Chapter 7
Technical Criteria for Converting Biomass to High Liquid Bio-Oil Yields

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Abstract Rising energy demands and depletion of fossil fuels have led the research community to investigate alternative fuel sources. Green and renewable biofuels have evolved to substitute for a non-renewable energy source. Biomass can be utilized as a raw material for producing low-carbon fuels. Although biomass-based fuels can replace fossil fuels, direct use is limited due to the low quality of the fuels and expensive process costs. An unrivaled solution to this problem is an integrated biorefinery concept involving generating hydrocarbon-grade fuels and valuable chemicals from pyrolysis-derived bio-oil. The chapter examines recent breakthroughs in bio-oil up-gradation processes and moisture removal techniques and bio-oil recovery of valuable compounds. One of the widely used and well-developed techniques for producing bio-oil is the fast pyrolysis of biomass. The catalytic cracking process has been identified as a viable technology for converting bio-crude to liquid fuel in bio-oil upgrading. The chapter examines recent trends and advances in the fast pyrolysis technique to improve overall profitability of the process. Critical analysis of the potential and existing techniques and necessary future steps are essential for adopting these methods industrially and in a feasible manner.

Keywords Pyrolysis · Upgraded fuel · Green fuel · Biomass

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Abbreviations

CHNS-O	Analyzer
CO_2	Carbon dioxide
DSC	Differential scanning calorimetry
SEM	Scanning electron microscope; Py-GC/MS- Pyrolysis-gas chromatography/mass spectrometry
FTIR	Fourier transforms infrared spectroscopic analyzer
NMR	Nuclear magnetic resonance spectroscopy
NO_x	Nitrogen oxides
SO_2	Sulfur dioxide (SO_2)
TGA	Thermogravimetric analysis analyzer
XRD	X-ray diffraction analyzer

7.1 Introduction

Biomass is a promising eco-friendly alternative renewable energy source in today's energy landscape. The present global energy supply is primarily dependent on fossil fuels such as oil, natural gas, and coal, with limited reservoirs (Smith et al. 2018; Goswami et al. 2021a). Thus, it has become necessary to evaluate an alternative long-term energy source that can meet the demands of the growing global population and the increasing per capita energy consumption. Also, the evidence of increasing global warming due to greenhouse emissions has raised concern for most developed and developing countries. All these concerns have increased the importance of research for fossil-free alternatives.

Biomass is a renewable energy source that is widely available (Sarkar and Praveen 2017; Agrawal and Verma 2022). Due to environmental concerns and rising energy demands worldwide. Biomass utilization in mainstream energy usage attracts much attention. Biomass is composed of hemicellulose (20–35 wt.%), cellulose (30–50 wt.%), and lignin (15–35 wt.%) (Cheng et al. 2016; Kumar et al. 2020). Apart from carbon-based components, biomass also contains a small amount of nitrogen, sulfur, and inorganic composition ash. As a result, when compared to conventional fossil fuels, biofuel burning produces fewer toxic gas pollutants such as nitrogen oxides (NO_x), sulfur dioxide (SO_2), and soot. Furthermore, biomass fuel combustion can produce zero or negative carbon dioxide (CO_2). emissions since CO_2 generated from bio-oil combustion can be recycled back into the plant through photosynthesis (Debalina et al. 2017; Goswami et al. 2020a, 2021b).

Different routes are available by which biomass can be converted into biofuel. These include thermal, biological, and physical processes. Among the different available processes, pyrolysis has emerged as a promising technology for producing liquid fuel products due to its storage, transport, and versatile applications such as combustion engines, boilers, and turbines. Managing solid biomass and waste is a complex and cost-intensive task that encourages pyrolysis research. However, it is still in its early stages of development and faces various technological and economic challenges to compete with existing fossil fuel-based technologies (Tang et al. 2020; Goswami et al. 2020b). An extensive investigation of the production of bio-liquids and other products using different biomass species has been carried out in the past.

The quality bio-oil production from different biomass is challenging and requires the application of advanced technologies such as catalytic pyrolysis. Thermochemical conversion techniques can efficiently and economically transform biomass into energy-rich compounds used in various applications (Mandapati and Ghodke 2021). Different routes are available for converting biomass into usable fuel. These technologies include thermochemical conversion of biomass via combustion, pyrolysis, and gasification. The disadvantage of the gasification process is that the produced synthesis gas needs to be utilized at the place of production as it becomes economically inviable or costly for storage and transportation through pipelines (Mandapati and Ghodke 2020).

The chapter discusses the different routes of pyrolysis and its technical specifications and the advances in the pyrolysis technology used for biomass conversion. The chapter covers a detailed description of the pyrolysis technique, its technical specifications, and the technology involved. Pyrolysis has emerged as an essential technology in turning biomass into solid, liquid, and gaseous fuels. A yield of around 60–65% bio-oil production has been reported in literature through the pyrolysis process utilizing a fluidized bed reactor.

7.2 Pyrolysis

Pyrolysis is the process in which both thermal and chemicals effects the conversion of organic materials in an oxygen-depleted atmosphere such as nitrogen. It is an endothermic reaction (Basile et al. 2015). The term pyrolysis was derived from two Greek words: pyro, which means fire, and lysis, which denotes degradation into essential components. During pyrolysis, components of biomass begin to decompose at 350 °C–550 °C due to rapid heating and progress to 700 °C–800 °C, resulting in the generation of a variety of products such as liquids, solids, and gases (Das et al. 2015). Biochar and bio-oil are the solid carbon-rich product and the volatile fraction of pyrolysis that is partly condensed to a liquid fraction product, respectively. The pyrolysis process produces hydrogen, carbon dioxide, methane, and carbon monoxide, among other gases (Moorthy Rajendran et al. 2020). These products are intriguing because they could be used as alternative energy sources. Pyrolysis has emerged as a critical method in converting biomass into solid, liquid, and gaseous fuels. The literature reported a yield of roughly 60–65 wt.% bio-oil generation through the fast pyrolysis process using a catalytic fluidized bed reactor. However, pyrolysis-produced bio-oil has numerous unfavorable qualities that directly use bio-oil as an engine fuel challenge. Thus, bio-oil is enhanced by the hydrotreating or catalytic cracking process to make it compatible as a drop-in fuel molecule (Shihadeh and Hochgreb 2000).

7.2.1 Different Routes of Pyrolysis

Pyrolysis processes may work efficiently under a variety of conditions. Thus, there are various pyrolysis processes, such as fast, slow, flash, intermediate, ultra-flash, vacuum, and catalytic pyrolysis (Wei et al. 2021). Especially, vacuum pyrolysis occurs at negative or low pressures, whereas another pyrolysis of biomass occurs at atmospheric or controlled positive pressure (Chintala et al. 2018). The ideal primary fuel for the pyrolysis process is waste material, such as forest debris, woody biomass, and agricultural waste. Longer residence times and high temperatures increase biomass conversion to gas. Pyrolysis conditions can be varied depending on the desired product type (Bridgwater 2012; Dhyani and Bhaskar 2017). Several different modes of biomass pyrolysis depending on conditions, such as heating rate and residence time of biomass, are being actively developed (Hu and Gholizadeh 2019; Kiliç et al. 2014; Adelawon et al. 2021; Dhyani and Bhaskar 2017). However, the most generally used classification of pyrolysis processes is slow, fast, and flash pyrolysis.

7.2.1.1 Slow Pyrolysis

Slow pyrolysis or conventional pyrolysis has been used to convert diverse feedstock biomasses into charcoal or biochar at slow heating rates for a lengthy residence time, around 5–30 min, and at temperatures below 300 °C since the beginning of the pyrolysis process (Ahmad et al. 2014). Feedstocks, wheat straw, pinewood, dried algae, and green garbage were employed. This procedure can also make bio-oil or liquid fuels. Slow pyrolysis is typically carried out at atmospheric pressure. The heat required for the process is provided from an external source, usually produced from partial combustion or combustion of the produced gases or biomass feedstock (Ghodke and Mandapati 2019). The process results in the development of vapor phase components that continue to react, resulting in the formation of charcoal and other liquid products. Slow pyrolysis produces roughly 35 wt.% biochar, 30 wt.% bio-oil, and 35 wt.% gaseous products. However, due to technological restrictions such as cracking of the primary product due to high residence time (Demirbaş 2005; Jahirul et al. 2012), bio-oil is produced through slow pyrolysis is not suitable for direct use as a liquid fuel.

7.2.1.2 Intermediate Pyrolysis

Intermediate pyrolysis is a type of pyrolysis that occurs halfway between fast and slow pyrolysis. It has an excellent product distribution and may be employed in the coproduction of biochar, bio-oil, and gas (Meng et al. 2019). Intermediate pyrolysis is flexible to diverse materials and has good product distribution. The product is a two-phase separable bio-oil, high quality, and biochar compared to other pyrolysis categories (Bridgwater 2003; Kumar et al. 2021). Researchers have also discovered that it has easily distinguishable liquid phases, with the organic phase exhibiting biodiesel-like qualities. The organic phase can be combined with up to 50 wt.% (Xiong et al. 2009). Its aqueous phase, which comprises C2–C6 sugars, hydroxy acids, oligomers, and water-soluble phenols, is also effective in manufacturing biogas and ethanol. The process has the advantage of requiring less bio-oil upgrading than quick pyrolysis oil and allowing for complete usage of all products. Because of the extensive interaction with steam, intermediate pyrolysis can treat high moisture content feedstock, and when this happens, the biochar takes on the properties of activated carbon (Gao et al. 2020).

7.2.1.3 Fast Pyrolysis

Fast pyrolysis is the rapid thermal degradation of biomass at more excellent heating rates, such as 1000 °C min^{-1}. Fast pyrolysis has a short vapor residence time of less than 2 s (Bhattacharya et al. 2009). Bio-oil is the main product of rapid pyrolysis. However, the amount of product created depends on the feedstock composition, ranging from 60% to 75% oily products, and 10–20 wt.% gaseous (CH_4, CO, CO_2, H_2, and light hydrocarbons), and 15–30 wt.% solids products. Rapid heating and quenching produce bio-oil, and the high reaction rates reduce char formation and favor the generation of either gas or liquid products. Higher temperatures, heating rate, short vapor residence time, rapid cooling of vapors for high bio-oil production, and precise control of reaction temperature are the essential characteristics of the fast pyrolysis process (Collins and Ghodke 2018). Furthermore, a fast pyrolysis process requires reducing the water content of feedstock and reducing the particle size to less than 2 mm. In fast pyrolysis, rapid and systematic separation of solids (char), rapid gas removal, and cooling pyrolysis product favor the formation of bio-oil or liquid products (Ponnam et al. 2021). This liquid product can be readily and inexpensively transported and stored, decoupling solid biomass handling from consumption (Malode et al. 2021).

7.2.1.4 Flash Pyrolysis

Ultra-fast pyrolysis is another name for the process. Flash pyrolysis is a thermal breakdown of large molecules into smaller molecules that occurs in an inert

Table 7.1 Summary of the classification of the pyrolysis method

Method	Residence time	Temperature (°C)	Heating rate (°C/s)	Major bioproducts
Slow pyrolysis	5–30 min	400–500	10	Char, bio-oil (tar), gases
Ultra-fast/flash pyrolysis	<0.5 s	750–1000	>500	Bio-oil and gases
Fast pyrolysis	0.5–2 s	500–650	100	Char, good bio-oil, gases

atmosphere such as nitrogen at a rapid heating rate of 1000–10,000 °C per minute and residence time is less than 1 s. An excellent feed particle size (2 mm) is required to perform this procedure at an optimal rate. The degradation of biomass produces a significant amount of coke and aerosol vapors during flash pyrolysis. A dark brown liquid (bio-oil) is produced after cooling and condensation, with a heating value of half diesel. In contrast to prior procedures, this is a novel technology with well-regulated parameters that generate high liquid yields (Gandidi et al. 2018). Flash pyrolysis in fluidized bed reactors can produce a high liquid output of up to 75 wt.% bio-oil (Gómez et al. 2018). However, there are certain drawbacks to flash pyrolysis, such as low thermal stability, particles in the oil, and the oil's corrosiveness, which results in the generation of oils with high viscosity, density, low calorific value, and carbon residues (Huang et al. 2013). Table 7.1 depicts the summary of different pyrolysis technologies available and can be used to produce different bioproducts.

7.2.2 Technical Specifications: Pretreatment, Characterization, and Mechanism

7.2.2.1 Pretreatment

Pretreatment is an important stage in the biochemical and thermochemical conversion of biomass. It requires structural changes to overcome biomass's recalcitrance. Improved biomass features are necessary to increase the biomass's energy use efficiency (Wu et al. 2021; Bhardwaj and Verma 2021). The primary treatment process requires the heating of lignocellulosic biomass (cellulose, hemicellulose, and lignin) to convert into polymeric and aromatic constituents. In contrast, the heterogeneity in atoms and inorganic oxides element components of biomass act as catalysts, resulting in the generation of a biofuel product with different carbon structures and significant reforms that increase yield during the bioconversion process (Kim 2018; Kumar and Verma 2020a, b). Current pretreatment systems have two significant challenges: high costs and obtaining a processed product with essential component degradation. Past and ongoing research and development efforts have failed to meet these problems. Pretreatment treatments must be tailored to the type of biomass and how it will be utilized in bioconversion and biorefinery

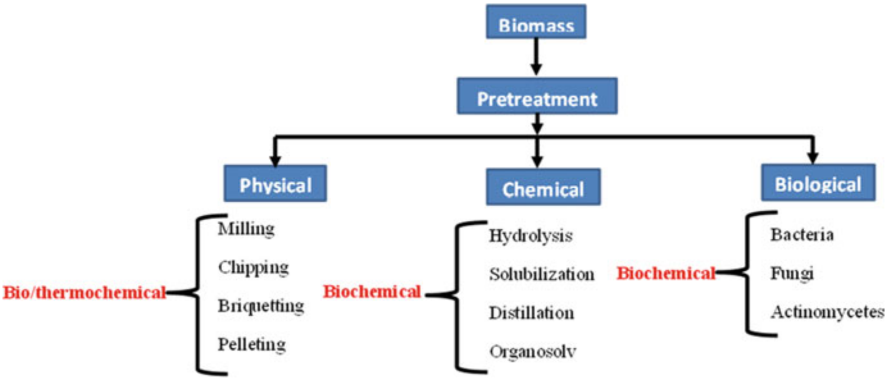

Fig. 7.1 Different pretreatments methods for biomass

processes. Figure 7.1 depicts the types and pretreatment processes required for biomass conversion technologies (physical, chemical, and biological). The subsections that follow go into the various types of preprocessing in greater depth.

Physical Treatment

Physical pretreatment of biomass aims to improve the surface area and pore size by reducing particle size through mechanical comminution. Physical processing reduces cellulose crystallinity and polymerization degree in lignocellulosic materials. Prior to both enzymatic and thermochemical biofuel production, this step is required. However, little is known about how physical preprocessing procedures function, particularly how biomass chemical content or bond structure are affected. The lignocellulosic biomass application determines the physical pretreatment technology to be undergone or utilized. Biochemical conversion of lignocellulosic biomass, for example, should undergo a reduction in particle size through milling, shredders, and cutters in order to improve biochemical digestibility. Milling of biomass is necessary before use in the thermochemical conversion process to reduce the size of biomass. Palletization, densification, and heat treatment torrefaction are the prior pretreatment process of thermochemical conversion technologies. Prior size reduction is essential in both biochemical and thermochemical conversion pathways to minimize mass and heat transfer constraints. Another physical pretreatment approach is chipping when employing waste wood biomass or agricultural residue as a feedstock in thermochemical conversion technologies. The thermochemical conversion technologies require feedstock with 50 mm or less diameter, feedstock with 50 mm or less is required.

Torrefaction, densification, and pelletization are examples of physical pretreatment procedures for biomass (Reckamp et al. 2014; Chi et al. 2021). These preprocessing procedures use heat to cause changes in the biomass, resulting in improved biomass characteristics. The physical pretreatment procedure has the drawback of removing the lignin content from lignocellulosic biomass materials, rendering the cellulose composition inaccessible. Another disadvantage is the high heat-energy requirements for pretreatment and not economically feasible commercial use. According to research findings, the process of removing lignin from lignocellulosic biomass materials can be led to an increase in the energy demand. Thus, thermal pretreatment treatment method could influence the total energy effectiveness/cost of a biorefinery process (Lewandowski et al. 2020).

Chemical Pretreatment

In chemical pretreatment methods, organic or inorganic chemical compounds are used to disrupt the chemical bonds of lignocellulosic biomass by interacting with the intrapolymer and interpolymer bond connections of the organic components are known as chemical pretreatment of biomass. Biomass, particularly lignocellulosic components, is considered recalcitrant because it is resistant to chemical breakdown. The structural diversity and complexity of biomass such as its crystalline nature and the degree of lignification, all contribute to its recalcitrance (Mai et al. 2014; Bhardwaj et al. 2020). In preliminary chemical pretreatment method, the chemical structural recalcitrance of the lignocellulosic nature of biomass is disrupted, resulting in cellulose crystalline phase reduction along with lignin breakdown. Before biochemical conversion, chemical preprocessing of biomass, particularly lignocellulosic biomass, is frequently employed to extract the biopolymeric constituents of the feedstock. Acids, alkalis, organic solvents, and ionic liquids are some of the chemicals that have been used to pretreat biomass chemically and have had a significant impact on its structure (Basak et al. 2020).

Biological Pretreatment

Biological preprocessing/pretreatment of the organic composition of biomass is always related to the activity of synthetic enzymes or enzymes produced from an organism that potentially can break down or depolymerize the hemicellulose, cellulose, and lignin components of biomass. The biological pretreatment method has many benefits over other physical/chemical pretreatment processes are particularly uses energy consumption and produces little or no toxic chemical. Biological pretreatment produces a high yield of required/valuable products. But major disadvantages are substrate and process reactions are very sensitive (Cao et al. 2013; Agrawal and Verma 2020). However, its significant drawbacks in biological pretreatment are that the method chosen was too slow and requires meticulous management of fungus growth conditions and the enormous amount of area required to complete the process (Kan et al. 2016). It was observed from the literature that the residence period or time required for biological activities in pretreatment was between 11 and 15 days. Moreover, because microorganisms consume the organic components of biomass, biological pretreatment operations have technological challenges and are seen as less economically appealing than other pretreatments (Robak and Balcerek 2018; Chintala et al. 2019). In the biological pretreatment of biomass, different fungi such as white-rot, brown-rot, and soft-rot fungi are used widely. Apart from fungi, actinomycetes and bacteria are used to pretreat the biomass. The fungi are notably applied to eliminate hemicellulose and lignin composition of biomass while causing minor damage to cellulose biomass. White-rot and brown-rot fungi have a wide degradation mechanism for gaining access and destroying the lignocellulosic biomass such as waste wood and agricultural residue. Their extraordinarily powerful metabolism or mechanism has been successfully employed in industrial commercial operations. White-rot and brown-rot fungi have been demonstrated to brighten hardwood kraft pulp, potentially lowering bleaching chemical costs and reducing the environmental effect of paper manufacturing operations (Phillips et al. 2017; Ghodke and Mandapati 2017; Bhardwaj et al. 2021).

Even though various preprocessing methods have been studied and more are in progress, evaluating pretreatment technologies is challenging. The primary reasons for challenging pretreatment techniques are upstream and downstream processing of biomass. Additionally, capital expenditure, waste treatment systems, and complicated chemical recycling (Shen 2015; Ghodke 2021).

The thermochemical conversion uses a variety of feedstocks, including wood waste, energy crops such as sweet sorghum, short rotation forestry, and agricultural residues. The critical technical parameters for thermochemical processing suitability are ash, moisture, and other physical characteristics. The two most essential economic elements are cost, including collecting, production, transportation, and availability. Competing uses such as pulp and combustion, board manufacture, recycling, and material recovery, rather than energy recovery, are also a concern.

7.2.3 Feedstock Drying

In most circumstances, pyrolysis necessitates a feedstock with a moisture level of less than 15 wt.% although there is a trade-off between moisture levels and conversion production efficiency. The moisture content essential for conversion differentiates between conversion plants. When biomass is delivered, the moisture level will be 50–60 wt.% range (Praveen et al. 2015).

Passive drying during summer storage can cut this by 30%. The moisture content of a silo can be reduced to as low as 12 wt.% with active silo drying. Drying can be done in various ways, including near-ambient solar drying, waste heat flows, and specially constructed dryers that operate at the location. Commercial dryers come in various shapes and sizes, but rotary kilns and shallow fluidized bed dryers are the most prevalent.

7.2.3.1 Characteristics of Feedstocks

Table 7.2 summarizes the essential physical features of biomass. Notably, the relatively low bulk density, high moisture content, and wide particle size range are notable traits.

7.2.3.2 Biomass Characterization

Biomass heterogeneity is still a natural feature. The biomass quality determines the possibility and viability of extracting products from it. The two conversion techniques such as biochemical and thermochemical conversions are primarily applied to recover commercially valuable products from biomass. The attributes of biomass also affect the conversion route chosen. Thus, characterization is required to effectively understand the underlying physicochemical properties of biomass. Depending on its characteristics, one can evaluate its suitability for bioconversion. The physical properties are critical for the efficient use of biomass in biofuel production methods (Dutta et al. 2015).

However, the fundamental organic components of biomass influence its features, which vary based on the source of biomass composition, biomass source, species, soil condition, climatic condition, and other factors. Depending on the end-use of biomass, proximate and final analyses are routinely determined and reported using a variety of analytical processes. The data is crucial for assessing biomass's diverse application potential, notably its energy production potential when third-generation biomass is used as a biofuel in thermochemical conversion operations (Sharma et al. 2020). Among the characteristics analysis techniques used in physicochemical characterization investigations involving organic composition are the following:

- XRD- X-ray diffraction analyzer
- FTIR- Fourier transforms infrared spectroscopic analyzer
- TGA- Thermogravimetric analysis analyzer
- NMR- Nuclear magnetic resonance spectroscopy
- CHNS-O analyzer
- DSC-Differential scanning calorimetry
- SEM-Scanning electron microscope
- Py-GC/MS- Pyrolysis-gas chromatography/mass spectrometry

Table 7.2 Essential physical features of biomass

Feedstocks	Forestry residues	Poplar tree	Waste wood	MSW	Straw
Moisture content (%)	20–50	10–40	5–30	20–30	5–25
Density (kg/m^3)	350	450	350	450	250

7.3 Future Prospects

The replacement of fossil fuels with biomass resources on a wide scale is a hot topic not just for energy generation but also for manufacturing chemicals, bioproducts, and materials. Moreover, and since biomass is extensively accessible, commercial products/biofuels from lignocellulosic materials can be produced in most geographic locations. Biomass characteristics determine the economic viability and effectiveness of the value-added product production, the primary treatment method used. However, biomass heterogeneity, high capital and operating costs associated with bioconversion, and the mechanisms underlying the biomass conversion process are all issues with using biomass for heat, chemical products, and fuels generation. As a result, efforts should be made at all levels to build more user-friendly and cost-effective technologies to stimulate the broad use of biomass and attract investment in this field. Furthermore, because ideal biomass pretreatment conditions are rarely published, nothing is known about them.

7.4 Summary

Biomass preprocessing and characterization is critical in determining that biomass materials are utilized effectively in biofuel production. An improved comprehension is required of the origins of biomass and its recalcitrance. Further the impact of primary treatment to maximize the different biofuel production pathways. It requires an assessment of biomass using cutting-edge analytical techniques capable of providing knowledge. Based on the features of the pyrolysis products, criteria for assessing the feasibility of biomass for a pyrolysis conversion process to produce solid, liquid, and gaseous fuels are developed. The applicability of various biomass for pyrolytic transformation is investigated using this technique. It is discovered that various biomass is suitable for diverse applications such as combustion of fuel, liquefaction, gasification, and the production of char adsorbents depending on the chemical composition of biomass.

Conflict of Interest All the authors declare that they have no competing interests.

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