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Chapter 1

Pyrolysis bio-oil upgradation to fuels

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1.1 Introduction

Industrialization, urbanization, and domestic use increase the global energy demand derived from fossil-based fuel. The global energy demand is likely to increase by 28% in 2040 resulting in their rapid depletion from the nature. The exacerbation of the fuel import by economically developing countries motivated the development of alternate renewable sources for fuel and chemicals (Azeez et al., 2010). Moreover, the increasing greenhouse gas emission by fossil-based fuel combustion is another important concern for the search of carbon-neutral fuels. Various sources of renewable energy such as wind, solar, water, and geothermal power are being utilized; however, the source for liquid fuel is of utmost importance especially in the transportation sector. Despite the fact that electric vehicles are of interest at present that utilizes electrical energy, they are still in early adoption phase. Biomass utilization for fuels has been proven to be a boon for the society (Negahdar et al., 2016). They are mainly obtained from municipal waste, agricultural wastes, wood, industrial, and forest residues. The conversion of biomass to biofuel has a potential to solve the global and environmental issues (Cao et al., 2018). The utilization of lignocellulosic biomass to produce second-generation biofuels (i.e., biofuel obtained from nonfood crop including the waste from food crops, agricultural residue, wood chips, and waste cooking oil) has not only promoted efficient waste management but also addressed the global pollution problems (A. V. Bridgwater, 2012). Further, biomass utilization provides a carbon-neutral process in terms of greenhouse gas emissions in comparison to fossil fuels (Czernik & Bridgwater, 2004).

The lignocellulosic biomass is majorly composed of lignin, cellulose, and hemicellulose as shown in Fig. 1.1. Extractives (nonstructural components

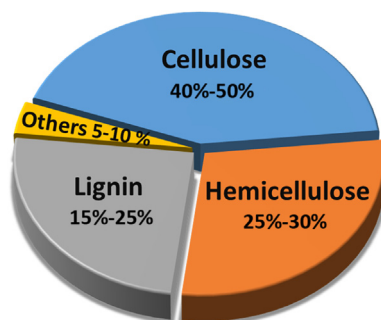


FIGURE 1.1 The percent constitution of the components of lignocellulosic biomass.

including fats, phenolics, resin acids, waxes, and inorganics) and ash are found in a small percentage ($\sim 5\%–10\%$). Lignin is a complex aromatic phenolic compound polymer present in $\sim 15\%–25\%$ of the total biomass. Cellulose is the biosphere's most abundant carbon form present as $\sim 40\%–50\%$ of the biomass. It forms the structural framework of plant cells. Cellulose is a linear polymer formed by $\beta \rightarrow 1,4$ -glycosidic linkages between 6-carbon glucose units. Hemicellulose, the second highest abundant carbon form, is a branched heteropolymer composed of six-carbon sugars (D-glucose, D-galactose, D-mannose), five-carbon sugars (L-arabinose, D-xylose), and uronic acid. It constitutes $\sim 25\%–30\%$ of the total biomass (Ramage & Scurlock, n.d.).

The cellulose and hemicellulose have been industrially utilized for the production of second-generation biofuel such as bioethanol (Em, 2015; Venderbosch & Prins, 2010; Yoo et al., 2018). Cellulose and hemicellulose polymers are interconnected with lignin in a heterogeneous matrix to make lignocellulosic structure. Their amount varies depending on the type of biomass source as shown in terms of weight percentage in Table 1.1. Both cellulose and hemicellulose are polymers of sugar moieties that can be broken down by hydrolytic enzymes. On the other hand, the phenolic compounds present in lignin inhibit the hydrolysis process; hence, lignin-rich biomass is unsuitable for biochemical conversion process (Chen et al., 2003).

Agricultural feedstock includes paddy straw, rice husk, sugarcane bagasse, wheat chaff, corn cobs, nut shells, cereal straw, etc. These feedstocks have high potential for biofuel production at relatively reasonable prices from their respective costs such as labor and land (Kumar & Singh, 2015). The economic viability of the process can further be ensured by utilizing whole crop biorefineries for harvesting value-added products. For example, harvesting whole crops of oil seed rape for cooking oil and high-protein food for poultry (Chen et al., 2003). Whereas, wood and forest residues mainly include primary forestry waste such as bark, off-cuts, sawdust, and shavings. Unlike agricultural residues, wood and forest residues contain high lignin content and

TABLE 1.1 Selected lignocellulosic feedstocks' chemical composition (Bhagwan Goyal et al., 2008; Kumar & Singh, 2015).

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Corn stover	37	21	13
Corn cob	45	35	15
Barley straw	37	44	11
Wheat straw	34	28	18
Rice husk	50	–	25–30
Bagasse	40	25	25
Oat straw	37	25	15
Sorghum straw	36	26	8
Switch grass	31	20	18
Bamboo dust	41–49	–	25–28
Sawdust	31–64	71–89	14–34
Paddy straw	28–48	–	12–16
Maize stalk straw	38	26	11
Nut shells	25–30	25–30	30–40
Coconut fiber	36–43	2–3	41–45
Hardwood stems	40–45	18–40	18–28
Softwood stems	34–50	21–35	28–35
Municipal solid waste	21–64	5–22	3–28
Poplar	49	17	18
Eucalyptus	43	32	25
Miscanthus straw	45	30	21

low moisture. These characteristics are attributed to their favorable thermochemical processing for biofuel production. Presently, recovered forest residues are burned to produce heat and electricity (Bhagwan Goyal et al., 2008).

These biomass resources can be utilized to make renewable fuel and important chemicals through several biomass conversion routes such as thermochemical, biochemical, and chemical routes. These routes are based on the methodology and technology used as well as the final products. The biochemical route involves the microbial digestion and fermentation of pretreated, hydrolyzed soluble sugars into biogas and bioethanol or biobutanol,

respectively. However, the biochemical transformation of biomass involves a series of time-consuming and challenging metabolic reactions such as hydrolysis and acidogenesis (Das, 2019). The chemical route undergoes different chemical reactions such as esterification and hydrolysis of biomass components over different catalysts to produce several platform chemicals. The lignin component of the biomass is recalcitrant to chemical and biochemical conversion, which makes these processes unsuitable for biomass conversion. The biomass conversion by thermochemical route includes either a direct approach or an indirect approach. The direct thermochemical conversion is executed by the combustion of biomass into electricity and heat. The indirect approach includes gasification and pyrolysis that gives synthesis gas (syngas: $\text{CO} + \text{H}_2$) and bio-oil as the final product, respectively. Although the thermochemical route is an energy-intensive process, it is an efficient and prospective way for a complete transformation of biomass into biofuel and chemicals. Among the different thermochemical routes, pyrolysis is an eco-friendly, efficient, and economical process for the production of a good yield of energy-rich liquid fuel and chemicals. This process has high commercial advantage due to its compatibility with the existing refinery infrastructure and machineries. Pyrolysis reaction is performed at high temperature in the absence of air that yields liquid bio-oil ($\sim 80\%$), char, and gases. The bio-oil is composed of phenolic compounds derived from lignin, sugars and furfurals from cellulose and hemicellulose, and light oxygenates. The comparison of properties of pyrolysis bio-oil and fossil-derived oil is shown in Table 1.2.

Though a good quantity of pyrolytic bio-oil is obtained from the pyrolysis process, this bio-oil cannot be used directly as a commercial fuel due to certain limitations such as high oxygen functionality, high water content, acidic nature, free-flowing, smoky smell, and less stability. Moreover, the heating value of bio-oil is very low (16–21 MJ/kg) as compared with fossil-based fuel (~ 43 MJ/kg) (Czernik & Bridgwater, 2004). In order to meet the commercial fuel standard, bio-oil is subjected to various upgrading techniques such as steam reforming, catalytic cracking, hydrodeoxygenation (HDO), esterification, and supercritical fluid. In addition, carbon addition strategies are implemented to increase the carbon number of pyrolytic oils in the range of commercial fuels. Among the mentioned methods, HDO process at high hydrogen pressure is widely applied to upgrade the quality of final fuel and chemicals.

This chapter thoroughly examines thermochemical processes for biomass conversion, encompassing two key stages: pyrolysis of biomass to generate liquid bio-oil, followed by upgrading of bio-oil to produce high-quality bio-fuel or chemicals. The discussion initiates with an analysis of biomass composition at the molecular level, aimed at revealing the chemistry behind its decomposition. Building on this foundational knowledge, the chapter systematically explores various techniques for biomass conversion, providing a

TABLE 1.2 Comparison of properties of pyrolysis bio-oil and fossil-derived oil (Czernik & Bridgwater, 2004; Das, 2019; Oasmaa & Czernik, 1999).

Physical property	Units	Bio-oil	Diesel	Heavy fuel oil
Water	wt.%	15–30	0–0.001	0.1–7
Ash	wt.%	0–0.2	0–0.01	0.03–0.1
Carbon	wt.%	44–58	86	85–86
Hydrogen	wt.%	5.5–7.2	13	11–12
Nitrogen	wt.%	0–0.2	–	0.3
Oxygen	wt.%	35–50	0	0–0.1
Sulfur	wt ppm	<400	10–500	10,000–21,000
Stability	–	Unstable	Stable	Stable
Viscosity (40°C–50°C)	cSt	13–100	1.9–4.5	140–380
Density (15°C–40°C)	kg/L	1.1–1.3	0.82–0.85	0.96–1.02
Flash point	°C	50–100	>52	65–100
Pour point	°C	–36 to –9	–20	15–21
HHV	MJ/kg	16–21	43	38–41
pH		2.4–3.2	–	–

nanced exploration of the advantages and disadvantages associated with each method. Within the realm of thermochemical methods, the chapter emphasizes that pyrolysis followed by upgrading stands out as the preferred technique for producing liquid fuel or valuable chemicals followed by comparison of physicochemical properties of the bio-oil obtained through pyrolysis using different biomass sources. The subsequent exploration delves into various upgrading techniques, with a particular focus on the highly efficient HDO process designed to reduce the high oxygen content present in bio-oil in the form of water molecules. A detailed catalytic study of this HDO reaction along with the effects of reactor configuration, reaction medium, and reaction conditions is also presented. Given the reliance of most bio-oil upgrading methods on heterogeneous catalysts, the chapter addresses the challenges in their development due to the diverse and complex structures of bio-oil. Finally, the chapter addresses the major technological aspects involved in scaling up and commercializing the developed processes, drawing insights from an extensive literature survey.

1.2 Constituents of biomass

The chemical constituents of biomass determine the conversion technique that should be employed for its conversion. The constituents of biomass are discussed in detail as follows:

1.2.1 Cellulose

Cellulose is a linear chain polymer of 1,4-D-glucopyranose units in β -configuration. Cellulose has a molecular weight of ~ 100 kDa (Trinh et al., 2013). Two glucose anhydride units make a cellobiose unit, which is the fundamental repeating unit of cellulose as shown in Fig. 1.2. Cellulose is crystalline and insoluble, containing residues in between 2000 and 14,000. Hydrogen bonds in the molecules at $O_3-H \rightarrow O_5'$ and $O_6 \rightarrow H-O_2'$ and at strand $O_6-H \rightarrow O_3'$ retain the polymer structure flat forcing the hydrophobic ribbon faces to stack (Fig. 1.2). Cellulose is soluble in unique solvents such as aqueous *N*-methylmorpholine oxide, CdO/ethylenediamine (cadoxen), LiCl/*N,N'*-dimethylacetamide, some ionic liquids, and near supercritical water (Mohan et al., 2006; Swatloski et al., 2002).

1.2.2 Hemicellulose

Hemicelluloses are branching polysaccharides that are present in conjunction with cellulose in cell walls. They vary greatly depending on the type of biomass (Table 1.3). They constitute of monosaccharides such as glucose, mannose, xylose, and arabinose, and uronic acids such as glucuronic acids and galacturonic acids, with a molecular mass of $<30,000$ Da (Fig. 1.3).

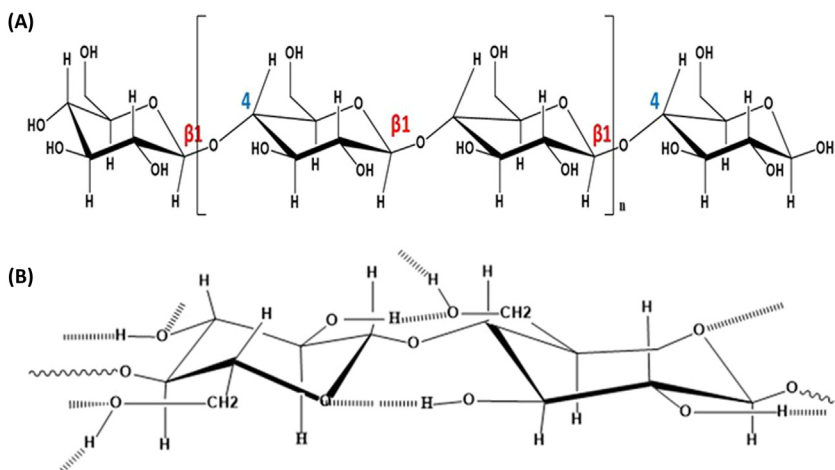
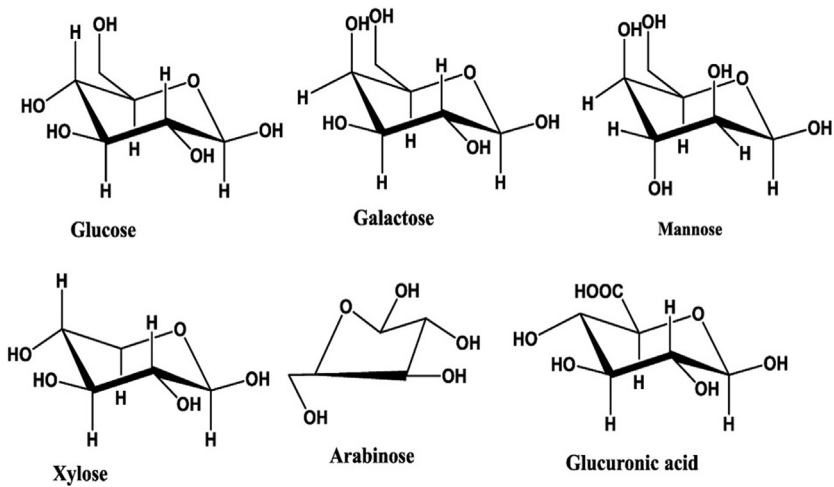


FIGURE 1.2 (A) Structure of cellulose and (B) hydrogen bonding in cellulose.

TABLE 1.3 Chemical compositions of different types of woods (Delbecq et al., 2018).

Feedstock type	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood	40–45	25–30	25–30
Softwood	40–45	30–35	20–25
Eucalypt	45	20	30

**FIGURE 1.3** Main components of hemicellulose.

Hemicellulose is less thermally stable than crystalline cellulose. Hardwood hemicellulose contains a large amount of xylan, whereas softwood hemicellulose contains a large amount of galactoglucomannan and a very small amount of xylan. They can be degraded through slow pyrolysis at temperatures starting from 130°C, where most of the degradation occurs above 180°C (Delbecq et al., 2018; Swatloski et al., 2002).

1.2.3 Lignin

Lignins are large-molecular-weight complex aromatic amorphous polymer structures and are mainly found in woody biomass accounting for 23–33 wt.% in softwood and 15–16 wt.% in hardwood. They act as a binder to bundle up the cellulose fibers and provide them protection against microbes and fungus. Lignin is a complex array of unordered hydroxyl and methoxy

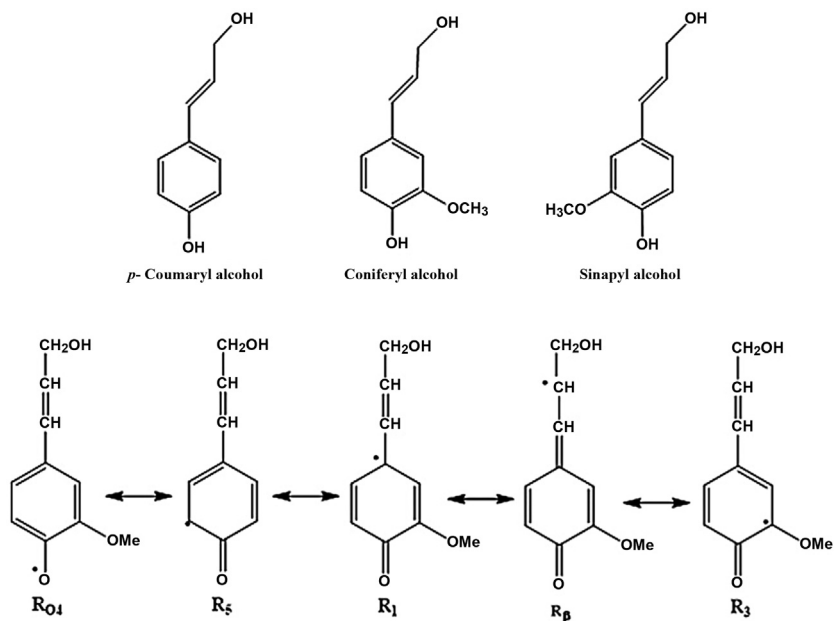


FIGURE 1.4 Structures of *p*-coumaryl, coniferyl, and sinapyl alcohol and resonance hybrid radicals of phenoxy from coniferyl oxidation. Reprinted from Barcelo, A. R., Gomez Ros, L. V., Gabaldon, C., Lopez-Serrano, M., Pomar, F., Carrion, J. S., & Pedreño, M. A. (2004). *Phytochemistry Reviews*, 3, 61–78. <https://doi.org/10.1023/B:PHYT.0000047803.49815.1a>.

functionalized polyphenolics. It is a heteropolymer structure of *p*-hydroxyphenylpropanoid monomer units, named monolignols. The monomeric units present in the form of *p*-coumaryl, coniferyl, and sinapyl alcohol are shown in Fig. 1.4. They are formed from the precursors guaiacyl, syringyl, and *p*-hydrophenyl, respectively. In lignin formation, these structures undergo radical resonance by oxidation to form dimerized structures and further oligomerized and polymerized structures. Softwoods are mostly composed of “guaiacyl” lignin, resulting from coniferyl unit polymerization. Hardwoods are composed of “guaiacyl-syringyl” lignin, resulting from coniferyl and sinapyl unit’s copolymerization (Delbecq et al., 2018). The lignin units are majorly linked by ether bonds along with some carbon – carbon bonds. In case of polysaccharides, acetal functions are dominant (Barcelo et al., 2004). Owing to the high carbon content, lignin contains approximately 40% of the total biomass energy.

1.2.4 Other extractives

Small amounts of minerals are present in the biomass that forms ashes during pyrolysis. Some organic extractives such as fats, proteins, waxes, gums,

and resins are also present that can be extracted from wood by using polar or nonpolar solvents.

1.3 Biomass conversion techniques

The biomass can be transformed into several types of valuable energy through different conversion techniques. The existing biomass conversion technology consists of physical, chemical, thermochemical, and biochemical methods as shown in Fig. 1.5 (Chen et al., 2003). Any particular technique is selected depending on the feedstock, end-user energy requirement, economic viability, and environmental considerations (Garca-Pèrez et al., 2002; Liu et al., 2017; McKendry, 2002).

1.3.1 Physical method

1.3.1.1 Biomass briquetting

Briquetting, also known as densification, is the process of compacting waste material into a higher-density product of any shape or size as per consumer requirement (Adhikari et al., 2006). Biomass densification is a collection of processes for converting biomass to fuel (Kaliyan & Vance Morey, 2009; Zhu et al., 2020). Briquetting of agricultural, forest, and other biomass waste enhances their efficiency and handling, increases the volumetric calorific value, confirms the environment purity, and reduces the transportation cost (Majhi et al., 2012; Oladeji, 2015). Biomass briquettes can be used in several domestic and industrial applications such as cooking fuel as coal substitute, residential heat systems, industrial furnaces, and heat generation in boilers (Oladeji et al., 2015).

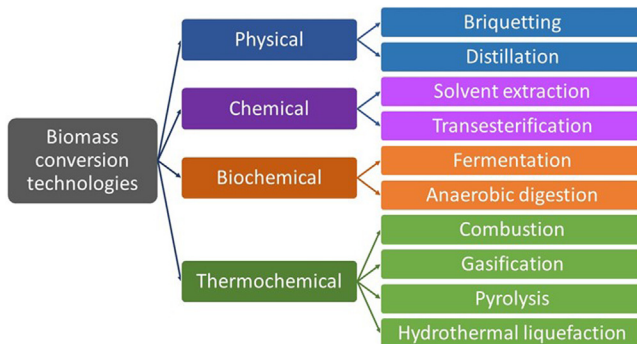


FIGURE 1.5 Biomass conversion technologies. Reprinted from McKendry, P. (2002). *Energy production from biomass conversion technologies*. Bioresource Technology, 83, 47–54.

1.3.1.2 *Steam distillation*

Steam distillation is a component separation method based on the boiling point and further condensing the vapor into liquid. This process is extensively used in industries to extract oil from plants, e.g., eucalyptus oil and orange oil are produced commercially using the steam distillation method. Distillation is also used for obtaining distilled beverages from fermented products or for producing bio-oil after pyrolysis as explained in the following sections (Oladeji, 2015).

1.3.2 **Chemical method**

1.3.2.1 *Solvent extraction*

Solvent extraction is the separation of components based on their solubility in two immiscible liquids. The system consists of an extract phase and a raffinate phase. The extract phase is the solvent that is rich in the solute (i.e., the desired component), and the solute depleted phase is called raffinate (Ndiema et al., 2002). The common solvents used for extraction of chemicals present in bio-oil are alkaline solutions, ethyl acetate, water, toluene, supercritical CO₂, ketones, ethers, and *n*-hexane. Several chemicals such as terpenoids, sterols, and waxes can be extracted from biomass (Oladeji, 2015).

1.3.2.2 *Trans-esterification*

Trans-esterification is the chemical reaction between triglycerides present in animal fat/plant oil/used cooking oil and alcohol (commonly methanol or ethanol) to form first-generation biodiesel (Topare et al., 2011). The concept of breaking triglycerides in fats and oils and utilizing the resultant esters as a source of energy has been considerable for long time. Walton, in 1938, suggested the splitting of triglycerides, and also, there is a report of fatty acid esters being used as fuel in the Congo in 1937 (Graboski & McCormick, 1998; Suppes et al., 2004). Following that, there have been several instances of plant oil/diesel mixes in engines. In 1980, sunflower oil esters were prepared that improved the quality (such as viscosity) of the untreated oil (Konthe, 1980). The trans-esterification can convert up to 98% of triglycerides into biodiesel. Since trans-esterification is a well-established process in petroleum refineries, it can be easily implemented for biomass conversion to biodiesel (Oladeji, 2015).

1.3.3 **Biochemical method**

1.3.3.1 *Fermentation*

Fermentation is the bacterial conversion of biomass into liquid fuel (ethanol, butanol), gaseous fuel (hydrogen), and/or value-added chemicals (acetic acid, lactic acid). Bioethanol is one of the earliest biofuels to be obtained from the

fermentation of sugar/starch in the presence of yeast (Keera et al., 2011). *Schwanniomyces castelli*, *Saccharomyces cerevisiae*, *Endomycopsis burtonii*, and other yeast strains are used in the production of bioethanol. *S. cerevisiae* is the most common species that is readily available and economical for fermentation reactions. The yield of bioethanol can further be improved by adding nutrients such as alkaline amino acids, epsom salt, vitamin B12, and other minerals (Hossain & Jalil, 2018; Vohra et al., 2014).

1.3.3.2 Anaerobic digestion

Anaerobic digestion is used to break a variety of organic matter into biogas or biomethane in the absence of air. It mainly includes hydrolysis, acid generation, acetogenesis, and methanogenesis. The deterioration of sewage sludge by anaerobic digestion has been investigated; however, it further has the potential to become an alternative to the traditional activated sludge technique as it also generates electricity while treating wastewater. Biogas offers numerous advantages over liquefied petroleum gas including the fact that it is easier to recover since the gas separates from the substrate automatically. Biogas also creates enhanced organic manure, which may be used to complement or even replace artificial fertilizers. It can be a source of decentralized power generation in rural regions. This technique may also be used to dispose of home trash and bio-oil waste beneficially and healthfully. However, significant environmental and economic hurdles must be overcome for this technology to be a viable alternative to present fossil fuels (Zuber & Dwivedi, 2013).

1.3.3.3 Bioelectrochemical systems

Bioelectrochemical system combines biological and electrochemical technology to directly transform the energy contained in biomass into electricity (Mata-Alvarez et al., 2000). The system uses a specific type of bacteria known as exoelectrogens that can interact and donate electrons to the solid electrode surface. Conventional fuel cells are converted to microbial fuel cells such that the organic substrate or biomass acts as the fuel and the microorganisms act as catalysts. It contains two half cells (anode and cathode) that are connected by an ion-exchange membrane. By the action of microbes, the energy stored in the biomass is oxidized to CO₂, protons, and electrons that when connected to an external circuit recombine at the cathode to generate electricity or hydrogen depending upon the terminal electron acceptor present at cathode (Sleutels et al., 2012).

1.3.4 Thermochemical method

Different thermochemical processes lead to different product forms. Gasification process converts biomass into synthesis gas. Combustion burns the biomass in

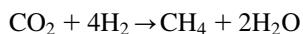
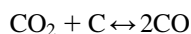
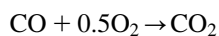
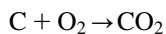
the presence of air to form heat or electricity. Liquefaction occurs at high pressure and low temperature over some catalysts in hydrogen flow to form liquid product. Pyrolysis is the process of heating biomass in the absence of oxygen to form liquid bio-oil along with biochar and synthesis gas (Logan et al., 2006). The bio-oil, after upgrading, has the potential to replace hydrocarbon fuel such as diesel and other heavy fuels (Chen et al., 2003).

1.3.4.1 Combustion

The energy content in the biomass is transformed into heat, water, and carbon dioxide in the presence of air by the combustion process. Hot gases are produced during combustion in a temperature range of 850°C – 1050°C. Combustion is used at a small scale for domestic purposes such as heating and cooking. Industrial-scale combustion process is carried out in boilers, furnaces, steam turbines, etc. (Gao et al., 2016). Biomass combustion requires initial treatment of straw, wood, etc., by compressing, grinding, chopping, etc. Moreover, the high amount of moisture in the biomass increases the cost of large-scale biomass power generation systems (Nussbaumer, 2003).

1.3.4.2 Gasification

Gasification has been used to convert carbonaceous fossil fuels to gaseous products by supplying limited amounts of oxygen, air, or steam at high temperatures (Patil et al., 2015). The same process is implemented for biomass conversion to synthesis gas or producer gas. Gasification of biomass is conducted at high temperatures in the range of 800°C – 900°C. Synthesis gas is composed of CO and H₂. Producer gas is a mixture of several gases such as CO, CO₂, H₂, CH₄, and N₂ (Bhowmik & Roy, 1983). During the gasification reaction, the reactor undergoes the following reactions:



The generated gas has poor calorific value (4–6 MJ/m³), which is further burnt or used as a fuel for gas engines and gas turbines (Asadullah et al., 2002; Molino et al., 2016). Hydrogenation (HYD) is mostly used to produce methane by hydro-gasification. One of the methods starts with the formation of synthesis gas followed by a hydrogen-based reaction to produce methane.

1.3.4.3 Liquefaction

Liquefaction is a process that is operated at high pressure and low temperature in the presence of a catalyst to produce liquid products. High pressure facilitates efficient heat transmission in the liquid system. This process is lesser focused upon as compared with gasification due to the need of a complex and expensive reactor system and the handling of sticky and tarry lumps of liquefied heavy oil (Demirbas, 2004).

1.3.4.4 Pyrolysis

Pyrolysis is the heating of feedstock in the absence of air to produce products in liquid, solid, and gaseous phases. Lignocellulosic biomass is utilized as feedstock materials in biomass pyrolysis to produce liquid bio-oil, noncondensable gases, and biochar with initial biomass decomposition at 300°C and reaching up to 600°C–700°C (Demirbas, 2001). Currently, pyrolysis and gasification are the most researched and applicable techniques as they are environmentally benign processes and provide higher-quality products (Afreen & Upadhyayula, 2021).

The thermochemical methods for biomass conversion are summarized as follows.

1.3.5 Pyrolysis of biomass

Biomass pyrolysis is one of the most efficient thermochemical techniques to produce a viscous liquid called bio-oil along with char and some gases (Al-Sabawi et al., 2012; Bridgwater, 1994; Bridgwater, 2006; Capunitan & Capareda, 2013; Czernik & Bridgwater, 2004; Fan et al., 2017; Hu et al., 2013; Karge, 2001; Li et al., 2014; Majhi et al., 2012; Mura et al., 2013; Okajima & Sako, 2014; Paenpong et al., 2013; Pearce & Othmer, 1978; Pidasang et al., 2013; Qi et al., 2007; Salehi et al., 2011; Scragg, 2009; Vispute et al., 2010). The quality and yield of bio-oil are dependent on the composition of biomass and the operational parameters such as temperature, pressure, residence time, reaction time, and heating rate. For example, medium temperature and small residence time are favorable for high bio-oil yield, low temperature and long residence time give more biochar, and high temperature and long residence time produce high amounts of gases (Pearce & Othmer, 1978). Some of the properties of the bio-oil obtained from wood pyrolysis are given in Table 1.4. Degradation of cellulose on heating includes two fundamental processes: heating at lower temperature degrades and decomposes into biochar while heating at higher temperature leads to volatilization into the formation of levoglucosan. Hemicellulose degradation is faster than that of cellulose on heating. Initial lignin decomposition starts at ~280°C, and it decomposes better at ~450°C–500°C. Two methods have been established for lignin decomposition. First, two-step depolymerization

TABLE 1.4 Properties of bio-oil produced from wood (A. V. Bridgwater, 1994).

Property	Value	Comments
Moisture	25%	From moisture in feed
pH	2.5	From moisture in feed
Specific density	1.2	Dense compared to other fuels
Elemental analysis	C 57%; H 6%; O ₂ 37%; N ₂ Trace	–
Ash	0%	Stays with char
Viscosity (40°C)	50 cp	Can vary from 20 to 1000 cst
Solids	0.2%	Char
High heating value	18 MJ/kg	–

followed by deoxygenative hydroprocessing that results in hydrocarbons, gasoline, naphthenes, paraffin, C₇–C₁₁ alkyl benzenes, etc. Second, depolymerization followed by nondeoxygenating hydrotreatment that results in reformulated, partly oxygenated gasoline.

Pyrolysis, utilized for thousands of years, initially for charcoal production through the thermal decomposition of organic materials, has evolved into a modern, versatile process applied for biofuel generation, waste treatment, and valuable chemical production from biomass, contributing to renewable energy and sustainable resource management. The pyrolysis of biomass exhibits variations determined by the residence time of solid feedstock in the reactor, with methods such as slow pyrolysis, flash pyrolysis, and fast pyrolysis; traditionally conducted in earthen, brick, and steel kilns, this process results in the production of biochar (A. V. Bridgwater, 1994). The slow pyrolysis process occurred at low temperatures and prolonged time. Whereas, fast pyrolysis offered quick, more appropriate, and more advantageous over the other methods. Fig. 1.6 shows the various pyrolysis types with their properties.

The basic events that occur during pyrolysis are as follows:

- Transfer of heat from a source to raise the temperature of the fuel.
- Increasing temperature initiates the primary pyrolysis resulting in the formation of volatiles and char.
- Heat transfer between the hot-flowing volatiles and the upcoming cooler unmodified solid fuel.
- Heat transfer results in condensation of certain concentrations of volatiles and further secondary reactions create tar.

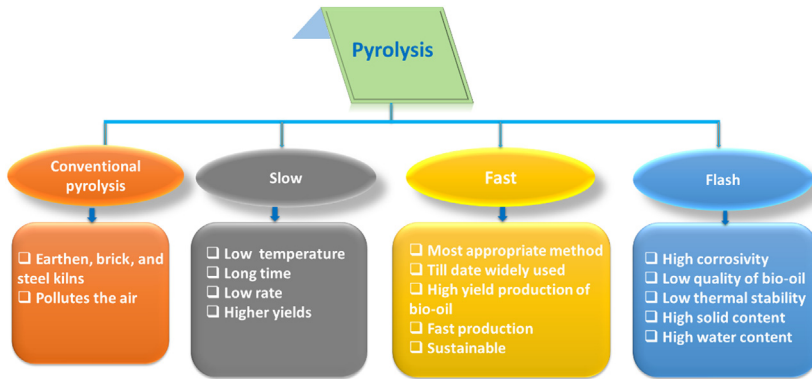


FIGURE 1.6 Schematic representation of pyrolysis and their types.

TABLE 1.5 Different pyrolysis processes (Scragg, 2009).

Pyrolysis process	Temperature (°C)	Heating rate (°C/m)	Residence time	Major products
Slow pyrolysis	400 – 600	0.1 – 0.3	30 – 60 min	Bio-oil, char, gas
Fast pyrolysis	600 – 1100	10 – 100	10 s	Bio-oil
Flash pyrolysis	1100 – 1300	>1000	1 s	Bio-oil

- Competitive secondary pyrolysis in parallel with primary pyrolysis reactions.

Operational parameters mediated reactions such as decomposition, reforming, recombination, dehydration, and water – gas shift.

1.3.5.1 Types of pyrolysis

The pyrolysis process is classified into three main categories, i.e., slow, fast, and flash pyrolysis based on operating conditions such as temperature, residence time, and heating rate. The product distribution of different types of pyrolysis is given in Table 1.5.

Since 1990, fast pyrolysis has been employed for bio-oil production, involving the decomposition of biomass components (cellulose, hemicellulose, and lignin) into approximately 65% liquid, 20% solid, and 15% gases at temperatures around 600°C (Karge, 2001; Salehi et al., 2011). Literature indicates that multiple parameters influence pyrolysis, such as temperature, biomass composition, heating rate, reactor design, and various catalytic systems.

1.3.5.2 Advantages of fast pyrolysis

Fast pyrolysis is a crucial technique for enhancing bio-oil through diverse methods, given its ability to efficiently convert a larger proportion of biomass into direct liquids. Till date, biomass stands as the primary and sustainable source, serving as a renewable alternative to crude oil. Biopolymers found in biomass, including cellulose, hemicellulose, and lignin, possess diverse uses and constitute a significant portion of biomass composition. As per reports, fast pyrolysis is an adaptable technology to transform solid biomass into fuels through various catalytic approaches, as illustrated in Fig. 1.7 (Bridgwater, 2012). The pyrolysis liquids obtained exhibit higher volumetric density. However, the fast pyrolysis oils have few negative properties such as less hydrogen and carbon ratio. Additionally, these oils have low stability during heating. Nonetheless, researchers continually exert efforts to enhance these properties through ongoing advancements. Several successful technologies have been explored, and the search for improvements is ongoing. Especially noteworthy is the exploration of catalysts and their versatile applications in catalytic pyrolysis (Qi et al., 2007).

1.4 Bio-oil upgradation

Bio-oil upgradation refers to the process of enhancing the quality of bio-oil derived from biomass, such as wood, agricultural residues, and other organic materials, through various techniques. Also known as pyrolysis oil, bio-oil has potential as a renewable energy source, but it often requires upgrading to optimize its properties for different applications. This upgrading is essential to increase its suitability and ensure its effectiveness in a variety of uses.

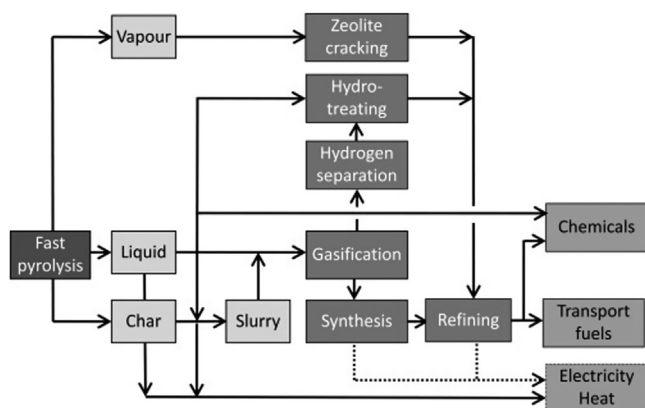


FIGURE 1.7 Schematic representation of fast pyrolysis upgradation of bio-oil to fuel and chemicals. Reprinted from Bridgwater, A. V. (2012). *Review of fast pyrolysis of biomass and product upgradation*. Biomass and Bioenergy, 38, 68–94. <https://doi.org/10.1016/j.biombioe.2011.01.048>.

1.4.1 Bio-oil general upgradation reactions

Various catalytic processes, including catalytic cracking, (Al-Sabawi et al., 2012) HYD (Czernik & Bridgwater, 2004), emulsification (T. Bridgwater, 2006), and supercritical technology, are being explored in the quest for advancement in biomass conversion (Fan et al., 2017). These approaches offer numerous advantages, with catalytic HYD emerging as a promising alternative. The catalyzed upgrading followed by a hydrotreatment process, typically carried out at a temperature of 100°C–400°C and a hydrogen process of 1400–4200 PSI. As per the literature reports, the catalytic hydrotreatment at more than 300°C is not good due to instability and depolymerization of labile groups. However, at temperatures below a certain threshold, labile groups remain stable, preventing polymerization from occurring (Ali et al., 2016). To date, catalytic reactor systems play a crucial role in bio-oil production, with raw bio-oils typically containing over thousands of organic compounds. Notably, the raw materials include acids, aldehydes, esters, ethers, and ketones, and the diverse classifications of these crucial molecules are depicted in Fig. 1.8. Besides, oligomers with molecular weights in the range of MW = 900–2500 also exist in the bio-oil with a large amount (Choudhury et al., 2014). These compounds' distribution is mainly determined by biomass type and pyrolysis route, which is related to the physico-chemical properties of bio-oil (Adjaye & Bakhshi, 1995; Varma et al., 2019).

1.4.2 Properties of bio-oil

The fundamental properties of raw bio-oil and petroleum fuel oil are compared and illustrated in Fig. 1.9 (Baker & Elliott, 1989; Czernik & Bridgwater, 2004; Hew et al., 2010). Obviously, the bio-oil contains significantly high level of oxygen and H₂O contents, which leads to lower heating value. Higher heating values (HHV, MJ/kg) of the pyrolysis bio-oils from

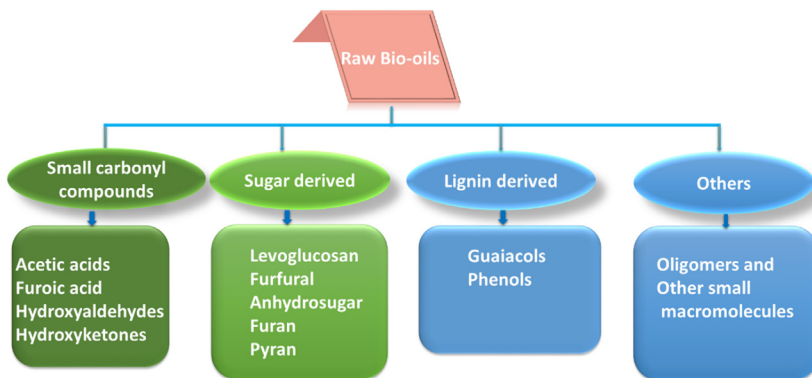


FIGURE 1.8 Upgrading raw bio-oil to specific products.

Bio-oil comparison properties

Carbon (wt.%)	54-58	85
Hydrogen (wt.%)	5.7-7.0	11
Oxygen (wt.%)	35-40	1.0
Nitrogen (wt.%)	0-0.2	0.3
Water content (wt.%)	15-30	0.1
pH	2.5	-
Viscosity (at 50°C) (mPa s)	40-100	180
Distillation residue (wt.%)	50	1
HHV (MJ/kg)	16-19	4

FIGURE 1.9 Schematic representation of bio-oil and their properties (He et al., 2019).

wood usually ranged from 16 to 19 MJ/kg. Petroleum fuel oil typically exhibits a higher heating value of 40 MJ/kg compared with bio-oil. The low quality of raw bio-oil resulted from its high oxygen and water contents with some solids components, high viscosity, low pH value, and thermal instability with poor combustion properties (Hew et al., 2010). The primary reason for the low heating value of bio-oil is its elevated oxygen content. Moreover, the unsaturated components, such as phenols and aldehydes, in bio-oil are inherently unstable and can readily undergo polymerization, especially under acidic conditions, leading to increased viscosity and reduced liquidity.

Indeed, as discussed earlier, catalytic HYD and catalytic cracking are the primary technological routes for the upgrading of bio-oil. There are two processes for the upgrading of bio-oil: *in situ* catalytic and *ex situ* catalytic pyrolysis upgrading. In an *in situ* catalytic process, catalysts are mixed with biomass. Catalysts utilize their pores to interact with pyrolysis vapors in the upgrading process. That interaction goes with different forms of reactions such as aromatization, condensation, and deoxygenation. In *ex situ* catalytic process, biomass and catalysts interact separately in the reactor as shown in Fig. 1.10.

There are different types of reactions involved in bio-oil upgradation producing more than 200 products. Processes such as dehydration, decarboxylation, cracking, aromatization, ketonization, condensation, and polymerization are notably involved, with the selection of a suitable catalytic system and its modifications tailored for the upgrading of specific or different bio-oils. For example, zeolite having a Brønsted acid site possesses aromatic

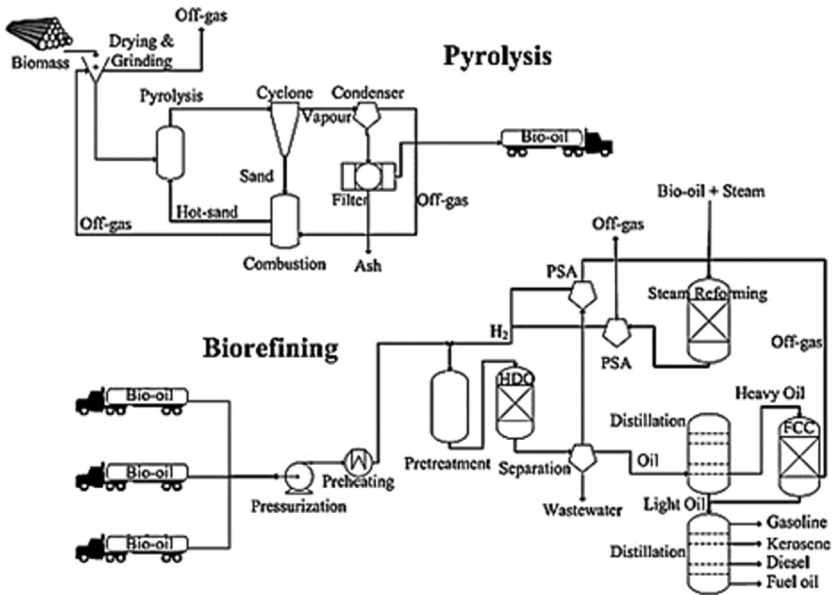


FIGURE 1.10 Schematic representation for production biofuel based on catalytic upgradation techniques. Reprinted from Mortensen, M., Grunwaldt, J.-D., Jensen, P. A., Knudsen, K. G., & Jensen, A. D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. Applied Catalysis A: General, 407, 1–19.

compounds such as toluene and benzene. Therefore, conducting parameter studies of catalysts, biomass, and other factors plays a crucial role in the reactions involved in the upgrading of bio-oil (Tang et al., 2009).

1.4.3 Catalysts

To date, the various techniques used for upgrading using solid catalysts are HDO, hydrodesulfurization, hydrodenitrogenation, hydrodemetallization, and HYD. Table 1.6 reviews the parametric studies of catalysts, degree of deoxygenation (DOD), and product yield for bio-oil upgradation through HDO reaction. It has been observed that various catalytic systems are applied for upgrading, providing the reader with insights into the choice of operating conditions in conjunction with catalysts. Remarkably, zeolite-based catalysts have huge advantages over the other catalysts demonstrated in Table 1.7. The design and fabrication of zeolites and their huge applications occurred in the high-quality production of bio-oil.

1.4.3.1 Zeolite

Zeolites are the microporous aluminosilicates having various cations Na^+ , K^+ , Ca^+ , and Mg^+ . Zeolites are widely utilized in ion-exchange materials

TABLE 1.6 Catalytic bio-oil upgradation through HDO reaction (Wildschut et al., 2009).

Catalyst	Bio-oil source	Setup	Time [h]	P [bar]	T [°C]	DOD [%]	O/C [molar]	H/C [molar]	Y _{oil} [wt.%]	References
Co-MoS ₂ /Al ₂ O ₃	Beech	Batch	4	200	350	82	0.07	1.20	26	Mortensen et al. (2011)
Co-MoS ₂ /Al ₂ O ₃	Beech	Batch	4	100	250	41	0.27	1.24	28	Mortensen et al. (2011)
Co-MoS ₂	Maple and oak	Continuous	4	≤ 300	370	99.9	0.00	1.82	33	Sheu et al. (1988)
Ni-MoS ₂	Maple and oak	Continuous	–	≤ 300	370	97	0.00	1.79	34	Sheu et al. (1988)
	Beech	Batch	4	200	350	74	0.10	1.24	28	Mortensen et al. (2011)
Ni-MoS ₂ /Al ₂ O ₃	Beech	Batch	4	100	250	37	0.31	1.48	31	Mortensen et al. (2011)
Ni-MoS ₂ /Al ₂ O ₃	Pine	Continuous	–	87	400	28	–	–	84	Wang et al. (2014)
Ni-MoS ₂ /Al ₂ O ₃	Pine	Continuous	168–192	96	330	100	0.00	1.18	–	Badawi et al. (2011)
Ni-MoS ₂ /Al ₂ O ₃	Wood	Continuous	6	100	300	100	–	2.1	–	Mante et al. (2016)

Ni-MoS ₂	Pine	Continuous	13–16	100	350	94	0.01	1.06	64	Boscagli et al. (2015)
Ni-MoS ₂	Pine	Continuous	73–97	138	300	60	0.07	1.39	73	Boscagli et al. (2015)
Ni-MoS ₂	Pine	Continuous	117–132	138	290	62	0.07	1.37	82	Boscagli et al. (2015)
Ni/SiO ₂	Wheat straw	Batch	4	130–180	250	51	0.25	1.46	15	Cheng et al. (2017)
Ni/ZrO ₂	Wheat straw	Batch	4	130–180	250	41	0.21	1.36	13	Cheng et al. (2017)
Fe ₂ O ₃ /SiO ₂	Pine	Batch	5	>35	300	31	0.30	1.05	33	Guo et al. (2018)
Co ₃ O ₄ /SiO ₂	Pine	Batch	5	>35	300	17	0.39	1.22	31	Guo et al. (2018)
Fe ₂ O ₃ Co ₃ O ₄ /SiO ₂	Pine	Batch	5	>35	300	26	0.31	1.21	27	Guo et al. (2018)
NiP/AC ^B	Hardwood	Batch	3	110–170	300	65	0.11	1.29	63	Elliott et al. (2009)
NiRuP/AC ^B	Hardwood	Batch	3	110–170	300	48	0.19	1.39	59	Elliott et al. (2009)
<i>(Continued)</i>										

TABLE 1.6 (Continued)

Catalyst	Bio-oil source	Setup	Time [h]	P [bar]	T [°C]	DOD [%]	O/C [molar]	H/C [molar]	Y_{oil} [wt.%]	References
CoP/AC ^B	Hardwood	Batch	3	110–170	300	62	0.12	1.26	60	Elliott et al. (2009)
CoRuP/AC ^B	Hardwood	Batch	3	110–170	300	48	0.19	1.37	63	Elliott et al. (2009)
Pd/C	Beech	Batch	4	200	350	85	0.06	1.26	65	Mortensen et al. (2011)
Pd/C	Beech	Batch	4	100	250	56	0.19	1.30	44	Mortensen et al. (2011)
Pd/C	Mixed wood	Continuous	–	138	340	63	0.12	1.49	62	Bjelić et al. (2020)
Pt/Al ₂ O ₃ -SiO ₂	Pine	Continuous	–	87	400	45	–	–	81	Wang et al. (2014)

HDO, Hydrodeoxygenation.

TABLE 1.7 Various zeolites screening for upgrading bio-oils (Wildschut et al., 2009).

Zeolites	DOD %	Y _{oil} wt.%
GaHZSM-5	–	18
H-mordenite	–	17
H–Y	–	28
HZSM-5	50	24
MgAPO-36	–	16
SAPO-11	–	20
SAPO-5	–	22

Note: Setup: batch and continuous, Feed: bio-oil, Time: 0.2–0.5 h, Temp: 300°C–400°C, Pressure: 1 bar.

and catalysts. Zeolites such as beta, Y, SSZ-55, ZSM-5, ZSM-23, and ZSM-11 with variable pores have been highly investigated for bio-oil upgrading. In the studies of zeolite-based upgrading of bio-oil, it is essential to investigate zeolite properties such as the balance of acidic and basic strength, shape, pore size, surface area, and other relevant characteristics. However, the calculation of the conversion of each component of the oil is difficult. The conversion of oil was done by using the DOD. As per the literature reports, for operating conditions, high pressure is in a range from 80 to 300 bar and the temperature up to 400°C (Blanco, Dongil, et al., 2020).

1.4.3.2 Hierarchical zeolites

Zeolites are promising catalysts attracting a lot of research work due to their ordered microporous framework, high surface area, tunable acidity and porosity, hydrophobicity, hydrothermal stability, etc. Hence, they find a wide range of commercial applications such as in petrochemicals, oil refineries, pollution control, and fine chemistry (Arora et al., 2020; Blanco, Dongil, et al., 2020; Blanco, Rosenkranz, et al., 2020; Bredenberg et al., 1989; Christensen et al., 2003, 2007; He et al., 2019; Jeong et al., 2021; Jia et al., 2018; Jongerius et al., 2012; Karge, 2001; Lachos-Perez et al., 2023; Li et al., 2020; Liu et al., 2020; Long et al., 2020; Rocha et al., 2017; Saidi & Baharan, 2020; Shu et al., 2020; Sirous-Rezaei et al., 2019; Song et al., 2020; Wu et al., 2020; Yue et al., 2020; Zhao et al., 2020). However, the micropores restrict the inward and outward diffusion of bulky reactant and product molecules resulting in lower reaction rates and high deactivation. When mesopores and macropores are introduced in the zeolite framework,

hierarchical zeolites are formed that enhance the reaction rates as well as reduce catalyst deactivation. The pores introduced are either intra- or inter-crystalline. They can be formed by presynthesis or postsynthesis routes as shown in Fig. 1.11. The presynthesis method has better structure control but has certain limitations such as a complex process, economic unavailability, and long time that prevents its commercial use. The postsynthesis method is therefore majorly utilized, which has the simple procedure of modification, shorter duration, higher efficiency, scalability, versatility, and economic viability. The advantages of hierarchical zeolites over microporous zeolites are as follows:

- Ease of bulk molecule diffusion at the active site inside the secondary pores.
- Knudsen diffusion offers a shorter diffusional length (Christensen et al., 2007; Jia et al., 2018; Karge, 2001).
- Extended zeolite applications as numerous reactions with a wide range of molecule sizes are possible by steric hindrance minimization.
- Resistance to coke deposition by providing extra active sites and limiting the secondary reactions (Karge, 2001).

Additionally, zeolites are employed in the catalytic pyrolysis of biomass for bio-oil production, aiming to increase the production of aromatic products. The mechanism pathway for the generation of these aromatic products through catalytic pyrolysis of lignocellulose with zeolites is depicted in the

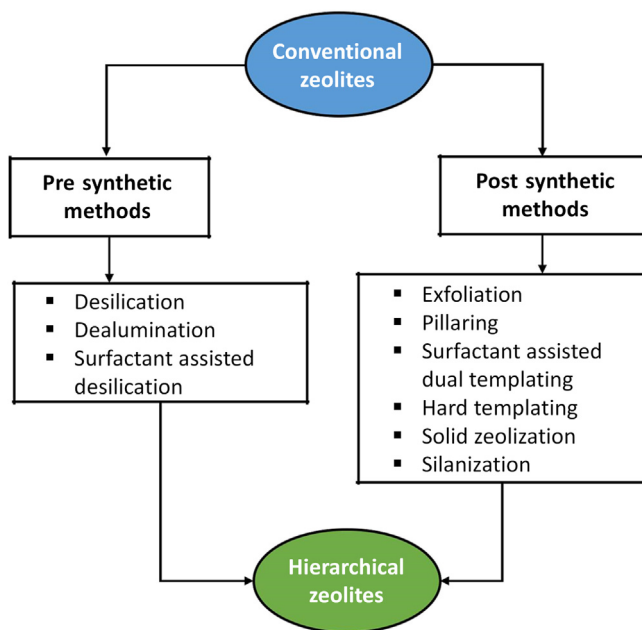


FIGURE 1.11 The schematic representation of various hierarchical zeolite formation strategies.

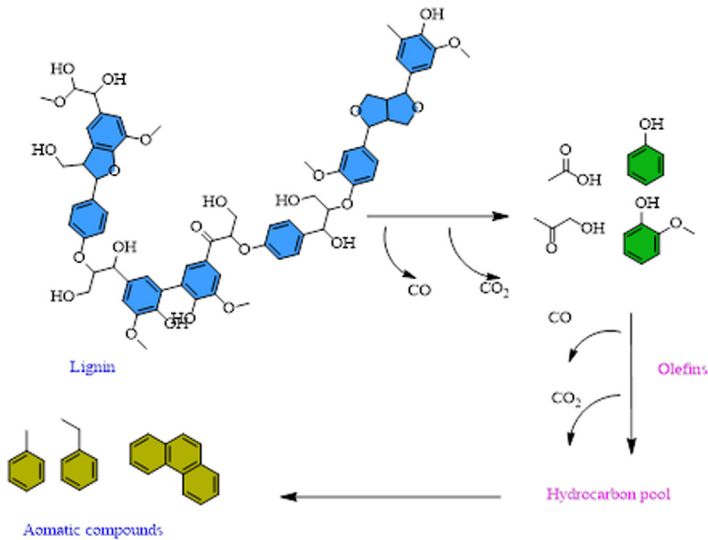


FIGURE 1.12 Proposed mechanism for the formation of aromatics from lignocellulosic feedstock through catalytic pyrolysis proposed mechanism for the formation of aromatic compounds.

reaction scheme as Fig. 1.12. It is noteworthy that selecting an appropriate catalytic system is essential to achieve optimal yields or specific product.

1.4.4 Bio-oil upgrading technologies

Reflecting on the aforementioned part about upgrading bio-oil, it has been observed that the unsought properties restrict its purposes to transportation fuels and chemicals. Certainly, upgrading or enhancing the quality of bio-oil is essential for continual improvement. Moreover, this upgrading process is crucial for making bio-oil a viable ingredient in chemicals and achieving a standard comparable with petroleum-based liquid fuels. In this section, diverse separation techniques for bio-oil upgrading are explored, encompassing new challenges and technologies, as illustrated in Fig. 1.13. Hydrotreating contains more hydrogen to improve the quality of petroleum-based bio-oils. The process involving the addition of hydrogen and the removal of oxygen is known as HYD, and in the context of bio-oil upgrading, it is often referred to as HDO. This process is crucial for reducing the oxygen content in bio-oil, improving its stability, and making it more suitable for use as a liquid fuel or chemical feedstock. Another process is catalytic cracking or hydrocracking, in which the thermal method is used for upgrading. This method involves the removal of oxygen in the form of carbon dioxide and water, resulting in the breakdown of bio-oil into light olefins. Steam reforming can be employed in this process to produce synthesis gas (CO/H_2) for further upgrading.

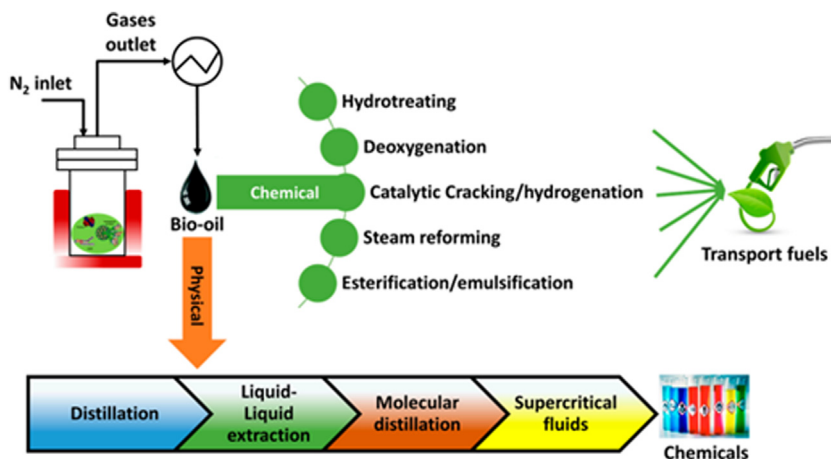


FIGURE 1.13 Bio-oil upgrading techniques reaction conditions and technical feasibility of the current upgrading techniques of bio-oil. Reprinted from Lachos-Perez, D., Martins-Vieira, J. C., Missau, J., Anshu, K., Siakpebru, O. K., Thengane, S. K., Morais, A. R. C., Tanabe, E. H., & Bertuol, D. A. (2023). Review on biomass pyrolysis with a focus on bio-oil upgrading techniques. *Analytica*, 4, 182–205.

The production of hydrogen has garnered attention due to its favorable characteristics and utility as a fuel. According to reports, steam reforming stands out as an innovative pathway for upgrading bio-oil into hydrogen. There are catalytic and noncatalytic approaches for significant conversion of bio-oil. Furthermore, bio-oil contains huge oxygenated compounds and easily breaks due to low stability limiting its application in transportation fuels. In the esterification process, the polar alcohols based on methanol, and ethanol with organic acids take part in their corresponding esters to increase the quality of bio-oil. Distillation, as noted in consideration of the properties of bio-oil with over 300 produced compounds, poses challenges for purification. The distillation technique, often conducted under vacuum conditions, has been employed for the recovery and purification of these compounds. In addition to distillation, supercritical fluid extraction, emulsification, liquid – liquid extraction, and other techniques are extensively studied for the upgrading of bio-oil (Arora et al., 2020; Blanco, Dongil, et al., 2020; Blanco, Rosenkranz, et al., 2020; Bredenberg et al., 1989; He et al., 2019; Jeong et al., 2021; Jongerius et al., 2012; Lachos-Perez et al., 2023; Li et al., 2020; Liu et al., 2020; Long et al., 2020; Rocha et al., 2017; Saidi & Baharan, 2020; Shu et al., 2020; Sirous-Rezaei et al., 2019; Song et al., 2020; Wu et al., 2020; Yue et al., 2020; Zhao et al., 2020).

1.4.5 Application of bio-oil

In this chapter, as we explored various techniques, catalytic systems, different biomass sources, and pyrolysis methods for the upgradation of bio-oil, it

is crucial to emphasize their diverse applications. Undoubtedly, biofuels have widespread applications, including transportation, heating, and electric generation. Upgraded bio-oil can be directly used as fuel or for power generation. Furthermore, bio-oil holds substantial potential for varied applications as a renewable feedstock for hydrogen production, carbon-based products, and other chemicals. The production of bio-plastics, binders, and polyurethane foam is also achievable through bio-oil. It's essential to acknowledge that the hydrogen generation from bio-oil faces several technological and economic challenges that hinder its commercialization. Nevertheless, bio-oil can be directly utilized for various chemical productions through distillation and solvent extraction, generating chemicals with diverse industrial applications as intermediates or end products. Through distillation and solvent extraction, bio-oil can yield valuable organic molecules such as phenols, organic acids, and aldehydes. However, these types of carbon-based components serve as essential building blocks in the synthesis of a wide range of products. The production of carbonaceous materials from bio-oil is a recent exploration, and while the conversion process is simple and cost-effective, achieving precise control over the final properties can be challenging. Another drawback is the relatively low conversion yield of bio-oil into solid carbonaceous materials. Despite the potential application of these carbonaceous materials, such as in electrodes, a comprehensive technoeconomic study is needed to assess the process's cost and identify potential bottlenecks. In the current scenario, it may not be considered an optimal solution to use bio-oil for this potential application.

1.4.6 Conclusion and future directions

Among all the biomass conversion routes, the pyrolysis process can be considered as an exquisite route, especially for the biomass with high lignin content. Pyrolysis is a robust process that operates at high temperatures in the absence of oxygen, which can suitably decompose the complex lignin structures along with cellulose and hemicellulose. The pyrolysis oil is acidic, viscous, unstable and contains a high amount of oxygen functionalities. All these properties result in its low heating value and hinder its direct use as an alternative fuel. This in turn necessitates the bio-oil upgradation step to bring them to par with commercial fuels. The pyrolytic bio-oil is upgraded to meet the commercial fuel standard by different methods such as steam reforming, catalytic cracking, HDO, esterification, and supercritical fluid. Among the various upgrading techniques, hydrodeoxygenation has gained a lot of attention because of more favorable results. Hydrodeoxygenation can be tailored to produce different types of products based on the desired application, such as transportation fuel (diesel and jet fuel), specialty chemicals (polymers, resins, plastics, and various high-value organic chemical), or feedstocks for other processes.

Indeed, the success of the process for producing carbonaceous materials from bio-oil heavily relies on the choice of catalysts and operating conditions. Various research groups are actively working to identify the most suitable catalyst for HDO by removing the oxygen from specific functional groups (hydroxyl, acids, and other carbonyl groups) to produce hydrocarbons. Zeolites, among the various catalysts employed for HDO, have garnered attention due to their shape selectivity, resistance to coke formation, and corrosion resistance. In spite of this, the microporous networks of zeolites hinder the movement of bulky reactants and products. To combat this problem, research is being conducted on hierarchical zeolites that incorporate macroporous and mesoporous, along with the microporous network of zeolites. In future, a significant challenge lies in the search for more effective catalysts that are not only greener but also multifunctional, to be utilized in bio-oil upgrading techniques. Notably, exploring innovative catalytic techniques such as nanocatalysis holds promise in achieving more precise control over the upgrading reactions and improving overall conversion yields. The development of such types of catalysts with enhanced environmental sustainability and versatile functionalities is crucial for advancing the efficiency and eco-friendliness of the bio-oil upgrading process. Moreover, the development of novel spectral and chemical characterization techniques for both catalysts and bio-oil is crucial. Scaling-up production and purification processes on a bulk scale are also essential aspects of bio-oil upgradation.

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