

Chapter 1

Introduction

1.1 Background and problem statement

The economic and social development of a nation is decided by the resources and its utilization for production of energy. The demand for energy in the world is increasing day by day due to increasing global population and ever-increasing living standard of people (Singh et al., 2020a). Considering worldwide population from 2015 to 2040, World Bank predicted that total population will increase from 7.3 to 9.1 billion (Fig. 1.1a). In recent years the world is facing major energy crisis. According to international energy outlook (IEA) 2016, total world energy consumption is projected to rise from 549 quadrillion Btu in 2015 to 812 quadrillion Btu in 2040 with an increase of around 48% (Fig. 1.1b) (Mokheimer et al., 2017). To fulfill our energy demand, we are highly dependent on the conventional sources of energy like coal, petroleum and natural gas. Fig. 1.2 clearly shows that fossil-derived fuels contribute to 87 % of total energy demand in India, while it contributes to 81.2 % of total energy demand of the world. The use of conventional energy resources like coal and crude petroleum produce greenhouse gases which severely affect the environment by increasing the temperature level of the earth. According to international energy outlook (IEA) 2016, world energy related CO₂ emission increases from 32.2 billion metric ton in 2012 to 43.2 billion metric ton in 2040 with an increase of around 34% (Mokheimer et al., 2017). The reserves of fossil fuel such as coal, petroleum, and natural gas are limited and large exploitation along with complete dependence on the fossil fuel can diminish the fossil fuel reserve. Also, application of fossil fuels severely affects the

environment by harmful emission such as SO_x , NO_x , greenhouse gas (CO_2) and particulate matters (Chen et al., 2011; Phanphanich & Mani, 2011; Yue et al., 2017).

Hence, the world is moving towards the exploration of non- conventional energy sources.

The major thrust on research and technology of present era is how to extract maximum amount of energy from renewable energy resources in the most efficient, economical, and sustainable way. Though we have wind, solar, geothermal, hydrothermal etc. as renewable energy sources, however, among them biomass is the most abundant worldwide and easily available. The consideration of biomass as a carbon-neutral fuel and its quality to emit lesser amount of sulfur and nitrogen makes it important source for the production of bio-energy (Giudicianni et al., 2013).

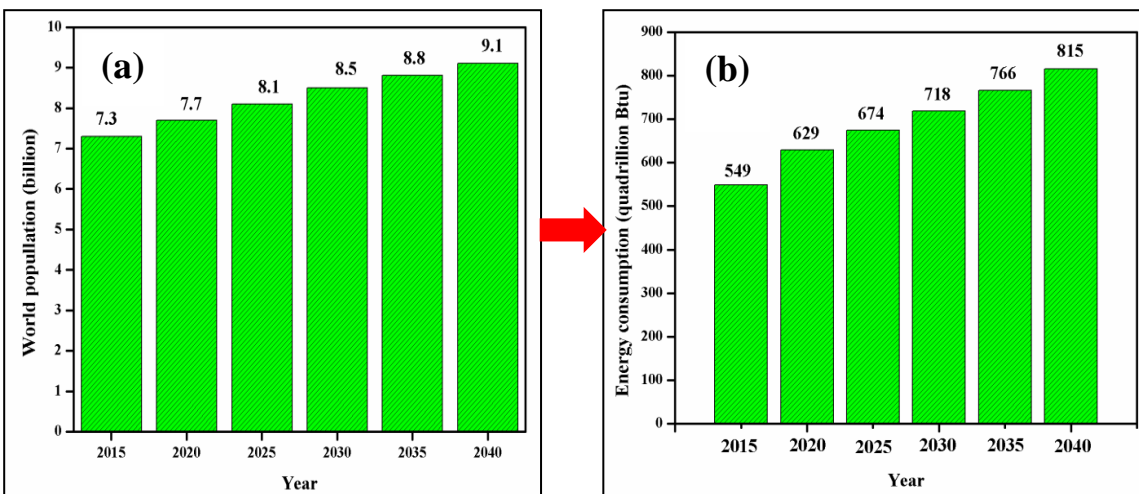


Figure 1.1 (a) Trend of increase in world population from 2015 to 2020 and (b) increase in demand of energy from 2015 to 2020

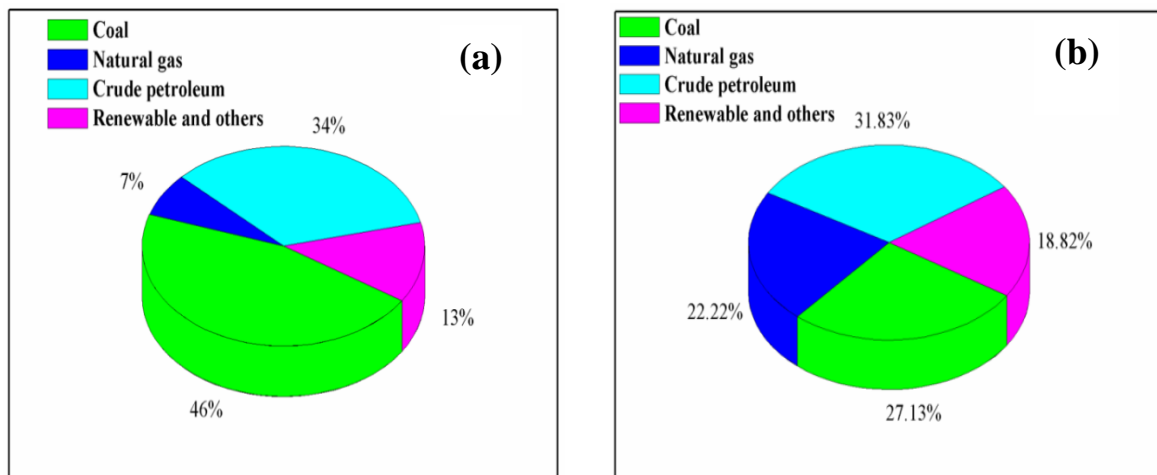


Figure 1.2 Major sources of energy in (a) India and (b) World

1.2. Biomass as a source of renewable energy

As the name suggests, biomass is biological mass i.e., the organic matter which is derived from living or recently living organism is called biomass. It can be microorganism, plant or animal in a given area of the ecosystem at a particular time. Various examples of biomass include food crops, crops for energy like switch grass or prairie perennials, crop residues like corn stover, wood waste and by-products (both mill residues and traditionally noncommercial biomass in the woods), and animal manure. In recent years the concept of biomass has widened and includes construction debris, municipal solid waste, algae, yard waste and food waste. Woody biomass is preferred over food crop biomass since it contains larger amount of energy than food crop biomass and lower application of fertilizer and pesticides for woody biomass (van der Stelt et al., 2011).

1.2.1 Components of biomass

Basic components of biomass can be classified as lignocellulosic and non-lignocellulosic. The lignocellulosic part of the biomass consists of mainly non-starch and fibrous part of the plants which are mainly polymer and joined with each other to different degree and with varying composition depending on the type and source of biomass. It consists of cellulose, hemicellulose and lignin which account for 40-60, 20-40 and 10-25 wt % of the total lignocellulosic biomass (Agbor et al., 2011; Carere et al., 2008; Chandra et al., 2007; Yang et al., 2007). Typical composition of various biomass samples are presented in Table 1.1. Non- lignocellulosic part of the biomass, on other hand, contains non-cellulosic material like sugar, starch, protein and fat. Cellulose, hemicellulose, and lignin are the main fiber cell-wall components present in the biomass and they show different reactivity during thermochemical conversion processes (Chen et al., 2013).

Table: 1.1 Constituents of selected biomass (wt% composition)

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Wheat straw	41.3	30.8	7.7	(Bridgeman et al., 2008)
Reed Canary Grass	42.6	29.7	7.6	(Bridgeman et al., 2008)
Rice Straw	34.0	27.2	14.2	(Mohan et al., 2006)
Birch Wood	40.0	25.7	15.7	(Mohan et al., 2006)
Corn cobs	50.5	31.0	15.0	(Worasuwannarak et al., 2007)
Cotton linter	89.7	1.0	2.7	(Dorez et al., 2014)

Sugar cane	51.8	27.6	10.7	(Dorez et al., 2014)
Switch grass	35.8	21.5	21.1	(Jung et al., 2015)
Bamboo	54.6	11.4	21.7	(Dorez et al., 2014)
Willow	42.4	20.6	21.1	(Stolarski et al., 2013)
Coconut	51.3	11.7	30.7	(Dorez et al., 2014)

1.2.1.1 Cellulose

Long chain polymers of saturated linear polysaccharide (glucose) which are linked together by inter-molecular and intra-molecular hydrogen bonding are called cellulose (Ghetti et al., 1996; Pordesimo et al., 2005; Tillman, 2000) Cellulose molecules are having fibrous macromolecular structures with smooth surface and composed of semi crystalline arrays of β -1,4 glucan chains having molecular weight of 500,000 in which D- Glucose is linked together by β -Glucosidic linkage (Chen & Kuo, 2010; Raveendran & Ganesh, 1998). Crystalline structure of cellulose provides higher packing density which increases the strength of biomass (Mohan et al., 2006).

1.2.1.2 Hemicellulose

Hemicelluloses, also known as polyose (Mohan et al., 2006) are generally heteropolysaccharides like hexoses which contain glucose, mannose and galactose which account for 25-35% by mass in dry wood, 28% in softwood, and 35% in hardwood (Mohan et al., 2006; Raveendran & Ganesh, 1998; Scurlock et al., 2000). Hemicelluloses are those polysaccharides which provide strength to the plant wall. The important constituents of hemicellulose are xyloglucons, xylans mannans, glucomannans and β -glucanes. Hemicelluloses are highly branched, amorphous and irregular in structure and cracks are

found on the surface which makes it weakest part of the biomass (Huber et al., 2006; Raveendran & Ganesh, 1998; Yang et al., 2007). Hemicellulose has lower degree of polymerization in comparison to cellulose hence it undergoes thermal degradation easily.

1.2.1.3 Lignin

The third major constituent of biomass is lignin whose amount depends on the type of biomass (23-33% for softwood and 16-25% for hardwood) (Bridgewater, 2004; Mohan et al., 2006). Three dimensional irregular, amorphous polymers which are dominant in C-O-C and C-O linkage are generally known as lignin and mainly attached with four or more phenylpropane unit and different type of alcohol such as p-coumaryl, coniferyl and sinapyl as a basic constituent of lignin (Goyal et al., 2008; Huber et al., 2006; Jenkins et al., 1998; Khan et al., 2009; Mohan et al., 2006; Tillman, 2000). Lignin having hemispherical shape (Raveendran & Ganesh, 1998) embedded into the cellulose, consists of large group of aromatic polymers and it acts as a binder for the agglomeration of cellulosic component of biomass and it hold the micro fibrils with greater rigidity and provide strength to the cell wall of the biomass (Goyal et al., 2008; Mohan et al., 2006; Scurlock et al., 2000; Yaman, 2004). Thermal degradation of lignin occurs at wide range of temperature since different oxygen functional groups have different thermal stability.

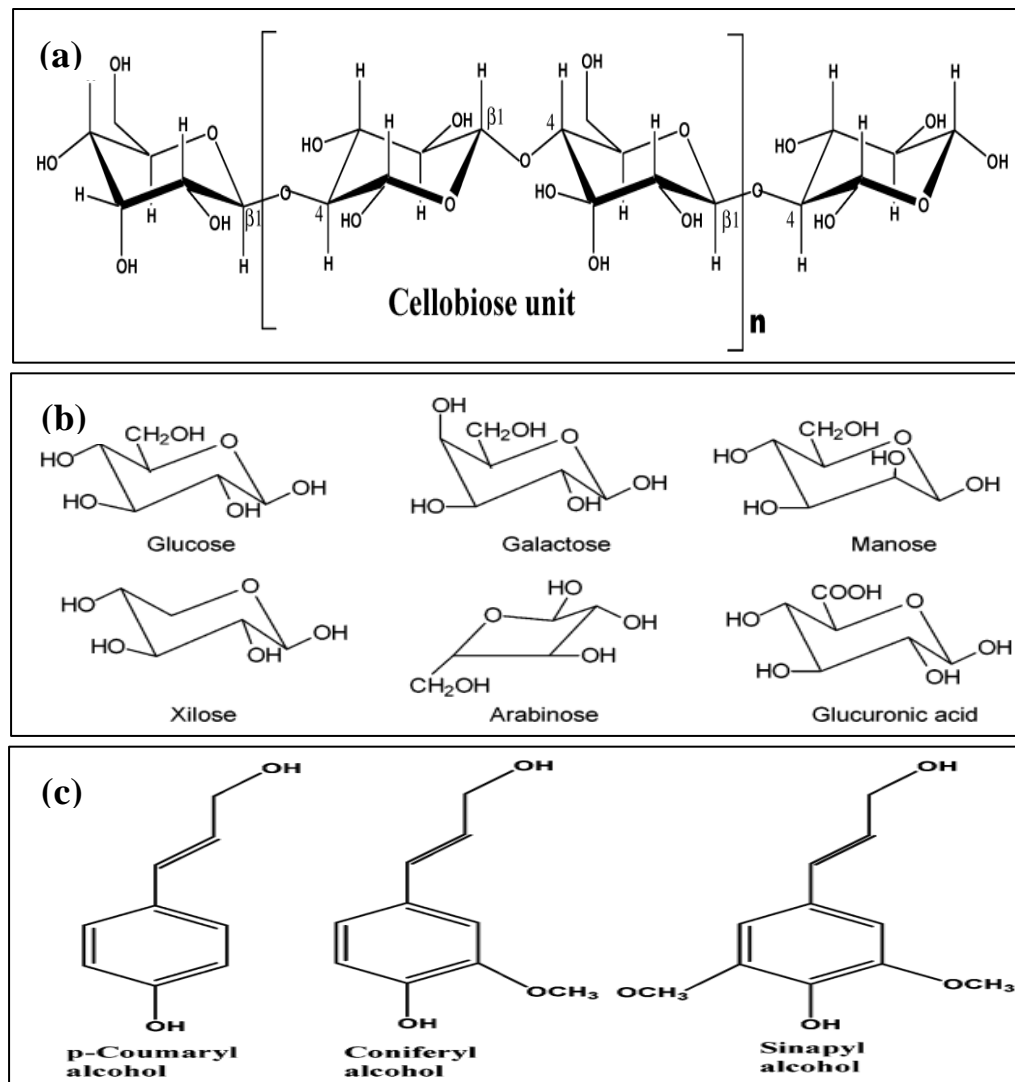


Figure 1.3 Major constituents of biomass (a) cellulose (b) hemicellulose and (c) lignin

1.2.1.4 Organic extractives

Biomass also contains some organic extractive materials. These materials can be identified in polar solvent (water, alcohol, methylene chloride) as well as non-polar solvent (toluene, n-hexane). The common extractive materials which are present in biomass are waxes (polyalkanes which is solid at room temperature), fats (polyalkanes which may be solid or

liquid at room temperature), alkaloids, proteins (amino acid, amines and carboxylic acid), phenolic, gum, resins (Mohan et al., 2006). These extractive materials act as intermediates in metabolism and as energy reserves. These extractive materials protect the biomass from external attack of microbes and insects (Mohan et al., 2006).

1.2.1.5 Inorganic minerals

Many inorganic minerals or metals are also present in biomass, which get concentrated in biochar after thermochemical process like torrefaction and pyrolysis. The common minerals present in the biomass are potassium (K), magnesium (Mg), calcium (Ca), phosphorus (P), and sodium (Na). The presence of these inorganic materials opens a wide range of application of bio char in different fields like catalysis, adsorption and fertilizer production.

1.3 Extraction of energy from biomass

Generally, energy from biomass can be extracted via two processes such as thermochemical conversion and biological conversion. However, thermochemical conversion of biomass has gained dominance over biological conversion because of its fast and efficient nature, higher conversion efficiency (Singh et al., 2020b), etc.

1.3.1 Thermochemical conversion of biomass

1.3.1.1 Pyrolysis of biomass

Pyrolysis is the thermal decomposition of lignocellulosic biomass in the presence of inert atmosphere. Temperature during the pyrolysis may vary from 200-1000 °C. The term devolatilization is also used as equivalent to pyrolysis but it is usually understood that devolatilization implies the presence of an oxidizing agent. The major products from

pyrolysis of biomass are bio-oil (liquid), biochar (solid) and noncondensable gases (Goyal et al., 2008). The process parameters which generally affect pyrolysis are temperature, retention time, heating rate, atmosphere inside the reactor, pressure and type of reactor. The products from pyrolysis of biomass depend on the process parameters and the composition of biomass. The pyrolysis gas contains mainly hydrogen, carbon dioxide, carbon monoxide, methane and light saturated and unsaturated hydrocarbons (Volpe et al., 2018). The liquid product from pyrolysis consists mainly of polyaromatic hydrocarbons (PAH), oxygenated aromatic compounds such as phenol and water (due to the moisture content of the fuel) (Yang et al., 2015). It is also called pyrolysis oil or bio-oil and can be upgraded to hydrocarbon liquid fuels for combustion engines, or directly used for power generation or heat (Kumar et al., 2020).

1.3.1.2 Combustion of biomass

Combustion means the complete oxidation of the biomass feedstock (Demirbas, 2007) in presence of stoichiometric or excess air/oxygen. It is one of the most traditional processes for extraction of energy from lignocellulosic biomass (Zhang et al., 2010). The process produces very hot gases that can be used to generate steam or to provide heat to a Sterling engine. The combustion process of biomass is far better known than the other thermochemical processes as far as the heat generation is concerned; however, many harmful gaseous products (NO_x and SO_x emissions) are generated during combustion of biomass.

1.3.1.3 Liquefaction of biomass

The liquefaction of biomass is similar to pyrolysis, while, it differs in operating conditions (Zhang et al., 2010). The process takes place at low temperatures (250-350 °C) and high pressure (100-200 bar) (Demirbaş, 2000). During liquefaction, biomass gets converted to water and fragments of small molecules which finally get converted into bio-oil by re-polymerization reaction (Demirbaş, 2001). With respect to pyrolysis, liquefaction has been considered as more complex and challenging process because of operating conditions, feedstock conditions and operational cost (Demirbaş, 2001).

1.3.1.4 Gasification of biomass

The gasification of biomass is an endothermic process where carbonaceous biomass is transformed mainly into mixture of combustible gases such as CO, CO₂, CH₄, and H₂ in presence of partial supply of O₂, CO₂ and H₂O (Zhang et al., 2010). When O₂ is used in gasification process, it is similar to combustion; however, partial combustion of biomass takes place in case of gasification. Also, the aim of combustion is to generate heat from biomass, while, gasification is used for generation of valuable gaseous products which can be used for direct combustion or can be used for other purposes (Rezaiyan & Cheremisinoff, 2005). In addition, gasification can be considered as more environmental-friendly process because of lower emissions of toxic gases like SO_x and NO_x (Rezaiyan & Cheremisinoff, 2005).

1.4 Demerits of raw biomass

Regardless of large availability, easy accessibility, and inexpensive in nature, biomass is burdened with many inherent disadvantages. Table 1.2 presents various drawbacks

associated with raw biomass and their effect on process as well as products. These drawbacks hinder the direct application of biomass in thermochemical conversion processes. It is therefore essential to improve the quality of biomass through pretreatment process and check the suitability of treated biomass in term of fuel and flow properties, before it can be used in thermochemical conversion process efficiently.

Table: 1.2 Demerits of raw biomass (adopted from (Bach & Skreiberg, 2016), (Dai et al., 2019))

Parameter	Associated drawbacks
High moisture content	<ul style="list-style-type: none"> ● Reduces the efficiency of the process ● Increases drying energy requirement ● Increases corrosion because of condensation of water in flue gas ● Possibility of biological degradation ● Reduces the heating value ● Increases storage and transportation cost
Heterogeneity	<ul style="list-style-type: none"> ● Creates wide variation in the property
High Oxygen content	<ul style="list-style-type: none"> ● Reduces the number of high energy C-H bond ● Reduces heating value and thermal stability ● Creates poor energy density
Poor Grindability	<ul style="list-style-type: none"> ● Increases the grinding energy ● Poor grindability produces coarser particle
Hygroscopic nature	<ul style="list-style-type: none"> ● Prone to biological degradation due to absorption of moisture
Low bulk and energy density	<ul style="list-style-type: none"> ● Increases the storage and transportation cost ● High feeding capacity required

1.5 Pretreatment of raw biomass

The raw biomass commonly requires certain physical and chemical modification to improve its inherent characteristics prior to its utilization in any thermochemical processes such as pyrolysis, gasification, combustion, etc. Generally, the pretreatment of biomass can be done through four methods namely; (1) physical methods, (2) thermal treatment, (3) chemical treatment, and (4) biological treatment (Kumar et al., 2020). Fig. 1.4 represents various types of pretreatment steps and their effects on structure of biomass.

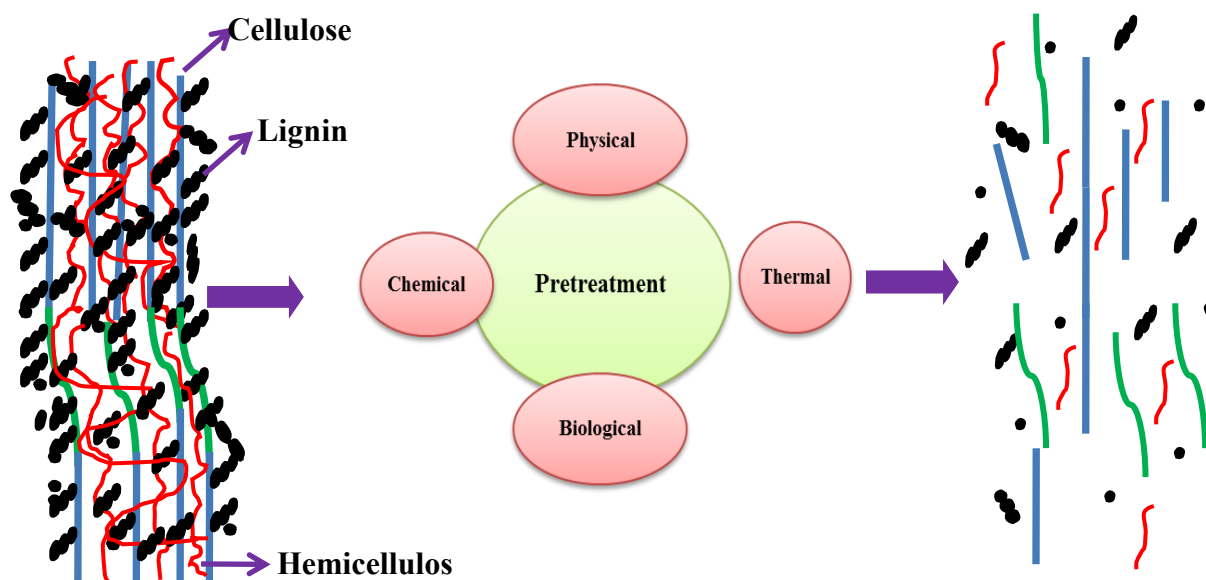


Figure 1.4 Effect of pretreatment on structure of biomass

1.5.1 Physical pretreatment

Generally, the physical pretreatment of biomass is associated with size reduction and/or densification. The size reduction of biomass particles facilitates better heat and mass transfer during thermochemical conversion process (Kumar et al., 2020). The size reduction of biomass also decreases the crystallinity of biomass (Alvira et al., 2010). The size reduction of biomass requires variety of resources such as milling, grinding, extrusion, and chopping machine which makes the process costly (Kumar et al., 2020). The prime concern of size reduction is to disintegrate the large biomass particles into smaller particles having uniform particle size and enhanced surface area. The higher surface area of biomass facilitates easy access to bacterial and enzymatic degradation of biomass, while in case of thermochemical processes, it provides better heat and mass transfer which provide uniform temperature distribution inside the particles (Kan et al., 2016). The densification of biomass increases the density and simplifies its storage and transportation. The densification of biomass is performed through compaction process by applying mechanical force on biomass and converting it into solid lumps called as briquettes.

1.5.2 Biological pretreatment

The biological pretreatment of biomass has been considered as the most economic, cost effective and environmental-friendly pretreatment process as it occurs at ambient temperature and atmospheric pressure and does not involve any chemical (Sindhu et al., 2016; Vasco-Correa et al., 2016). There are various microorganisms such as bacteria and fungi which have high potential to degrade biomass; however white and brown rot fungi have been utilized for pretreatment of biomass (Yang et al., 2011; Yu et al., 2013). Due to

action of microorganism, the complex lignocellulosic biomass unit such as lignin and cellulose break into their monomeric units through degradation or depolymerization. Subsequently, the activation energy of pretreated biomass decreases during thermochemical conversion (Vasco-Correa et al., 2016). The biological pretreatment process has certain drawbacks such as (1) time-consuming process, (2) microorganisms are very temperature-sensitive, (3) large space is required for biological pretreatment, (4) some amount of biomass can be consumed by microorganisms which lead to the decrease in mass yield of pretreated biomass (Agbor et al., 2011). These drawbacks limit the application of biological pretreatment process at industrial scale.

1.5.3 Chemical pretreatment

Chemical pretreatment of biomass is an important method that may overcome the recalcitrant nature of biomass. It involves the treatment of biomass with different kind of chemicals. Chemical treatment of biomass facilitates decomposition and decreases the thermal stability of biomass. Generally, acid and alkali treatment are the most prevalent treatments which fall under chemical pretreatment method. The biomass as a feedstock in thermochemical conversion process contains many inorganic minerals such as chlorides, sulphates, phosphates, and carbonates, etc. (Kumar et al., 2020). These minerals might affect the thermochemical processes through its catalytic activity or soluble minerals may be present in the products. For instance, presence of minerals in bio-oil may decrease the stability and create aging and corrosiveness in bio-oil through polymerization or condensation reaction. Therefore, removal of these minerals is of prime importance to increase the applicability of bio-oil. The pretreatment of biomass with dilute acids such as H_2SO_4 , HNO_3 , H_3PO_4 and HCl can be potentially used to remove the minerals present in

biomass (Lloyd & Wyman, 2005). The acid pretreatment of biomass basically cleaves the chemical bonds associated with hemicellulose, cellulose and lignin. In similar manner, the alkali pretreatment of biomass may also be carried out with the help of chemicals such as NaOH, KOH, and Ca(OH)₂. The alkali pretreatment of biomass facilitates the removal of lignin and increases the digestibility of cellulose (Kumar et al., 2020). Basically, the alkali treatment of biomass breaks the ester and glycosidic bonds between hemicellulose and lignin, while keeping most of the cellulosic part of biomass intact (Mohammed et al., 2017a). The treatment of biomass with alkali results in swelling of cellulose, which can reduce the degree of polymerization and decrystallization of cellulose leading to increase in surface area of biomass (Baruah et al., 2018). The major challenge associated with chemical treatment is corrosion of process reactor system for pretreatment, disposal of chemicals, and cost of chemicals which may increase the overall cost of chemical pretreatment process (Mohammed et al., 2017a).

1.5.4 Thermochemical pretreatment

The thermochemical pretreatment of biomass generally involves two processes; drying and torrefaction (Edelmann et al., 2005). Drying is used to remove the surface moisture from the biomass.

1.5.4.1 Torrefaction of biomass

Torrefaction is defined as the mild pyrolysis in the temperature range of 200-300 °C under the atmospheric pressure in the presence of inert with a low heating rate (< 20 °C/min). The retention time of biomass in the reactor should be around 15-60 min. After the torrefaction process, quantity of initial biomass reduces up to 40% and energy decreases around 10-

15% (Granados et al., 2016). Torrefaction occurs via drying, decomposition, devolatilization and depolymerization of biomass. In drying process most of the bound water is released and this takes place below 200 °C. According to Deng et al. (Deng et al., 2009a) during torrefaction, drying is supposed to be more destructive since it breaks the inter and intra molecular hydrogen bonds, C-O and C-H bonds which lead to the removal of hydrophilic and oxygenated compounds and makes the biomass black in color, hydrophobic in nature and high energy dense. Main products of torrefaction are torrefied biomass in solid form, permanent gases like hydrogen (H₂), Carbon dioxide (CO₂), Carbon monoxide (CO) and hydrocarbon like Methane (CH₄). Along with these products a condensable mixture containing mostly water, organic compound and lipid are also produced. Among all three products, torrefied biomass is the main product since it accounts for 70% weight of the total biomass and retains around 90% of the total energy of the biomass (Bach & Skreiberg, 2016). Unlike pyrolysis, the main aim of torrefaction is to maximize the yield of solid product, hence torrefaction is performed under low heating rate (Chen & Kuo, 2011). The main objective of torrefaction process is to enhance the quality of biomass for thermochemical process like pyrolysis and gasification. A torrefied biomass is quite suitable for pelletization, briquetting, pyrolysis, gasification and co-firing in thermal power plants (Bridgeman et al., 2010b; Felfli et al., 2005b). The limitations associated with biomass may be removed by torrefaction. It makes the biomass moisture free, hydrophobic solid product, decreases grinding energy, increases energy density, decreases O/C ratio and makes the biomass suitable for storage and transportation. Along with above improvements, it also enhances the particle size distribution, combustion with less smoke; in gasifier, combustion shifted to higher temperature zone, and increases

resistance to biological degradation. Torrefaction makes biomass brittle by removing fibrous and tenacious structure and hydrophobic nature. Due to this, grinding energy requirement for biomass reduces. Due to hydrophobic nature of torrefied biomass, it absorbs less moisture than the raw biomass which is around 3% (Chen et al., 2016b; Granados et al., 2016). Addition to above property, torrefaction provides uniformity, resistance to biological decomposition when exposed to external environment and high energy density to biomass (Granados et al., 2016). The decrease of O/C ratio and increase of energy density of biomass is mainly due to removal of volatile matter and light gases during torrefaction process.

1.6 Characteristics of torrefied biomass

Torrefaction is used as a pretreatment process to upgrade the quality of raw biomass. The most valuable product from torrefaction, considering it as a pretreatment, is torrefied biomass. The quality of torrefied biomass can be examined by its fuel and flow properties. The fuel properties of torrefied biomass can be interpreted by proximate and ultimate analyses, higher heating value, chemical composition and surface morphology. In addition, some fuel properties are also derived from proximate and ultimate analyses such as volatile ignitability, combustibility index, and fuel ratio. The flow properties of torrefied biomass such as Hausner ratio, cohesion coefficient, Carr compressibility index, and angle of repose play an important role during blending of torrefied biomass with other biomass, plastics co-pyrolysis and coal in co-firing in thermal power plants. The flow characteristics of raw and torrefied biomass can be characterized by Hausner ratio (HR), cohesion coefficient (C), Carr compressibility index (CCI) and angle of repose (Lumay et al., 2012). The angle of repose is defined as the steepest angle at which a stack of biomass particle can remain

stable without slumping (Rous et al., 2014). It may range from 0° to 90° . Different methods such as revolving cylinder method, tilting box method and fixed funnel method for analyzing the angle of repose have been described in literature (Cai et al., 2017; Rous et al., 2014). However, in this thesis ASTM-C144 associated with fixed funnel method was employed to investigate angle of repose. In fixed funnel method (Fig. 1.5), the biomass particles obtained after sieving were poured very slowly through a funnel which was fixed through a stand at a certain height (H) from the base. The biomass coming out of funnel takes the shape of a cone. The pouring from the funnel was stopped when cone pile touched the lower tip of the funnel which was at a predetermined height (H). By measuring the radius of base of the cone, the angle of repose can be calculated using Eqs. (1.1). Szalay et al. (Szalay et al., 2015) derived a correlation for cohesion coefficient and concluded that cohesion coefficient depends on angle of repose and particle size of biomass. The cohesion coefficient was calculated by Eqs. (1.2). HR and CCI vary with densities (bulk and tapped density) of biomass. HR and CCI of DAN and TAN were obtained by employing Eqs. (1.3) and (1.4).

$$\text{Angle of repose } (\theta) = \tan^{-1} \left(\frac{H}{R} \right) \quad \text{Where } R = D/2 \quad (1.1)$$

$$\text{Cohesion coefficient } (C) = \frac{1}{2}d \left(\sqrt{\cos^2\theta + \frac{4\sin\theta}{d}} - \cos\theta \right) \quad (1.2)$$

$$\text{Hausner ratio } (HR) = \frac{\rho_{Tb}}{\rho_b} \quad (1.3)$$

$$\text{Carr compressibility index } (CCI) = \left(1 - \frac{\rho_b}{\rho_{Tb}} \right) \times 100 \quad (1.4)$$

To evaluate the suitability of torrefied biomass as good quality solid bio-fuel, Conag et al. (Conag et al., 2017) mentioned combustion indices such as fuel ratio (FR), combustibility index (CI) and volatile ignitability (VI) and they were enumerated by using Eqs. (1.5)-(1.6).

$$\text{Fuel ratio, } FR = \frac{FC_{db}}{VM_{db}} \quad (1.5)$$

$$\text{Combustibility index } CI \text{ (MJ/kg)} = \frac{HHV_{db}}{FR} \times (115 - Ash_{db}) \times \frac{1}{105} \quad (1.6)$$

$$\text{Volatile ignitability, } VI \text{ (MJ/kg)} = \left[\frac{HHV_{db} - 0.338FC_{db}}{VM_{db} + M_{db}} \right] \times 100 \quad (1.7)$$

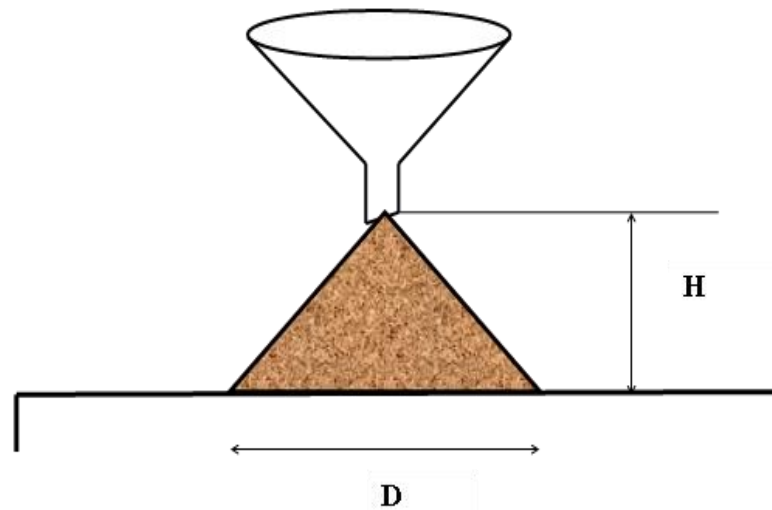


Figure 1.5 Schematic for calculation angle of repose

1.7 Application of biochar from pyrolysis of biomass

The pyrolysis of biomass yields three types of products, namely, bio-oil, biochar, and gaseous products. Nowadays, biochar has gathered colossal attention in wastewater treatment processes because it is chemically stable and environmentally friendly (Lyu et al., 2018; Zhang et al., 2020). It is a low cost adsorbent having high surface area, porosity, and higher carbon content (Trakal et al., 2014). The high functionality of biochar surface imparts adsorption potential for toxic substances present in wastewater (Uchimiya et al., 2010). Biochar from thermochemical processes has also been chemically engineered to improve its adsorption capacity (Lyu et al., 2018). However, chemically treated biochars have certain limitations, such as cost and associated problems of release of chemicals (Lyu et al., 2018).

1.8 Structure of thesis

This thesis entitled “**Pyrolysis of torrefied *Acacia nilotica* and application of biochar for removal of methylene blue dye from aqueous solution**” has been divided into eight chapters.

Chapter 1 is related to introduction section where general information about limitations of fossil derived fuels, basic information about biomass, extraction of energy from biomass, limitations of biomass, pretreatment of biomass, and application of biochar has been discussed.

Chapter 2 contains the detailed literature review of torrefaction process, pyrolysis process, and application of biochar for removal of methylene blue dye.

Chapter 3 is related to the torrefaction of *Acacia nilotica* in fixed-bed reactor and investigation of fuel and flow properties of torrefied biomass. The physicochemical

characteristics of raw biomass, torrefied biomass and coal have been compared to check the suitability of torrefied biomass in pyrolysis process.

Chapter 4 is related to pyrolysis of raw and torrefied biomass in thermogravimetric analyzer followed by estimation of kinetic parameters, thermodynamic parameters, and solid state reaction mechanism.

Chapter 5 is related to the optimization of process parameters (temperature, retention time, and heating rate) for torrefaction process using response surface methodology. The physicochemical characteristics of raw biomass and torrefied biomass obtained at optimum condition have been compared.

Chapter 6 is related to the pyrolysis of torrefied biomass obtained at optimum condition of torrefaction. The process parameters (temperature, retention time, heating rate, and sweeping gas flow rate) have been optimized using response surface methodology for maximum yield of pyrolysis oil. The pyrolysis of raw biomass at obtained optimum condition is also performed and characteristics of pyrolysis products (pyrolysis oil, biochar and pyrolytic gases) have been compared with products from pyrolysis of torrefied biomass at optimum condition.

Chapter 7 is related to the comparative study for removal of methylene blue dye from aqueous solution using biochar as an adsorbent from pyrolysis of raw and torrefied biomass obtained at optimum condition of pyrolysis for maximum pyrolysis oil yield.

Chapter 8 is related to the summary of results from thesis and scope of future work.