar surface and thus it decreases the further secondary recombination of volatiles with biochar which eventually provides more volatiles as bio-oil. Also, high heating rate leads to depolymerization and fragmentation of lignocellulosic components at a faster rate and concurrently accelerates the creation of lighter volatiles. This type of pyrolysis is being used in many other applications like certain chemicals or food flavor production, etc.

### **1.4.2.3 Intermediate pyrolysis**

Intermediate pyrolysis is considered as in between slow and fast pyrolysis as it makes balance between biochar and bio-oil yields. The primary product in case of slow pyrolysis is biochar whereas bio-oil is main output for fast pyrolysis. The operating conditions for this type of pyrolysis are: temperature 500 – 650 °C, heating rate 0.1 – 10 °C/min and residence time 5 - 40 min. The product contains 40 – 60 % bio-oil, 15–25 % biochar and 20–30 % pyrolytic gases (Kebelmann et al., 2013). Certain advantages of intermediate pyrolysis include less amount of reactive tar in the bio-oil that shows its direct use in engines or boilers and also the production of dry biochar which can be used in agricultural purposes (Mahmood et al., 2013).

#### 1.4.2.4 Flash pyrolysis

Flash pyrolysis is regarded as the enhanced or modified form of fast pyrolysis process. The temperature required for the flash pyrolysis ranges in between 900 to 1200 °C and the heat energy provided is for a very small period of time i.e. 0.1–1 s (Demirbas and Arin, 2002; Li et al., 2013). The product distribution is greatly affected by the heat and mass transfer, chemical kinetics and phase transition behavior of the biomass. The fast heating rate along with high temperature and low vapor residence time leads to high bio-oil and pyrolytic gas yield but the char yield gets decreased. Flash pyrolysis produces 25 - 40 % bio-oil, 50 - 60 % pyrolytic gases and 5 - 15 % biochar (Foong et al., 2020).

However, the challenge in using flash pyrolysis at industrial level is to construct a reactor for flash pyrolysis where the biomass can reside for a very small span of time under very high heating rate. Also, the stability and quality of the bio-oil produced with this pyrolysis is strongly affected by the presence of char/ash, as it can catalyze the polymerization reaction inside the bio-oil which may increase the viscosity of bio-oil (Canabarro et al., 2013).

#### 1.4.3 Pyrolysis products

Pyrolysis of biomass at elevated temperatures produces products in all three forms i.e. liquid (bio-oil), solid (biochar) and non-condensable gas (pyrolytic gas).

**Bio-oil** is the main product obtained after pyrolysis of biomass and it is a complex mixture of oxygenated organic compounds (Zhang et al., 2017). It is generally brown in colour but its physicochemical characteristics like density, HHV, viscosity, appearance etc are governed by the type of pyrolysis and also on feedstock. Bio-oil is a composite mixture of several numbers of organic compounds that includes acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers. Some of these

compounds are directly related to the undesirable properties of bio-oil. The advantages of bio-oil include its renewability along with low SO<sub>x</sub> and NO<sub>x</sub> emission when used as fuel, but high water content, acidity and chemical instability of bio-oil makes it unsuitable for direct use. It requires upgrading processes to enhance its properties for its direct use in industries as fuel. However, it also contains valuable chemicals which can be a source of feedstock for many industries.

In addition to bio-oil, **biochar** is also a solid value-added product obtained from pyrolysis. According to the definition given by International Biochar Initiative (Lehmann and Joseph, 2015), biochar is a carbon-rich stable solid material obtained after thermochemical conversion of biomass in oxygen limited environment and its properties depend upon various operating process parameters. The solid porous structure is developed when oxygen and hydrogen present in the biomass leaves at higher temperature. Various applications of biochar include waste management as it decreases the volume of waste, energy requirement for its transport and also reduces methane emission when land filled (Kwapinski et al., 2010; Hossain et al., 2011), solid fuel (Zhang et al., 2017a, b), high efficient low cost adsorbent for air and water pollutant (Mohan et al., 2011), catalyst (Lee et al., 2017) and in soil amendment (Cha et al., 2016). Thus, biochar serves as a multifunctional material.

**Non-condensable gases** are the other useful by-products obtained during pyrolysis. These non-condensable fractions are the mixture of useful gases such as hydrogen, methane, carbon monoxide, etc. which has high calorific value and they have their utility in the field of heat and power generation. In addition, these gases after cleaning can be a source of feedstock for the Fischer-Tropsh process in producing mixture of liquid hydrocarbons.

#### **1.4.4 Biomass selection criteria**

Although we have different products from biomass pyrolysis but it greatly depends the type of biomass we use for the process. Thus, the biomass selection criteria play an important role in the type of product and its quality.

Biomass should have low MC i.e. less than 10 %, as it reduces the extra energy requirement for drying. High VM is preferred in the biomass as it will provide more of the volatile products i.e. bio-oil. Higher amount of AC in the biomass brings down the energy value of the biomass, affects the burning rate and causes fouling problem, thus biomass should have low AC. HHV is the most significant properties of any fuel which explain the higher energy content and thus higher HHV of biomass is considered favourable for pyrolysis. Along with these compositional properties also plays an important role. According to many studies, low hemicellulose, higher amount of cellulose and lignin content are preferred for biomass pyrolysis. The higher amount of cellulose in the biomass adds to the advantage of the higher amount of bio-oil yield, and a moderate amount of lignin is better for biochar yield that has different utilities as described below.

### **1.5 Utility of biochar**

#### **1.5.1 Soil amendment**

Application of biochar in agricultural soil has gathered much attention these days. According to the literature survey, biochar has been proved to play beneficial role in enhancing crop yield when used as fertilizer and also as soil conditioner. The application of biochar in the soil increases the soil aggregate stability, soil pore characteristics which help in water holding and water retention capacity (Kavitha et al., 2018). In addition, biochar in the soil improves the soil fertility by facilitating the biochemical cycling of phosphorus and nitrogen (Gul and Whalen, 2016). Also, the

inorganic elements (e.g. N, P, K, Na, Fe, etc.) present in the biochar supply nutrients to the plant. The addition of biochar to the soil helps in the uptake of heavy metals and chemicals from the soil and thus, reduces the detrimental effect of these pollutants on plant growth.

### **1.5.2 Heavy metal removal**

Biochar is a carbon-rich material which can be prepared from various organic waste residues discussed earlier. The use of biochar for heavy metal (Cr, Pb, Ni etc.) removal has received growing attention due to its exclusive features such as high carbon content and cation exchange capacity, large surface area and stable structure (Wang and Wang, 2019). In addition, the functional groups present on the biochar surface plays a crucial role as well in the adsorption process by making complexes with the metal ions. The main process for the removal of heavy metals or any other organic pollutant is adsorption. However, the removal of heavy metals greatly depends upon its type as well as on the type of biomass.

### **1.6 Origin of the problem**

There has been continuous depletion of available fossil fuels all around the world which may cause shortage of energy sources for the coming generation. Although, these fossil fuels are available in limited amount but these are mostly exploited to get energy. Apart from this, the pollution caused by them increases the global warming. On the other side, biomass which is both cheap and carbon neutral, is available in plenty as waste material. However, biomass has required properties that can become as a substitute to fossil fuels. Thus, based on these findings, the problem of waste minimization as well as an alternative to fossil fuel was considered for the research work.

### **1.7 Objective of the present work**

Based on the above background, the objectives of the research work are summarized below:

- To study the feasibility of sagwan sawdust for pyrolysis and determine kinetic and thermodynamic parameters for sagwan sawdust pyrolysis.
- To study the effect of operating parameters for pyrolysis experiment (Temperature, packed bed height, feed particle size, sweeping gas flow rate).
- To optimize the pyrolysis process parameters using response surface methodology (RSM) and study the characteristics of pyrolysis products (bio-oil, biochar and pyrolytic gas).
- To utilize the biochar as adsorbent for Cr(VI) removal from aqueous solution, optimize the adsorption process parameters using RSM and study the mechanism of the adsorption process.

To fulfil the above mentioned objectives, recent literatures were reviewed as discussed in the next chapter.



# CHAPTER 2

## Literature review

Through decades the bio-energy generation from biomass through pyrolysis has been studied by many researchers. The study focuses mainly on the conversion of biomass to value added products and their utilization in different fields. Mostly, the studies have been done in packed bed system varying different parameters to establish optimum experimental conditions for the product yield. Literature review dealing with the pyrolysis of biomass to useful products and utilization of biochar for Cr(VI) removal in batch mode is reported in this chapter. This chapter includes detailed review on selection of biomass for pyrolysis, mechanism of biomass pyrolysis, effect of process parameters on pyrolysis product characteristics and adsorption of Cr(VI) using biochar.

### **2.1 Literature review on biomass selection**

Biomass is defined as the complex bio-residue organic or non-organic solid products obtained from living or dead organisms which are available naturally. Key properties which a biomass should have for pyrolysis have been discussed in section 1.4.4. Based on these properties, the following section discusses some of the biomass used by many researchers for pyrolysis. **Table 2.1** shows the characteristics of some of the biomass which was taken as feedstock for pyrolysis by other researchers. Generally the higher energy content in solid fuels is found with higher carbon content. However, in reverse, high amount of MC and AC would lead to decrease of energy content in biomass.