Chapter-2

Literature Survey

2.1 Biomass classification

Because of the significant disparities in biomass variety and amount, as well as their diverse

compositional features, there is no unambiguous manner of classifying biomass; therefore, they

can be classed differently, depending on purpose and scope. Biomass is often categorized into

different groups based on its origin, function, and end products (Fig. 2.1). The typical chemical

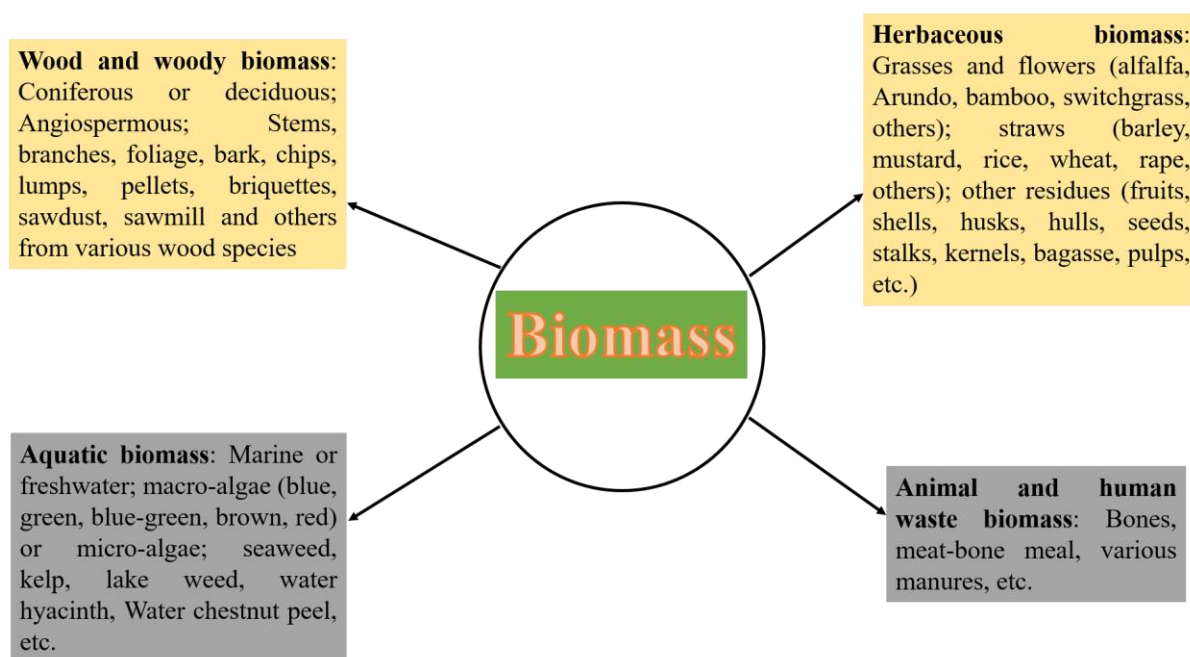compositions of several biomass classes are listed in Table 2.1.

Wood and woody biomass: Coniferous or deciduous; Angiospermous; Stems, branches, foliage, bark, chips, lumps, pellets, briquettes, sawdust, sawmill and others from various wood species

Herbaceous biomass: Grasses and flowers (alfalfa, Arundo, bamboo, switchgrass, others); straws (barley, mustard, rice, wheat, rape, others); other residues (fruits, shells, husks, hulls, seeds, stalks, kernels, bagasse, pulps, etc.)

Aquatic biomass: Marine or freshwater; macro-algae (blue, green, blue-green, brown, red) or micro-algae; seaweed, kelp, lake weed, water hyacinth, Water chestnut peel, etc.

Animal and human waste biomass: Bones, meat-bone meal, various manures, etc.

Fig. 2.1: Biomass classification: groups, varieties, and species

Table 2.1: Typical chemical composition of different biomass groups

Properties	Wood & woody	Herbaceous	Aquatic	Animal & human waste
Carbon (%)	49-57	42-58	27-43	57-61
Hydrogen (%)	5-10	3-9	4-6	7-8
Nitrogen (%)	<1-1	<1-3	1-3	6-12
Sulfur (%)	<1-1	<1-1	1-3	1-2
Oxygen (%)	32-45	34-49	34-46	21-25
Moisture (%)	5-63	4-48	8-14	3-9
Volatile matter (%)	30-80	41-77	42-53	43-62
Ash content (%)	1-8	1-19	11-38	23-34

Fixed carbon (%)	6-25	9-35	22-33	12-13

2.2 Physicochemical characterization of biomass

Physicochemical characterization of lignocellulosic biomass is the initial and most important step in demonstrating the biomass for conversion into sustainable fuels and valuable compounds. The values of these characteristics suggest whether biomass should be investigated further for conversion using an adequate thermal process. A substantial amount of published literature is available on the physicochemical characterization including proximate-ultimate analysis and fiber analysis of different types of biomass. Appendix A provides a detailed review of the available published literature. The values of moisture content varied between 1.3 – 24.6 wt. %, volatile matter (32.2 – 83 wt. %), ash content (0.18 – 42.3 wt. %), and fixed carbon (0.1 – 29.45 wt. %). The elemental composition has also fluctuated, ranging from 2.94 to 38.6% hydrogen, 6.7 to 76.83% carbon, 0 to 34.8% nitrogen, 0.1 to 63.03% oxygen, and 0.0 to 2.42% sulfur.

2.3 Kinetic analysis of biomass

For designing a pyrolysis reactor, it is necessary to achieve a good understanding of the kinetic parameter. The activation energy, pre-exponential factor, and reaction order are all essential kinetic factors. Thermogravimetric analysis (TGA) is a frequently used technique to understand the thermal degradation kinetic parameters and the prevailing reaction mechanism, utilizing only a small amount of the sample [56]. There are two types of thermogravimetric analysis: non-isothermal and isothermal. A non-isothermal TGA analysis is recommended over isothermal because isothermal procedures are not feasible at higher temperatures due to large non-isothermal heat-up and cool-down durations, the kinetic parameters at low heating rates are problematic because of weight loss during the heat-up time, and there is a nearly non-zero extent of conversions [57]. The TGA results are used to determine model-free and model-fitting

methods [58]. Though the application of the model fitting method allows the determination of a single value for activation energy throughout the process, increasing conversion changes pertaining to the reaction mechanism are difficult to determine and result in unrealistic values of kinetic parameters [59]. The application of the model-free methods permits the estimation of the activation energy value at different points during the conversion process [60]. The literature regarding the kinetic parameters of the previously published studies is presented in Appendix B.

2.4 Pyrolysis of biomass

Several researchers investigated the pyrolysis behavior of different types of biomasses in laboratory-based fixed and fluidized bed reactors using the information gained from TG/DTG analyses. Appendix C summarizes and discusses the operating conditions and results of available published work on batch pyrolysis studies.

Mishra et al., explored pyrolysis of different types of low-value waste seed biomass such as neem seed [61], *Manilkara zapota* seed [62], *Samanea saman* seed [63], *Cascabela thevetia* seed [64], *Madhuca longifolia* seed [65], and reported their excellent potential towards producing renewable fuel and chemicals. The optimum temperature for the pyrolysis of neem, *Manilkara zapota*, *Cascabela thevetia*, and *Madhuca longifolia* seed was 500°C; however, the optimum temperature for the pyrolysis of *Samanea saman* seed was 550°C. The optimum heating rate for the pyrolysis of neem, *Manilkara zapota*, *Cascabela thevetia*, and *Samanea saman* seed was 80°C/min; however, the optimum heating rate for the pyrolysis of *Madhuca longifolia* seed was 100°C/min. The optimum feedstock size for the pyrolysis of neem, *Manilkara zapota*, and *Samanea saman* seed was 0.5mm. The bio-oil obtained has been characterized based on their physicochemical characterization and it was found that bio-oil had higher oxygen, lower heating value, higher viscosity, and lower pH. The concentration of flue gases increased above the optimum temperature in all the cases because of the rapid

endothermic decomposition of biomass. The solid product decreased with increasing temperature (higher heat and mass transfer between biomass) because of increased combustion efficiency. Mishra et al., also noticed that, because of the higher heat and mass transfer efficiency between biomass particles, smaller particle sizes produced the most pyrolytic liquid, resulting in complete combustion of biomass. The generation of flue gases was higher at a smaller particle size (0.5 mm) due to rapid endothermic decomposition of biomass at optimum conditions, whereas the formation of char increased beyond 0.5 mm particle size due to partial combustion of biomass.

Goutam et al., [66] optimized the pyrolysis condition for the teak sawdust, such as temperature (400 – 700°C), sweeping gas flow rate (150 – 250 ml/min), bed height (2 – 8 cm), and particle size (0.18 – 0.60 mm). The optimum condition for the highest bio-oil yield (48.8%) was a temperature of 600 °C, an inert flow rate of 150 ml/min, a packed bed height of 8 cm, and a particle size of 0.18 – 0.25 mm. The FTIR analysis confirmed the existence of different functional groups and GCMS analysis confirmed the presence of aliphatic, aromatic, and oxygenated compounds in the bio-oil.

Biswas et al. [67] investigated the pyrolysis of conventional biomass in a fixed bed reactor at temperatures ranging from 300 to 350°C, 400°C, and 450°C. Agricultural residues such as corn cob, wheat straw, rice straw, and rice husk revealed optimum temperatures of 450, 400, 400, and 450°C, respectively. The highest bio-oil yields were obtained for corn cob, wheat straw, rice straw, and rice husk, which were 47.3, 36.7, 28.4, and 38.1 wt. %, respectively. The effects of pyrolysis temperature and biomass type on pyrolysis product yield and composition were investigated. All bio-oil contents were primarily oxygenated hydrocarbons. Corncob bio-oil contained higher percentages of phenolic compounds than other bio-oils.

Kumar et al., optimized the pyrolysis condition of peanut shells [68] and *Saccharum munja* [69] using the response surface methodology (RSM) based on a central composite design in a fixed bed tubular reactor. The optimized condition for the pyrolysis of peanut shell to attain maximum bio-oil yield (43.24 wt. %) obtained was temperature = 650°C, N_2 flow rate = 100 ml/min and heating rate = 20°C/min, whereas the optimum condition for the pyrolysis of *Saccharum munja* to attain highest bio-oil yield (46 wt. %) was temperature = 525°C and residence time of 60 min. Appendix C summarizes the published data on batch pyrolysis of different biomass.

2.5 Bio-oil yield operating parameters for biomass pyrolysis

The yield of pyrolysis products is determined by several factors, for example, type of biomass, catalyst employed, heating rate, size of the feedstock, sweeping gas (N_2) flow rate, reactor layout, and temperature. Several researchers have investigated the effects of these variables on product yield. These are discussed briefly below.

2.5.1 Temperature

One of the most important and necessary parameters for pyrolysis is temperature. It provides the necessary heat energy for the thermal decomposition of biomass components. With increasing temperature, the pyrolysis process becomes more efficient because more energy is available for breaking the bonds of the constituents of biomass. Various researchers have reported that the temperature to obtain higher liquid yields ranges from 450 to 550°C; however, this temperature range is no longer applicable to all biomasses used. The rise in bio-oil yield with temperatures upto 550°C was due to complete pyrolysis (highest heat and mass transfer). At relatively lower temperatures (450°C), biochar yield is enhanced. In contrast, gas and bio-oil yields were reduced, while at the temperature (>600°C), the gas yield was enhanced, and the bio-oil yield was reduced. This occurs as a result of partial pyrolysis (lower mass and heat

transfer) at lower temperatures, as opposed to fast endothermic degradation of biomass into condensable to non-condensable gases at higher temperatures.

Tsai et al. [70] found that increasing the temperature from 400 to 500°C increased the yield of bio-oil for rice husk pyrolysis from 11.26 to 35.92%. However, the yield increased at a slow rate with temperature, reaching up to 40% at 800°C. Though most researchers have reported an increase in bio-oil yield with increasing temperature, some have reported that beyond the optimum temperature, the yield decreases due to secondary reactions that result in increased gas formation. For example, Mishra et al., reported that, at optimum temperature (500°C) of pyrolysis of neem [61], *Manilkara zapota* [62], *Cascabela thevetia* [71], and *Madhuca longifolia* seed [65], the bio-oil yield was maximum. This is due to the total breakdown (highest mass and heat transfer) of biomass. However, when the temperature is lower than the optimal temperature, bio-oil yield decreases because heat and mass transfer between biomass particles is reduced, resulting in lower quantities of hot volatiles from the insufficiently heated biomass. Further, at elevated temperatures, gas yield is enhanced because of the rapid endothermic destruction of biomass.

2.5.2 Heating rate

Mishra et al., studied pyrolysis of *Manilkara zapota* [62], *Cascabela thevetia* [71], *Samanea saman* [63], and *Madhuca longifolia* seed [65] in the heating range of 50 to 120°C/min and reported optimum heating rate for pyrolysis of *Manilkara zapota*, *Cascabela thevetia*, and *Samanea saman* seed was 80°C/min; however, the optimum heating rate for the pyrolysis of *Madhuca longifolia* seed was 100°C/min. Tsai et al. [70] changed the heating rate from 100 to 500°C/min while studying the pyrolysis of rice husk in a fixed bed reactor and found that the bio-oil yield peaked at 200°C/min and remained constant at higher rates. With an increase in the heating rate, Uzun et al. [72] saw an augmented reduction in the water content in the bio-oil, resulting in a higher quality bio-oil. Fast heating most likely prevents secondary

dehydration reactions, resulting in a decrease in water content in the bio-oil. At higher heating rates, the oxygen content of the pyrolysis liquid product is also reduced.

2.5.3 Carrier gas (Inert) flow rate

The flow rate of inert gas during biomass pyrolysis is an important parameter that influences the yield of bio-oil and other pyrolysis products. It changes the residence time of the vapor formed inside the reactor during pyrolysis, affecting the vapor's ability to initiate secondary reactions such as thermal cracking, depolymerization, and condensation of the char residue, resulting in a decrease in bio-oil yield [73]. A higher inert gas flow in the process results in a shorter vapor residence time in the hot pyrolysis zone, which resists secondary reaction formation and, as a result, increases bio-oil yield. Pattiya et al. [74] discovered that increasing gas flow from 1 l/min to 1.5 l/min increased liquid yield, but increasing to 3 l/min had no effect on yield. Islam et al. [75] investigated the effect of vapor residence time in sugarcane bagasse pyrolysis in a fixed bed reactor and discovered that increasing the vapor residence time from 5 to 20s reduces the liquid and char yields while increasing the gas yield. Numerous studies investigated the effect of N_2 flow in pyrolysis discovered that increasing the flow of inert gas improves bio-oil yield. A high gas flow, on the other hand, reduces the liquid yield due to complete condensation of the vapors, which increases the gas yield in the process, and part of the biomass can also be swept out of the reactor before pyrolysis is completed [76].

2.5.4 Feedstock size

Because biomass is a poor conductor of heat, heat transmission during pyrolysis is sluggish. As a result, particle size has an impact on the bio-oil yield. It is also important to avoid heat transmission issues [73]. Mishra et al., [61] reported that due to inadequate heat and mass transport, larger particle size lowered liquid output, resulting in incomplete burning of biomass. Because of the better heat and mass transfer efficiency between biomass particles, smaller particle sizes created the most pyrolytic liquid, resulting in total biomass degradation. The

creation of char increased beyond 0.5 mm particle size owing to partial burning of biomass. Still, the generation of flue gases was more significant at a smaller particle size (0.5 mm) due to the fast endothermic degradation of biomass under optimal conditions. However, in the pyrolysis of palm shells, Abnisa et al. [77] discovered the opposite effect, when particle size was increased from 0.5 to 2 mm, there was an increase in liquid yield (69.6%). Smaller particles are desirable for pyrolysis because they heat up faster and more evenly. However, minute particles can limit the liquid yield in pyrolysis because biomass degradation happens fast, leaving little time for secondary reactions amongst vaporous products, resulting in an increase in gas yields and a drop in liquid and char yields [75].

2.5.5 Residence time

The pyrolysis product distribution is also influenced by reaction time. The reaction time of the pyrolysis process is the amount of time that the process is kept at a steady temperature. The reaction period in a batch (fixed bed reactor) pyrolysis process should be adequate to obtain the desired result. Secondary reactions of pyrolysis vapors, such as carbonization, gasification, and thermal cracking, result in decreased bio-oil output with longer reaction times [78]. Abnisa et al., [77] experimented with residence times ranging from 30 to 150 minutes. The bio-oil production grew steadily as reaction periods increased from 30 to 60 minutes, while the liquid yield remained constant after 60 minutes. The longer the reaction time, the higher the expense of the experiments.

2.6 Response surface methodology (RSM)

Converting biomass into bio-oil improves its efficiency in a variety of applications. As a result, optimizing by maximizing intended product quality and quantity while reducing costs and environmental issues is a critical challenge for engineers. For pyrolysis, optimizing these parameters is very necessary in order to get high efficiency, design, and economy of the reactor. Researchers generally used OFAT (one factor at a time) method to optimize the process

parameters. In this method, one factor varies, and the others remain constant. However, it is time-consuming and not feasible for complex processes such as pyrolysis [79]. As a result, the limitations of such traditional approaches may be avoided by optimizing the process parameters using statistical experimental design through response surface methodology (RSM). It is a statistical technique for optimizing process variables by considering several aspects simultaneously.

Mishra et al., studied the pyrolysis of *Cascabela thevetia* seed [71] to produce bio-oil. In this study, important pyrolysis parameters such as temperature, heating rate, and N_2 flow rate were optimized based on central composite design (CCD). The results determined that a temperature of 525 $^{\circ}$C, a heating rate of 75 $^{\circ}$C/min, and a nitrogen flow rate of 75 ml/min produced the most pyrolytic liquid (45.26 wt. %). The design of experiments revealed that reaction temperature was more important than heating rate and sweeping gas flow rate in the generation of pyrolytic oil.

Kumar et al., optimized the pyrolysis parameters (temperature and residence time) in the thermal degradation of *Saccharum munja* [69]. The central composite design based on RSM was utilized to optimize temperature and residence time impacts on bio-oil yield. The bio-oil yield was determined to be 46 wt. % under the optimal circumstances (T= 525°C, t = 60min). The ANOVA test revealed that the model was statistically significant (low p-value < 0.0001 and high F value).

Kılıc et al. [80] used response surface methodology (RSM) based on the CCD to optimize the experimental conditions for achieving the greatest bio-oil production from *Euphorbia rigida* by fast pyrolysis. The experimental design was used to optimize the reaction temperature, heating rate, and nitrogen gas flow rate. The most important element of each experimental design response was found using analysis of variance (ANOVA), and an empirical model in

terms of factors was developed. The best conditions were discovered to be at a reaction temperature of 600°C, a heating rate of 200°C/min, and a nitrogen flow rate of 100 ml/min. Under ideal conditions, the maximum bio-oil output was 35.3 wt. %.

2.7 Products of pyrolysis

2.7.1 Pyrolytic liquid (Bio-oil)

Bio-oil, also known as pyrolysis oil/liquid, is a dark brown liquid that contains a variety of oxygenated components and is used as a fuel/chemical. It is a multi-component combination of water and molecules of various sizes formed from the de-polymerization and fragmentation of three primary components of biomass such as cellulose, hemicellulose, and lignin. Small carbonyl molecules (acids, ketones, aldehydes), sugar-based compounds (furans and hydro sugars), and lignin-based compounds (phenols, aromatic oligomers) are the three broad groups of bio-oil. The lower heating value of bio-oil is due to the presence of a high H_2O component (15 – 30%). The water content in the bio-oil is due to the original moisture in the feedstock and the product of dehydration during the pyrolysis reaction and storage. Most of the water in pyrolytic oil is formed from the decomposition of cellulose and hemicellulose; however, some additional water is formed from lignin decomposition. The formation of water could be attributed to the dehydration of lignin aliphatic hydroxyl groups. The presence of water content has both negative and positive effects on the bio-oil properties. The water content lowers the heating value and flame temperature; on the contrary, water reduces the viscosity and enhances the fluidity, which is suitable for the atomization and combustion of bio-oil in the engine. Aside from the high O_2 level (35 – 40%) and moisture content, the presence of carboxylic acids decreases the pH value to 2 – 3.7, which is detrimental to bio-oil formation [81]. The acidity makes bio-oil very corrosive to common construction materials and extremely severe at elevated temperatures, which imposes more requirements on the construction materials of the vessels and the upgrading process before using bio-oil in transport fuels. The presence of

oxygen creates the primary issue for the differences between bio-oils and hydrocarbon fuels. The high oxygen content causes a lowering of energy density (heating value) than the conventional fuel by 50%. Due to the large amounts of oxygenated components present, the oil has a polar nature and does not mix readily with hydrocarbons. The presence of ash in bio-oil can cause erosion, corrosion, knocking problems in the engines and valves, and even deterioration when the ash content is higher than 0.1 wt. %. However, alkali metals are complex components of ash. More specifically, sodium, potassium, and vanadium are responsible for high-temperature corrosion and deposition, while calcium is responsible for hard deposits. Acid washing of biomass feedstock prior to pyrolysis can decrease the ash content and result in a better quality bio-oil. Furthermore, bio-oil can be used as a raw material in chemical production, such as phenols (resin synthesis), an additive in the fertilizer and pharmaceutical industries, and a taste enhancer (such as glycolaldehyde) in the food business, and a variety of other specialty chemicals.

2.7.2 Pyrolytic gases

Pyrolytic gases are primarily a combination of H_2, hydrocarbon gases (C1 – C4), CO_2, CO, and H_2S. Thermal degradation of carbonyl and carboxyl functional groups produces CO_2. In contrast, detachment of C–O–C and C—O bonds produce CO. Similarly, the breakage of the C–H and aromatics groups results in the production of H_2. Nonetheless, CO and CO2 are the predominant gaseous products at low temperatures. In contrast, lignin de-polymerization at high temperatures gives CH_4 as the main gaseous product.

2.7.3 Solid product (Biochar)

The solid product of lignocellulosic biomass pyrolysis, termed biochar, is a highly carbonaceous substance with high carbon content. The physicochemical property of solid biochar is substantially determined by the feedstock and process conditions influencing its widespread use. By contracting the bio-oil production, the biochar yield was determined to be

maximum during slow pyrolysis (<500 °C) [82]. Similarly, their micro porous nature, high specific surface area, and cation exchange capacity improve their ability to filter and adsorb harmful contaminants. They serve as precursors for the mass manufacture of activated carbon due to its adsorptive activity and rapid chemical activation [83]. They have also been used in catalysis, composting, fermentation, detoxification, and electrochemical energy storage. Because of its high nutrient retention capacity in soil and ability to produce a symbiotic habitat for microorganisms, biochar may also be utilized as an organic fertilizer.

Furthermore, it provides significantly more significant GHG reductions than direct biomass incineration due to the biochar effect on production and carbon sequestration [84].

2.8 Knowledge gaps and hypothesis

Different strategies can be taken to convert biomass into renewable fuel and other value-added goods. According to the literature, the following are the key knowledge gaps:

1. Complete physicochemical characterization of *Lagerstroemia speciosa* seed hull (LS), mustard straw (MS), and *Sesbania bispinosa* (SB) are not done.

2. Kinetic analysis of these selected biomasses using the isoconversional method is not reported so far.

3. Effect of different pyrolysis factors on the pyrolytic product yield and properties is not yet reported.

4. Physicochemical characterization of biochar of these biomasses was not studied extensively

2.9 Aim and Objectives

Based on the research gaps, the following research objectives are identified,

1. Physicochemical characterization of selected biomass towards producing renewable fuel and value-added chemicals.

2. Kinetic analysis (model-free and model fitting) of biomass using non-isothermal techniques.

3. Thermodynamic analysis of biomass.

4. Reaction mechanism using Criado's $z(\alpha)$ master plot and Coats Redfern (CR) method.

5. Thermal pyrolysis of selected biomass and its fuel properties evaluation.

6. Effect of various parameters on the pyrolytic products yields (liquid, char, and gases).

7. Optimization of process parameters using response surface methodology (RSM) based on central composite design (CCD) technique.

8. Physicochemical characterization of biochar obtained from the pyrolysis of selected biomass.