



FORESTRY BIOMASS IN A BIOENERGY PERSPECTIVE

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ABSTRACT

The demand for energy has been increasing in the current decade due to rapid industrialization and urbanization. Limited fossil fuel resources, rising fuel prices, and global warming are some of the factors leading to increased interest in lignocellulosic biomass to generate renewable fuels. Forestry residues which contain a major proportion of lignocellulosic matter are suitable candidates for conversion to liquid and gaseous fuels. This review highlights forestry biomass from a bioenergy point of view, focusing on its global applications, availability, chemical composition, and conversion. The conversion pathways discussed here are biochemical conversion to ethanol and butanol as well as thermochemical conversions, including pyrolysis, liquefaction, and gasification, to produce process-specific end products such as bio-oil and synthesis gas. A wide variety of woody biomass species are also discussed, indicating their variation in cellulose, hemicellulose, and lignin content; bio-oil, biochar, and gas yields through pyrolysis; and bioethanol and biobutanol yields through bioconversion.

INTRODUCTION

In the current decade, it is crucial to develop energy-efficient technologies to produce sustainable fuels and chemicals. This is due to socio-economic concerns such as exhaustion of petroleum resources and increased demand for fossil energy by developing nations combined with their political and environmental concerns [1]. This requires the use of alternative energy sources to produce renewable fuels. Although energy harnessed from sunlight, wind, or water could supply heat and electricity for domestic and industrial purposes, it cannot fuel motor vehicle engines. In this respect, waste plant biomass could be looked upon as the only source of renewable carbon and biofuels. In addition, biofuels have significantly less greenhouse

gas emissions and are considered carbon-neutral because CO_2 generated from their combustion is consumed by plants during photosynthesis to produce new biomass. The carbon-neutral cycle of biofuels in nature is illustrated in Fig 1.

Plant biomass, especially its non-edible residues, is an attractive resource for biofuel production because it does not create any “food-versus-fuel” conflicts, unlike starch-based feedstocks that are often linked with the risk of diverting farmlands for fuel production [2,3]. These non-edible plant residues are also called next-generation biofuel feedstocks or lignocellulosic biomass. After the edible parts (grains and other food/feed-based materials) have been harvested from the

plants, the remaining non-edible fraction is separated and can then be converted into transportation fuel. Biomass that is normally in low-density form can be densified in the form of bales, pellets, or briquettes and transported to biorefineries to be converted into fuels. Biomass densification not only saves the cost associated with transportation and other logistics, but also enhances the heating value of the solid fuel [4].

The term “lignocellulose” refers to the chemical nature of these feedstocks, which contain cellulose, hemicelluloses, and lignin in varying compositions. Lignocellulose makes up approximately half the plant matter produced through photosynthesis, averaging about 70% in plant cell walls. This makes it the most abundant renewable organic resource [5]. Bioenergy or biomass energy is the potential solution to the energy security challenges faced by the global economy due to its dependency on rapidly declining fossil fuel resources. Lignocellulosic biomass broadly includes waste residues from agriculture and forestry resources. Worldwide annual production of lignocellulosic biomass from terrestrial plants is approximately $17\text{--}20 \times 10^{10}$ tonnes [6]. It is essential to explore the properties of lignocellulosic biomass as a candidate for biofuel production



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to promote its eco-friendly use.

Lignocellulosic biomass can be converted into biofuels by three primary pathways: thermochemical, hydrothermal, and biochemical. Depending on the type of conversion pathway, the product (i.e., fuel or chemical) yields vary. Thermochemical conversion includes mostly pyrolysis and liquefaction, which convert biomass chiefly to bio-oil with certain amounts of biochar and gases. Hydrothermal conversion (sometimes included in thermochemical pathways) degrades biomass in supercritical water to synthesis gas (H_2 and CO) through gasification. This synthesis gas or syngas can be further converted to hydrocarbons (e.g., gasoline and diesel), methanol, ethanol, and butanol through various gas-to-liquid (GTL) conversions such as the Fischer-Tropsch process or syngas fermentation [7]. Through biochemical conversion, biomass is pretreated to monomeric sugars and further fermented to alcoholic fuels such as ethanol and butanol. These lignocellulose conversion pathways have been comprehensively described by Nanda et al. [7].

This review is focussed on current conversion methods available for lignocellulosic biomass, in particular forest-based residues, to synthesize transportation fuels. The review also highlights the worldwide geographical distribution of forested areas, with a special emphasis on United

States and Canadian statistics with their insights into possible use for biofuel production. Finally, the composition of various wood-based feedstocks is discussed, followed by their thermochemical and biochemical conversions.

FOREST RESOURCES – GEOGRAPHICAL STATISTICS

Global forest resources represent a total area of 4,033,060 hectares [8]. These forest resources have myriad uses, as shown in Fig. 2. For instance, out of total forest resources, 30% is used in the production of wood and timber; 8% helps to conserve soil and water resources (i.e., ecosystems); 12% aids in conserving biodiversity (i.e., flora and fauna); 4% is used for cultural services such as social or recreational needs (e.g., hunting, camping, and ecotourism); 7% is used in industry; and 24% has multiple uses [9]. The remaining 16% of forest resources remain unused. Industrial use of wood occurs primarily in mining and oil/gas recovery. Furthermore, the multiple uses of forest residues include production of biochemicals, biolubricants, biocomposite materials, adhesives, perfumes, cosmetics, furniture, plywood, and many other products.

Figure 3 gives a more detailed illustration of current and potential applications of forest resources. Forest resources

have long been used as timber and lumber to build infrastructure, furniture, and utility poles to support overhead power lines, fibre optic cables, transformers, and street lights. The traditional use of wood has been to produce heat energy for cooking and sustain rural livelihoods. Wood resources have also gained industrial attention for manufacturing pulp and paper, plywood, and wood-based composites along with laminates and packaging goods in small volumes for long- or short-distance freight or shipping. The agricultural and ecological benefits of forest residues include water retention in arid soils, preventing soil erosion, carbon sequestration, enhancing soil fertility, and preserving biodiversity. Carbon sequestration applications of biomass-derived char are gaining wide attention because they make the biofuel production process carbon-negative by capturing or holding carbon in soil for longer periods [11].

In addition, forest biomass has a huge potential to improve the economics of current biofuel refineries [12]. Because wood contains carbohydrates (mostly cellulose and hemicelluloses) in its cell wall, it is a candidate for conversion to hydrocarbon fuels. Through various thermochemical and biochemical routes, woody biomass can be converted to biofuels (e.g., bio-oil, ethanol, butanol, and syngas) and biochemicals (e.g., organic acids, solvents,

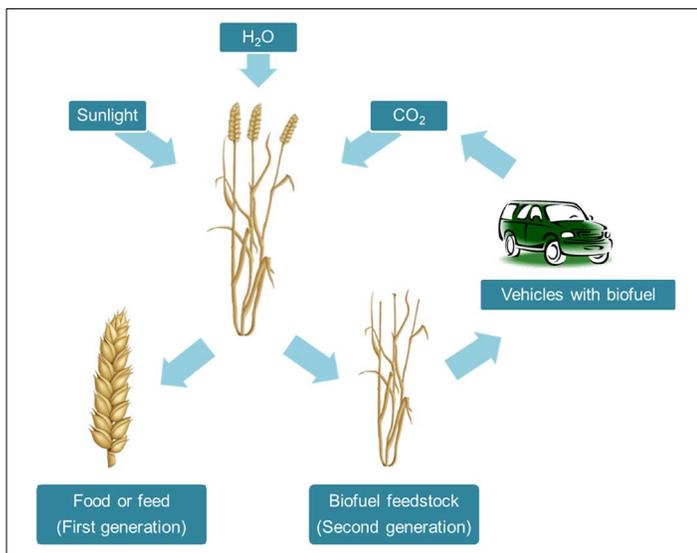


Fig. 1 - Carbon-neutral cycle of biomass and biofuels.

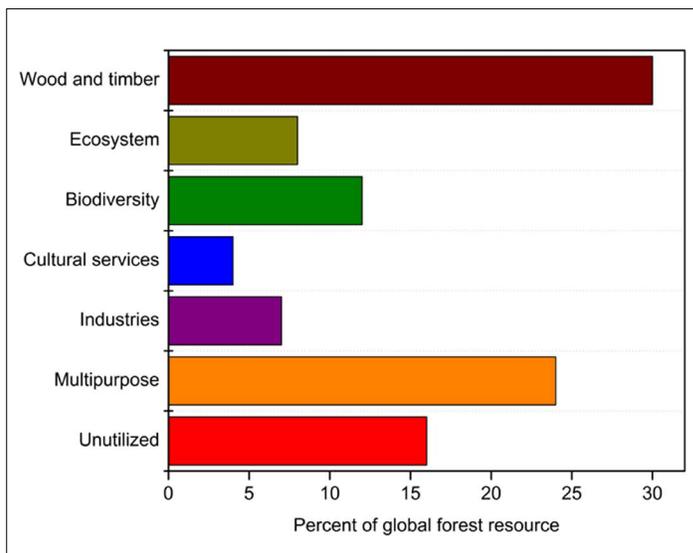


Fig. 2 - Diversity in use of global forest resources (Data source: [9].)

biolubricants, and adhesives). Recently, woody biomass has also found applications in production of advanced biomaterials such as carbon fibres [13], activated carbon, [14] and bioplastics [15] for multidisciplinary applications.

Figure 4 shows several countries with their variation in forest cover over the last two decades. The South American countries such as Brazil and Peru show a larger forested area than that of other countries in the comparison. Unlike most countries that show a steady increase in their forest land area, Brazil, Peru, and Mexico reveal a distinctive trend. A continuous decrease in total forest land area over the years is clearly visible in these three Latin American nations. The common reasoning for this scenario is deforestation. Deforestation is defined as the use of forested areas for alternative purposes such as agriculture and urbanization [9] and/or the excessive exploitation of wood resources. This usually occurs when forest lands are seen as a hindrance to the fulfilment of other societal needs related to economic development.

Brazil ranks first in tropical deforestation, eliminating an average forest land

area of 19,500 km² per year from 1996 to 2005 [16]. The chief purpose in this case of deforestation was forest conversion to pasture and farmland, which released 0.7–1.4 Gt CO₂ annually. To mitigate this CO₂ emission, Brazil has committed to reducing deforestation rates by 20% of its 1996 to 2005 rate through 2020. Mexico is a water-deficient country where forest trees function to regulate stream flows from watersheds [17]. Some of the reasons for deforestation in Mexico include poverty, communal land-tenure arrangements relating to local ownership, extraction of forest wood for profit, and price distortions that favor maize cultivation (after forest elimination) [17,18]. The degradation of Amazonian rainforest in Peru is influenced by poverty, unsustainable forestry activities by Brazilian nut harvesters, and gold mining in Madre de Dios [19, 20].

The worldwide wood production in 2009 was approximately 3267×10⁶ m³ [9]. About 72% (2368×10⁶ m³) of these forest residues were used as fuelwood as well as in charcoal and black liquor production. In 2009, total fuelwood use in developing nations (e.g., Asia, Africa, Oceania, Latin America, and the Caribbean) was 1657×10⁶

m³, whereas in developed nations (e.g., the United States, Canada, Europe, the former Soviet Union, Australia, New Zealand, Japan, etc.), it was 195×10⁶ m³ [9]. Klenk et al. [9] reported a reduction of 26% in fuelwood usage in the United States and Canada compared to their 1995 estimate. However, both countries saw a significant increase in black liquor recovery (116×10⁶ m³) by pulp and paper industries in 2009. It should be noted that many pulp and paper production facilities have closed operations recently in the United States and Canada [21], mainly due to increasing use of electronic communications media for business transactions.

Estimates of the annual lignocellulosic biomass availability (including forest residues, agricultural refuse, and energy crops) in the United States and Canada range up to 577 and 561 million dry tonnes respectively [22]. Both countries have bright prospects to address biofuel production if these vast reserves of lignocellulosic materials become accessible under economically viable scenarios. Softwood is one of the leading sources of lignocellulose in the Northern Hemisphere and is reported to be of interest for bioethanol

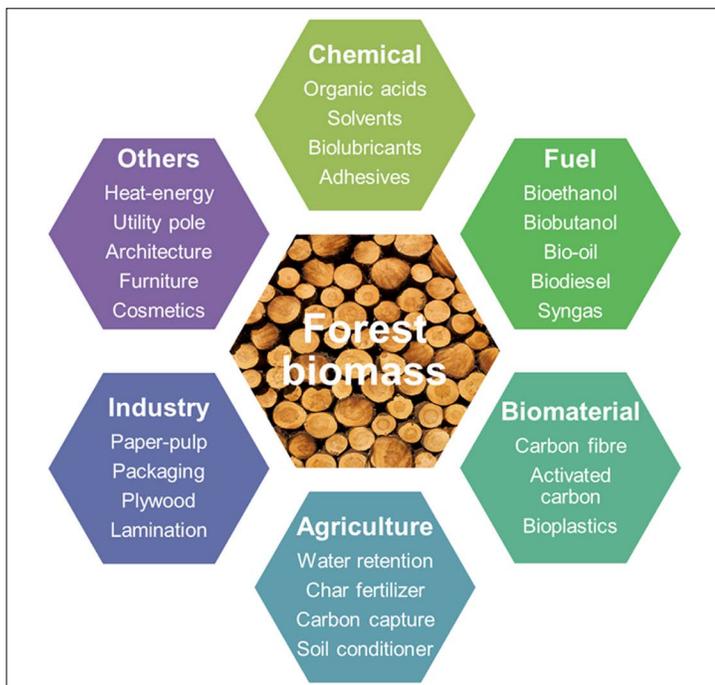


Fig. 3 - Potential applications of forest resources in various sectors.

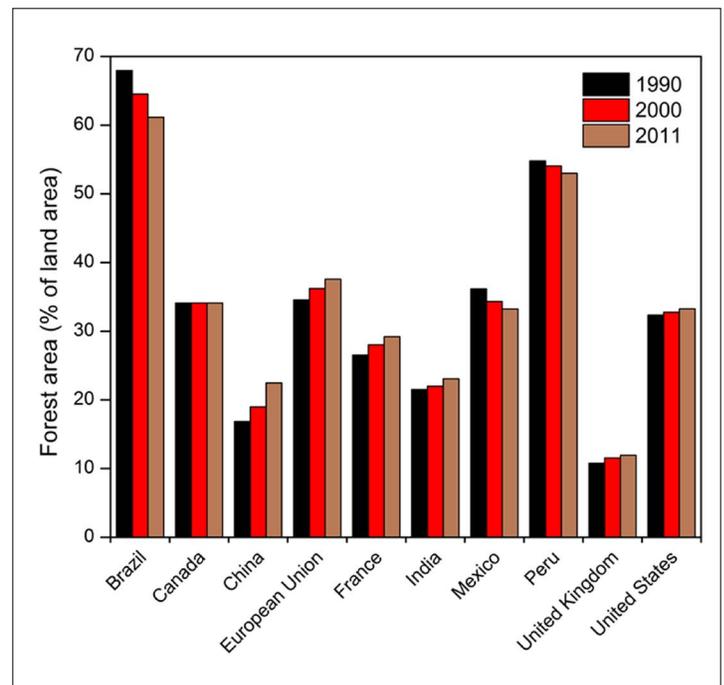


Fig. 4 - Worldwide forested areas through the years, 1990–2011 (Data source: [10]).

production in Canada, the United States, and Sweden [23]. Currently, the five major bioethanol-producing countries are the United States, Brazil, China, Canada, and France, although the United States and Brazil together produce over 90% of the world's bioethanol [7]. The greater accessibility of lignocelluloses (especially agricultural biomass) in the United States is due to the availability of 2.5 times more agricultural land than in Canada, which results in approximately 26 times more agricultural production in the United States [22]. Moreover, the northern climate of Canada is another factor in its relatively lower biomass production.

The total forest resources available every year in the United States are between 60 and 100 million dry tonnes, whereas in the case of Canada, this amount is between 19 and 25 million green tonnes [22]. The lower availability of forest resources in Canada could be due to forest fires, insect infestations, and limited forest management [24]. Forest (logging) residues in the United States and Canada could provide as much as 57 and 92 million green tonnes per annum respectively [22]. Every year, up to 135 and 17 million dry tonnes of wood mill residues are generated in the United States and Canada respectively. Forest harvesting operations in Canada produce substantial amounts of wood chips and particles ranging from 9.8 to 46 million dry tonnes, which offer the possibility of producing 1.2–13.8 billion litres of bioethanol per annum [25]. Currently, wood chips and particles are predominantly used in pulp and paper processing facilities across North America. Sawdust and wood flakes usually result from forest product manufacture or wood processing. In Canada, these residues are between 2 and 5.4 million dry tonnes, which have the potential for producing approximately 0.2–1.6 billion litres of ethanol per annum. However, biomass densification techniques such as pelletization and briquetting are reducing the availability of these residues.

In addition, a non-renewable source of forest biomass called disturbance wood or damaged wood is available in Canada.

This resource consists of trees killed by the mountain pine beetle in British Columbia, Canada. The mortality of lodgepole pine trees due to such insect infestation was between 36 and 43 million m³ in 2007 [25]. This damaged-wood biomass, which is available abundantly in western Canada, could potentially be used to supplement domestic biofuel production. Approximately 9.3 to 12.3 million dry tonnes of damaged wood are generated every year [24], corresponding to a prospective production of 2.8–3.6 billion litres of bioethanol [25].

CHEMICAL COMPOSITION OF WOODY BIOMASS

The basic organic constituents of lignocellulosic biomass that could be converted to renewable fuels and chemicals include cellulose, hemicellulose, lignin, and extractives. Chemically, lignocellulosic biomass forms a complex crystalline structure supported by covalent bonding, intermolecular bridges, and van der Waals forces, which makes it water-insoluble and robust to enzymes. Lignocellulosic materials typically contain 30%–60% cellulose, 20%–40% hemicelluloses, and 15%–25% lignin on a moisture-free basis [26]. Cellulose, hemicelluloses, and lignin make up about 90% of lignocellulosic dry matter, with the rest consisting of extractives and ash. Extractives are water- or solvent-soluble non-structural biomass components such as terpenoids, steroids, resin acids, fats, lipids, waxes, stilbenes, flavonoids, lignans, and tannins [7]. The mineral matter in biomass is represented by its ash, which includes both major elements (e.g., Na, Mg, K, Ca, and Si) and minor elements (e.g., Al, Fe, Mn, P, and S). The proportions of these elements in agricultural residues (e.g., straws and husks) and woody biomass are about 25 wt.% and 1 wt.% respectively [27].

Cellulose is a glucose polymer consisting of β (1,4)-linked D-glucose subunits and has cellobiose as its repeating unit. Hemicellulose is a polysaccharide mixture of pentose and hexose sugars such as glucose, xylose, galactose,

mannose, and arabinose along with sugar acids such as methylglucuronic and galacturonic acids. Lignin is an aromatic phenylpropane polymer linked with ether bonds and composed of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. As lignin tightly binds with cellulose and hemicellulose to provide structural rigidity to the plant cell, its presence makes the biomass recalcitrant towards hydrolysis and bioconversion [28].

The magnitude of oxidative polymerization of coumaryl alcohol (e.g., *p*-hydroxyphenyl propanol), coniferyl alcohol (e.g., guaiacyl propanol), and sinapyl alcohol (e.g., syringyl propanol) in woody biomass is influenced by the plant part, latitude, temperature, light intensity, available water, harvesting time, and biomass storage conditions [29]. Upon incorporation of the respective monolignol into the lignin polymer, formation of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) monomers occurs [30]. The lignin composition of the gymnosperm and angiosperm varies in terms of H, G, and S monomers. Gymnosperm cell walls are composed primarily of H and G monomers, whereas angiosperm cell walls (i.e., monocots and dicots) are composed of H, G, and S monomers. Whereas lignin in hardwoods consists mostly of G and S monomers with traces of H units, softwoods contain chiefly G monomers with low levels of H units [31,32]. On the other hand, herbaceous feedstocks such as grasses contain G, S, and H monomeric lignin [30].

Depending on the type and species of feedstock as well as local climatic conditions, the compositions of cellulose, hemicellulose, and lignin vary [33]. Table 1 summarizes a few wood-based feedstocks and their organic compositions. It is evident from Table 1 that cellulose, hemicellulose, and lignin contents are influenced not only by the feedstock type, but also by the part of the plant, i.e., stems, twigs, branches, etc. On average, wood (particularly stems) contained 48% cellulose, 22% hemicellulose, 22% lignin, and 4.7% extractives. In contrast, twigs (particularly branches) contained 15% cellulose, 32% hemicellulose,

22% lignin, and 2% extractives. Furthermore, bark (i.e., wood rind) on average contained 20% cellulose, 23% hemicellulose, 27% lignin, and 3% extractives. Hardwood stems generally contained 40%–55% cellulose, 24%–40% hemicellulose, and 18%–25% lignin, whereas softwood stems contained 45%–50% cellulose, 25%–35% hemicellulose, and 25%–35% lignin [5].

Hemicelluloses are usually found to be enriched in fast-growing plant tissues such as those in twigs, leaves, and even grasses [33]. Lignin content is characteristically higher in softwoods than in hardwoods. It is found to be augmented in the cells' middle lamellae and in wood bark, as

can be seen in Table 1. This is the case because of the polymeric property of lignin that protects the plants from physical and chemical agents such as invasion by pests and parasites, microbial or fungal growth, and decomposition by waterlogging.

Production of biofuels from woody biomass can be achieved through two primary routes, thermochemical and biochemical. Figure 5 illustrates various pathways for converting woody biomass to a wide range of liquid and gaseous products. Through thermochemical processing, wood residues undergo pyrolysis, liquefaction, and gasification to produce bio-oil and syngas. In the case of bioconversion, woody biomass is treated with a

series of dilute acids, enzymes, and microorganisms to produce monomeric sugars that could be further fermented to ethanol and butanol. Along with the major biofuels such as bio-oil, ethanol, butanol, and syngas, various value-added products including biochar, organic acids, organic solvents, phenols, aromatic compounds, etc., can also be obtained during the course of chemical reactions.

THERMOCHEMICAL CONVERSION

As a result of thermochemical conversion, wood-based biomass undergoes various chemical reforming processes that convert long-chain organic compounds in the biomass to short-chain oxygenated hydrocarbons. Thermochemical conversion can be achieved through pyrolysis, liquefaction, or gasification. Whereas pyrolysis produces bio-oil, biochar, and gases from wood, liquefaction results in bio-oil, and gasification leads to syngas production.

Pyrolysis can be defined as the disintegration of macromolecular organics at high temperatures in the absence of oxygen. Depending on operating temperatures, heating rates, and solid/vapor residence time, pyrolysis can be divided into three basic types: slow, fast, and flash [7]. Slow pyrolysis operates between 300°C and 700°C with heating rates ranging from 0.1°C/s to 1°C/s, whereas fast pyrolysis operates between 600°C and 1000°C with heating rates in the range of 10°C/s to 200°C/s [44]. In contrast, flash pyrolysis requires temperature ranges of 800°C to 1000°C and heating rates greater than 1000°C/s. The ranges of residence times for slow, fast, and flash pyrolysis are 10–100 min, 0.5–5 s, and < 0.5 s respectively. Although the biomass particle size for slow pyrolysis ranges from 5 to 50 mm, it is preferably less than 1 mm for fast and flash pyrolysis. Considerable amounts of bio-oil are obtained from both fast and flash pyrolysis, whereas in the case of slow pyrolysis, larger amounts of biochar are obtained [45]. The gases from all pyrolysis processes are made up of non-condensable gases such as H₂, CO, CO₂, CH₄, C₂H₄, and C₂H₆. These gases can be

TABLE 1 Lignocellulosic composition (in wt.%) of various wood residues.

Biomass	Cellulose	Hemicellulose	Lignin	Extractives	Reference
Wood					
Albizzia wood	58.3	8.1	33.2	1.9	[34]
Aspen wood	60.7	19.1	14.8	-	[35]
	47.6	18.4	18.4	-	[36]
Beech wood	44.2	33.5	21.8	2.6	[37]
Birch	56.5	24.8	12.2	-	[35]
Douglas fir	42.0	23.5	27.8	-	[38]
Eucalyptus wood	48.0	14.0	29.0	2.0	[1]
European birch	48.5	25.1	19.4	-	[38]
Hornbeam wood	53.4	31.4	15.3	-	[39]
Monterey pine	41.7	20.5	25.9	-	[38]
Oak wood	54.0	29.0	9.4	-	[35]
Pine chips	52.9	9.6	26.0	0.5	[40]
Pine pellets	45.0	11.4	23.2	0.5	
Pinewood	38.8	23.6	20.4	15.7	[26]
Poplar	43.8	14.8	29.1	-	[41]
Premna wood	63.2	10.5	21.1	3.5	[34]
Pterospermum wood	59.1	8.7	28.5	1.9	[34]
Sawdust	37.7	31.4	15.9	15.0	[42]
Scots pinewood	49.0	24.5	19.5	-	[39]
Spruce	43.0	29.4	27.6	1.7	[37]
Subabul wood	39.8	24.0	24.7	9.7	[27]
Syzygium wood	60.2	5.5	31.0	1.4	[34]
Walnut	53.0	27.0	20.0	-	[39]
White poplar	49.0	25.6	23.1	-	[38]
White spruce	44.8	30.9	27.1	-	[38]
White willow	49.6	26.7	22.7	-	[38]
Wood pulp ^a	20.8	44.7	-	-	[43]
Average	48.3	22.1	22.6	4.7	
Twigs					
Albizzia twig	15.4	32.8	22.2	1.9	[34]
Premna twig	19.4	29.6	20.0	2.0	[34]
Pterospermum twig	13.6	31.5	24.2	1.0	[34]
Syzygium twig	12.2	35.3	21.6	1.6	[34]
Average	15.2	32.3	22.0	1.6	
Barks					
Albizzia bark	21.5	16.7	31.1	4.5	[34]
Premna bark	18.5	34.7	20.1	2.6	[34]
Pterospermum bark	20.1	20.6	25.3	3.1	[34]
Syzygium bark	21.9	18.6	30.1	3.0	[34]
Average	20.5	22.7	26.7	3.3	

^a Wood pulp: mixture of maple, beech, and birch wood.

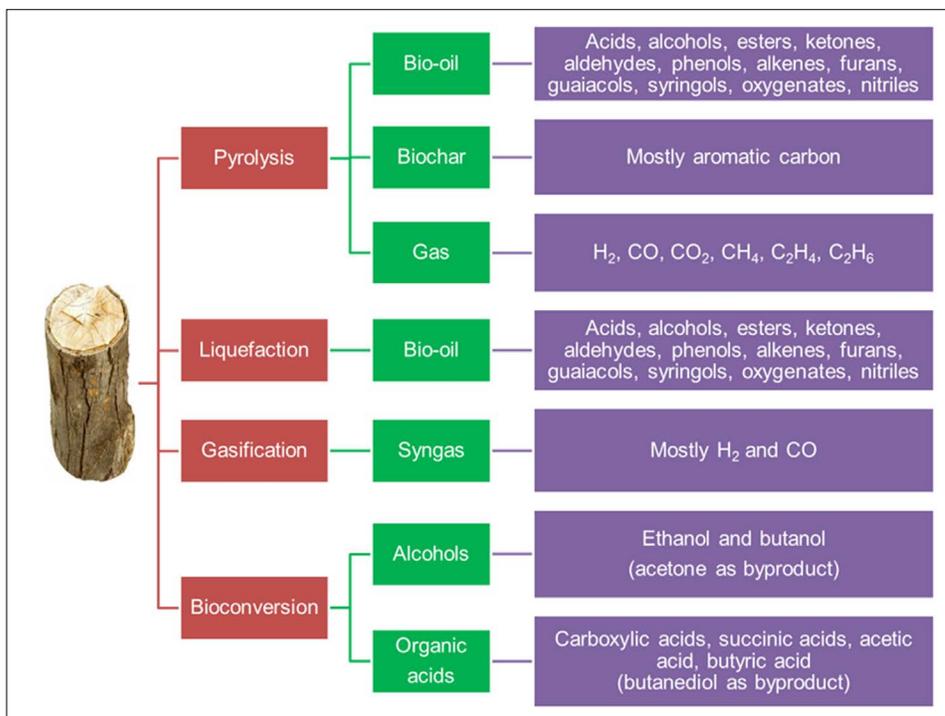


Fig. 5 - Evolutionary tree of woody biomass with conversion processes and products.

recycled for heat recovery during the pyrolysis process.

Compared to gasoline, bio-oil is largely composed of oxygenated compounds with negligible quantities of hydrocarbons, which makes its heating value just under half that of hydrocarbon fuels (e.g., gasoline: 42–44 MJ/kg) [7]. Table 2 summarizes the pyrolysis of various woody biomasses, highlighting the temperatures used and the yields of bio-oil, biochar, and gases. The liquid products obtained from pyrolysis can be further processed to separate the bio-oil fraction. Usually, the liquid product consists of aqueous and organic (or bio-oil) phases. The aqueous phase contains mostly carboxylic acids, acetic acid, methanol, and acetone, whereas the organic phase contains phenolics and carbonyl compounds [53]. A number of acids, alcohols, esters, ketones, aldehydes, phenols, alkenes, furans, guaiacols, syringols, and oxygenates along with traces of nitriles are found in the crude pyrolysis liquids. Because bark contains a greater amount of lignin (see Table 1), bio-oil derived from softwood bark contains considerably more phenolic compounds from lignin than bio-oil from hardwood bark [54]. The pyrolysis

products from cellulose and hemicellulose in bio-oil include acids, alcohols, aldehydes, esters, furans, ketones, sugars, and oxygenates, whereas lignin derivatives include phenols, guaiacols, and syringols [53].

Liquefaction of lignocellulosic biomass results in liquid fuels without gasification or pyrolysis. Unlike pyrolysis, liquefaction does not require biomass drying, which makes it more economically attractive [38]. Compared to pyrolysis-derived bio-oil, liquefaction-derived bio-oil has higher energy content due to its lower oxygen levels [1]. The temperatures and pressures in liquefaction are typically in the range of 250°C to 350°C and 5 to 20 MPa respectively [55]. Liquefaction leads to hydrogenation reactions and high-pressure thermal cracking of biomass into heavy oil and useful chemicals along with evolution of CO and H₂ [56]. In addition to bio-oil production, liquefaction of lignocellulosic materials also results in certain chemical compounds in the oil fraction that lead to generation of epoxy resins, polyurethane foams, and adhesives for plywood [55].

Liquefaction requires the addition of catalysts, which reduce the reaction temperature, improve reaction kinetics, and

enhance liquid product yields [55]. Catalysts that have been used for biomass liquefaction include alkalis, alkaline oxides, carbonates, bicarbonates, and metals (e.g., Zn, Cu, Ni, Ru, I, ZnCl₂, Fe(OH)₃, Co_xS_y, and formate) [1]. Catalysts such as Na₂CO₃ and K₂CO₃ along with CO and H₂ as supplemental reactants have been found to be helpful in enhancing liquefaction rates [57,58]. Liquefaction of wood sawdust in presence of catalysts such as NaOH, H₃PO₄, H₂SO₄, and toluenesulphonic acid has resulted in 70.6 wt.% to 99.4 wt.% liquid product yields [59].

Bio-oil obtained by liquefaction of lignin-rich wood is reported to contain higher amounts of low-molecular-weight phenolic compounds than bio-oil from cellulose [56]. The amount of solid product has also been found to be influenced by wood lignin content. Phenol is known to prevent any possible condensation reactions by lignin or polyphenol that could produce an insoluble polymerized material during acid-catalyzed liquefaction [60].

Bio-oil must be upgraded if it is intended to replace conventional diesel and gasoline-based fuels. Bio-oil can be upgraded into liquid transportation fuel by three major routes: (i) hydrodeoxygenation (with hydrotreating catalysts, e.g., sulphided CoMo or NiMo); (ii) zeolite upgrading; and (iii) emulsification with diesel [1]. Hydrodeoxygenation is performed by treating bio-oil at 300°C–600°C with high-pressure H₂ in the presence of heterogeneous catalysts, which result in a highly stable and energy-dense fuel [7]. Zeolite upgrading is performed at 350°C–500°C, ~0.1 MPa, and gas hourly space velocities of ~2 h⁻¹ and results in bio-oil with lower oxygen content and enhanced thermal stability [1]. Bio-oil blending with diesel is achieved using surfactants, leading to an upgraded fuel with improved ignition characteristics [61].

During gasification, wood or other carbonaceous materials react with air (oxygen), steam, or both to produce syngas containing mostly H₂ and CO along with CO₂, CH₄, and N₂. During primary gasification reactions, woody biomass forms water vapour and CO₂ along with oxygenated

vapours from cellulose and hemicellulose (e.g., levoglucosan and hydroxyacetaldehyde) and lignin (e.g., methoxyphenols) [1]. In secondary gasification reactions, the oxygenated vapours result in H₂, CO, CO₂, H₂O, olefins, phenols, and aromatics. Cracking of primary oxygenated vapours begins at 500°C, whereas the products from secondary reactions are initiated at 700°C–850°C. Heating of secondary products beyond 850°C produces tertiary products such as H₂, CO, CO₂, H₂O, methylnaphthalene, toluene, and indene. These secondary and tertiary reactions

also result in formation of soot, coke, and tar.

Generation of tars is a factor to be considered in thermal cracking of woody biomass because it leads to reactor plugging and compromised bio-oil yields. Efforts have been made to reduce tar formation during gasification of cedar wood, jute sticks, bagasse, and rice straw using solid catalysts such as Pd, Pt, Ru, and Ni supported on CeO₂/SiO₂ and dolomite; however, Rh/CeO₂/SiO₂ was found to be the most promising catalyst [62]. Alkali catalysts also investigated for tar reduction

include NaCl, KCl, ZnCl₂, AlCl₃•6H₂O, K₂CO₃, Na₂CO₃, Na₃H(CO₃)₂, Na₂B₄O₇•10H₂O, and CsCO₃ [1]. Although alkali catalysts decrease tar generation, they also enhance char formation. In addition, hydrogen can be generated from char and bio-oil through steam-reforming reactions.

BIOCHEMICAL CONVERSION

Bioethanol and biobutanol are the products of bioconversion of wood-based feedstocks. Biochemical conversion of lignocellulosic materials involves use of enzymes and microorganisms to convert fermentable sugars to alcohol-based fuels. To recover the fermentable sugars, biomass must be pretreated to depolymerize its cellulose-hemicellulose complex with lignin [63]. This results in removal of polymeric lignin and separation of carbohydrates. The cellulases (e.g., endocellulase, exocellulase, cellobiase, oxidative cellulases, and cellulose phosphorylases) and hemicellulases (e.g., xylanase) further break down the complex carbohydrates to monomeric sugars such as glucose and xylose. Finally, these simple sugars are fermented using diverse microorganisms (e.g., bacteria or fungi) to produce ethanol and butanol. Unlike pyrolysis, biochemical conversion of wood-based materials does not require biomass drying.

The pretreatment phase begins by pulverizing the woody biomass physically to increase its surface area along the fibres. A wide range of biomass pretreatments is available to separate cellulose and hemicellulose from lignin. Such pretreatments for woody biomass include acid or alkaline hydrolysis, ozonolysis, microwave digestion, organosolv, steam explosion, supercritical fluids, and a number of other methods [63–65]. This pretreatment is followed by enzymatic hydrolysis that breaks down cellulose and hemicellulose into sugar monomers. Unlike softwoods, hardwoods have more cellulose and less hemicellulose and therefore produce more glucose for easier bioconversion [66]. However, the hemicellulose in hardwoods contains more xylose that is difficult to hydrolyze.

TABLE 2 Pyrolysis products from various wood residues.

Biomass	Temperature (°C)	Bio-oil	Water	Gas	Biochar	Reference
		Yield (weight %)				
Aspen poplar	425	55.9	3.8	5.9	30.6	[46]
	465	67.2	5.5	8.5	18.9	
	500	71.1	6.6	12.1	11.2	
	541	63.6	7.4	21.2	9.0	
	545	57.5	-	9.6	11.3	
	555	45.2	-	13.1	-	
Chinese oak	550	40.2	39.6	-	-	[48]
Cunninghamia	500	53.9	31.4	-	-	[48]
Fir bark	482		48.9	12.3	39.3	[49]
Maple	482	60.6	6.3	6.3	20.9	[46]
	500	64.7	8.2	8.2	12.6	
	532	56.2	7.8	7.8	9.0	
Oil mallee	500	52.0	-	19.4	18.8	[50]
Pine chips	500	24.2	26.2	18.4	31.2	[40]
Pine pellets	500	26.9	30.9	12.1	30.0	
Pinewood	450	48.0	11.0	17.0	24.0	[45]
Pinewood (hydrolyzed)	600	22.3	11.1	24.9	41.7	[28]
Pinewood (Quartz sand)	450	27.3	5.4	52.0	15.3	[51]
Pinewood (H-Beta-25)		15.1	13.9	49.5	21.6 ^a	
Pinewood (H-Y-12)		9.0	16.7	51.1	23.2 ^a	
Pinewood (H-ZSM5-23)		20.7	13.0	52.1	14.2 ^a	
Pinewood (H-MOR-20)		17.6	14.4	48.1	19.9 ^a	
Rosewood	500	55.7	24.6	-	-	[48]
Sawdust	400	28.0	-	-	-	[42]
	475	52.0	-	-	-	
	550	44.5	-	-	-	
Subabul wood	500			75.4	24.6	[27]
Wood (general)	350		45.5	25.5	29.0	[44]
	400		44.9	28.7	26.1	
	500		43.4	32.7	22.9	
	550		41.1	36.4	21.1	
Wood chips	480		48.3	12.3	39.3	[49]
Wood shavings	400		65.5	10.2	24.1	[52]
	450		65.7	11.1	21.4	
	500		66.0	14.6	18.9	
	550		67.0	15.3	17.0	
	500		22.6	58.0	19.3	

Note: Acidic zeolite catalysts (H-Beta-25, H-Y-12, H-ZSM5-23, H-MOR-20); ^a Biochar + coke.

Cellulases, which are most commonly produced by soft-rot fungi such as *Trichoderma*, *Penicillium*, and *Aspergillus* species, are used for enzymatic hydrolysis of woody biomass [25]. Lignin-degrading enzymes such as lignin peroxidases and manganese-dependent peroxidases are produced by *Phanerochaete chrysosporium* [67] and could have wide application in degrading woody biomass that is rich in lignin. Azzam et al. [68] suggested that peroxidase enzymes could catalyze lignin biodegradation in the presence of H₂O₂. Some soft-rot fungi can also digest lignin because they degrade the plant cell wall and decrease the content of acid-insoluble material, i.e., lignin in angiosperm wood. Several white-rot fungi such as *P. chrysosporium*, *Trametes versicolor*, *Bjerkandera adusta*, *Pycnoporus cinnabarinus*, *Strobilurus ohshimae*, and *Xylaria polymorpha* have been found to degrade wood with production of lignin peroxidases, manganese-dependent peroxidases, laccase, xylanases, and cellobiose dehydrogenase [5].

Fermentation of the sugars generated from enzymatic hydrolysis of

biomass is another crucial step in bioconversion. Although half the mass of generated sugars is released as CO₂, all their energy is concentrated in the product ethanol [1]. Typically, after addition of basic microbial nutrients (i.e., salts, carbon sources, and energy sources) into the medium, fermentation is carried out with approximately 20 wt.% sugars at pH 4–5, temperatures of 30°C–38°C, and residence times of 28–48 h. However, the operating conditions may vary depending on the mode of fermentation, i.e., batch, fed-batch, or continuous [7].

Table 3 summarizes various microorganisms used in bioconversion of woody biomass to ethanol and butanol as fuels along with value-added chemicals. Some of the notable microorganisms producing ethanol from wood are fungi such as *Saccharomyces cerevisiae*, *Dichomitus squalens*, *Ceriporiopsis subvermispora*, *Pleurotus ostreatus*, *Coriolus versicolor*, *Pichia stipitis*, and *Phellinus* spp. *Zymomonas mobilis* and *Klebsiella pneumonia* are the bacteria known to produce ethanol along

with 2,3-butanediol from woody biomass [69,75]. The butanol-producing bacteria studied for wood bioconversion belong to the genus *Clostridium*, especially *C. acetobutylicum* and *C. beijerinckii*. Butanol fermentation is strictly anaerobic in nature, unlike ethanol fermentation, which is mostly an aerobic process.

Because wood-based feedstocks contain a significant amount of hemicelluloses (mostly xylose sugars for hardwoods and galactoglucomannans for softwoods), it is critically important for a biorefinery to consider their efficient conversion. This concern arises because *S. cerevisiae* and *Z. mobilis*, which are the most widely used microorganisms in alcohol fermentation, lack the tendency to ferment hemicellulose [66]. Moreover, microorganisms such as *Candida shebatae*, *Pachysolen tannophilus*, and *P. stipitis* can ferment xylose to ethanol, but their fermentation efficiencies are lower [78]. Higher concentrations of ethanol in the fermentation medium, sensitivity towards inhibitors, and lower pH also restrict their efficiency [79].

TABLE 3 Bioconversion of various wood residues to fuels and chemicals.

Biomass	Microorganism	Operating conditions	Products (concentration)	Reference
Aspen wood	<i>Saccharomyces cerevisiae</i> C495	37°C, 72 h	Ethanol (25.5 mg/mL)	[69]
	<i>Zymomonas mobilis</i> 22 (ATCC 29191)		Ethanol (22.3 mg/mL)	
	<i>Klebsiella pneumoniae</i>	37°C	Ethanol (2.6 g/L), butanediol (9.8 g/L)	[70]
	<i>Clostridium acetobutylicum</i> ATCC 824	30°C	Butanol (4.9 g/L), acetone (1.3 g/L), ethanol (0.6 g/L)	[36]
	<i>Clostridium acetobutylicum</i> ATCC 824	36°C	Butanol (18.1 g/100 g), acetone (8.6 g/100 g), ethanol (1.5 g/100 g)	
Beech wood	<i>Dichomitus squalens</i> CBS 432.34	28°C, 2–8 weeks	Ethanol (~15.8%)	[71]
	<i>Ceriporiopsis subvermispora</i> FP90031		Ethanol (~17.5%)	
	<i>Pleurotus ostreatus</i> K 2946		Ethanol (~12%)	
	<i>Coriolus versicolor</i> K 2615		Ethanol (~14%)	
Birch	<i>Saccharomyces cerevisiae</i> VTT B-08 014	30°C, 120 h	Ethanol (64.7 g/L)	[72]
	<i>Pichia stipitis</i> VTT C-10 876		Ethanol (10.4 g/L)	
Japanese cedar wood	<i>Ceriporiopsis subvermispora</i> FP-90031 (ATCC 90467)	28°C, 4–8 weeks	Ethanol (9.8 g/L)	[73]
	<i>Phellinus</i> sp. SKM2102		Ethanol (8.9 g/L)	
Monterey pine	<i>Clostridium acetobutylicum</i> NCIB 2951	30°C, 5–7 days	Butanol (5.7 g/L)	[74]
Oakwood	<i>Klebsiella pneumoniae</i>	32°C, 120 h	2,3-butanediol (11 mg/mL)	[75]
Pinewood	<i>Saccharomyces cerevisiae</i> ATCC 96581	30°C, 60 h	Ethanol (24.1 g/L)	[76]
	<i>Clostridium beijerinckii</i> B-592	35°C, 72 h	Butanol (11.6 g/L), acetone (5.2 g/L), ethanol (1.7 g/L)	
Poplar	<i>Saccharomyces cerevisiae</i> 424A (LNH-ST)	30°C	Ethanol (39.9 g/L)	[64], [77]
Spruce	<i>Saccharomyces cerevisiae</i> VTT B-08 014	30°C, 120 h	Ethanol (14.9 g/L)	[72]
	<i>Pichia stipitis</i> VTT C-10 876		Ethanol (34.1 g/L)	
Wood pulp ^a	<i>Clostridium beijerinckii</i> CC101	37°C	Butanol (13.5 g/L), acetone (4.2 g/L)	[43]

^a Wood pulp: mixture of maple, beech and birch wood

Several efforts to enhance xylose utilization by yeasts have been made, such as co-fermentation of pentose and hexose sugars [80], protoplast fusion [81], and other genetic modifications in *Saccharomyces* [82].

A major disadvantage in choosing bioconversion over thermochemical conversion is that the former is time-intensive due to longer digestion periods (hours to days) and cost-intensive due to use of expensive enzymes. Along with ethanol and butanol, several by-products are obtained from wood bioconversion (Fig. 5). These by-products include acetone, carboxylic acid, lactic acid, succinic acid, acetic acid, butyric acid, butanediol, and glycerol. Butanol fermentation, typically using ABE (or acetone-butanol-ethanol) fermentation, produces acetone, butanol, and ethanol in the ratio 3:6:1 [83]. ABE fermentation also produces acetic acid and butyric acid as liquid intermediary products and CO₂ and H₂ as gaseous intermediary products. More specifically, acetic and butyric acids are produced during the acetogenic growth phase of butanol-producing *Clostridia*, whereas acetone, butanol, and ethanol are produced during their solventogenic growth phase.

CONCLUSIONS

Forestry resources are useful not only for industrial and agricultural use, but also from a biofuel, biochemical, and biomaterial perspective. To use forest biomass for bioenergy, it could be converted into valuable energy products, especially to liquids that could replace fossil fuels. Wood residues have varying compositions of cellulose, hemicelluloses, lignin, and extractives. Pyrolysis and liquefaction of woody biomass result in superior bio-oil that can be upgraded to transportation fuels or used for combined heat and power. In the case of gasification, syngas is produced, which has potential as a high-energy gaseous fuel due to the presence of H₂. Although biochar is produced during thermochemical conversion, it could be used in agronomy or for carbon sequestration, making the overall biofuel production process attractive and carbon-negative.

Biomass conversion using enzymes and microorganisms leads to ethanol and butanol as the main end products, although various industrially important products such as organic acids and solvents can be obtained by fermentation. Although bioconversion does not require biomass drying, resulting in a significant cost saving, it does require pretreatment to hydrolyze the lignocellulosic network and release sugar monomers for fermentation. Bioconversion processes are also relatively expensive due to the cost of hydrolytic enzymes and time-consuming due to long fermentation periods. Compared to pyrolysis, liquefaction does not require biomass drying, but catalysts are required to produce high-energy-content bio-oil. Forestry residues are promising resources for producing next-generation biofuels, and hence significant efforts must be invested in their efficient use and conversion.

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REFERENCES

1. Huber, G.W., Iborra, S., and Corma, A., "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering", *Chemical Reviews*, 106:4044-4098 (2006).
2. Luque, R., Herrero-Davila, L., Campelo, J.M., Clark, J.H., Hidalgo, J.M., Luna, D., Marinas, J.M., and Romero, A.A., "Biofuels: A Technological Perspective", *Energy and Environmental Science*, 1:542-564 (2008).
3. Cassman, K.G. and Liska, A.J., "Food and Fuel for All: Realistic or Foolish?" *Biofuels, Bioproducts, and Biorefining*, 1:18-23 (2007).
4. Tumuluru, J.S., Wright, C.T., Hess, J.R., and Kenney, K.L., "A Review of Biomass Densification Systems to Develop Uniform Feedstock Commodities for Bioenergy Application", *Biofuels, Bioproducts, and Biorefining*, 5:683-707 (2011).

5. Sanchez, C., "Lignocellulosic Residues: Biodegradation and Bioconversion by Fungi", *Biotechnology Advances*, 27:185-194 (2009).
6. Pauly, M. and Keegstra K., "Cell-Wall Carbohydrates and their Modification as a Resource for Biofuels", *The Plant Journal*, 54:559-568 (2008).
7. Nanda, S., Mohammad, J., Reddy, S.N., Kozinski, J.A., and Dalai, A.K., "Pathways of Lignocellulosic Biomass Conversion to Renewable Fuels", *Biomass Conversion and Biorefinery*, 4:157-191 (2014).
8. FAO, Food and Agriculture Organization, *Global Forest Resource Assessment: Key Findings*, Rome, Italy, United Nations (2010).
9. Klenk, N.L., Mabee, W., Gong, Y., and Bull, G.Q., "Deforestation, Forest Management, and Governance", in Wiley, Chichester, UK (2012).
10. FAO, Food and Agriculture Organization, *The World Bank, World Development Indicators: Rural Environment and Land Use*. www.data.worldbank.org/indicator/AG.LND.FRST.ZS. Accessed on December 9, 2013.
11. Lehmann, J., Gaunt, J., and Rondon, M., "Bio-Char Sequestration in Terrestrial Ecosystems – A Review", *Mitigation and Adaptation Strategies for Global Change*, 11:395-419 (2006).
12. Chambost, V. and Stuart, P.R., "Selecting the Most Appropriate Products for the Forest Biorefinery", *Industrial Biotechnology*, 3:112-119 (2007).
13. Kadla, J.F., Kubo, S., Venditti, R.A., Gilbert, R.D., Compere, A.L., and Griffith, W., "Lignin-Based Carbon Fibers for Composite Fiber Applications", *Carbon*, 40:2913-2920 (2002).
14. Khezami, L., Chetouani, A., Taouk, B., and Capart, R., "Production and Characterisation of Activated Carbon from Wood Components in Powder: Cellulose, Lignin, Xylan", *Powder Technology*, 157:48-56 (2005).
15. Ben, M., Mato, T., Lopez, A., Vila, M., Kennes, C., and Veiga, M.C., "Bioplastic Production Using Wood Mill Effluents as Feedstock", *Water Science and Technology*, 63:1196-1202 (2011).
16. Nepstad, D., Soares-Filho, B.S., Merry, F., Lima, A., Moutinho, P., Carter, J., Bowman, M., Cattaneo, A., Rodrigues, H.,

- Schwartzman, S., McGrath, D.G., Stickler, C.M., Lubowski, R., Piris-Cabezas, P., Rivero, S., Alencar, A., Almeida, O., and Stella, O., "The End of Deforestation in the Brazilian Amazon", *Science*, 326:1350-1351 (2009).
17. Alix-Garcia, J., Janvry, A.D., and Sadoulet, E., "A Tale of Two Communities: Explaining Deforestation in Mexico", *World Development*, 33:219-235 (2005).
 18. Deininger, K.W. and Minten, B., "Poverty, Policies, and Deforestation: The Case of Mexico", *Economic Development and Cultural Change*, 47:313-344 (1999).
 19. Swenson, J.J., Carter, C.E., Domec, J.C., and Delgado, C.I., "Gold Mining in the Peruvian Amazon: Global Prices, Deforestation, and Mercury Imports", *PLoS ONE*, 6:e18875:1-7 (2011).
 20. Escobal, J. and Aldana, U., "Are Non-timber Forest Products the Antidote to Rainforest Degradation? Brazil Nut Extraction in Madre de Dios, Peru", *World Development*, 31:1873-1887 (2003).
 21. Mabee, W.E. and Mirck, J., "A Regional Evaluation of Potential Bioenergy Production Pathways in Eastern Ontario, Canada", *Annals of the Association of American Geographers*, 101:897-906 (2011).
 22. Gronowska, M., Joshi, S., and MacLean, H.L., "A Review of U.S. and Canadian Biomass Supply Studies", *Bioresources*, 4:341-369 (2009).
 23. Galbe, M., Liden, G., and Zacchi, G., "Production of Ethanol from Biomass: Research in Sweden", *Journal of Scientific and Industrial Research*, 64:905-919 (2005).
 24. Mabee, W.E., Fraser, E.D., McFarlane, P.N., and Saddler, J.N., "Canadian Biomass Reserves for Biorefining", *Applied Biochemistry and Biotechnology*, 129-132:22-40 (2006).
 25. Mabee, W.E. and Saddler, J.N., "Bioethanol from Lignocellulosics: Status and Perspectives in Canada", *Bioresource Technology*, 101:4806-4813 (2010).
 26. Nanda, S., Mohanty, P., Pant, K.K., Naik, S., Kozinski, J.A., and Dalai, A.K., "Characterization of North American Lignocellulosic Biomass and Biochars in Terms of their Candidacy for Alternate Renewable Fuels", *Bioenergy Research*, 6:663-677 (2013).
 27. Raveendran, K., Ganesh, A., and Khilar, K.C., "Influence of Mineral Matter on Biomass Pyrolysis Characteristics", *Fuel*, 74:1812-1822 (1995).
 28. Nanda, S., Azargohar, R., Kozinski, J.A., and Dalai, A.K., "Characteristic Studies on the Pyrolysis Products from Hydrolyzed Canadian Lignocellulosic Feedstocks", *Bioenergy Research*, 7:174-191 (2014).
 29. Hatfield, R.D. and Chaptman, A.K., "Comparing Corn Types for Differences in Cell Wall Characteristics and *p*-Coumaroylation of Lignin", *Journal of Agricultural and Food Chemistry*, 57:4243-4249 (2009).
 30. Ayyachamy, M., Cliffe, F.E., Coyne, J.M., Collier, J., and Tuohy, M.G., "Lignin: Untapped Biopolymers in Biomass Conversion Technologies", *Biomass Conversion and Biorefinery*, 3:255-269 (2013).
 31. Bose, S.K., Francis, R.C., Govender, M., Bush, T., and Spark, A., "Lignin Content versus Syringyl to Guaiacyl Ratio amongst Poplars", *Bioresource Technology*, 100:1628-1633 (2009).
 32. Boerjan, W., Ralph, J., and Baucher, M., "Lignin Biosynthesis", *Annual Review of Plant Biology*, 54:519-546 (2003).
 33. Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G., and Morgan, T.J., "An Overview of the Organic and Inorganic Phase Composition of Biomass", *Fuel*, 94:1-33 (2012).
 34. Katakai, R. and Konwer, D., "Fuelwood Characteristics of Some Indigenous Woody Species of North-East India", *Biomass and Bioenergy*, 20:17-23 (2001).
 35. Shen, D.K., Gu, S., Luo, K.H., Bridgwater, A.V., and Fang, M.X., "Kinetic Study on Thermal Decomposition of Woods in Oxidative Environment", *Fuel*, 88:1024-1030 (2009).
 36. Shah, M.M. and Lee, Y.Y., "Simultaneous Saccharification and Extractive Fermentation for Acetone/Butanol Production from Pretreated Hardwood", *Applied Biochemistry and Biotechnology*, 34/35:557-568 (1992).
 37. Demirbas, A., "Thermochemical Conversion of Biomass to Liquid Products in the Aqueous Medium", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 27:1235-1243 (2005).
 38. Toor, S.S., Rosendahl, L., and Rudolf, A., "Hydrothermal Liquefaction of Biomass: A Review of Subcritical Water Technologies", *Energy*, 36:2328-2342 (2011).
 39. Muller-Hagedorn, M., Bockhorn, H., Krebs, L., and Muller, U., "A Comparative Kinetic Study on the Pyrolysis of Three Different Wood Species", *Journal of Analytical and Applied Pyrolysis*, 68-69:231-249 (2003).
 40. Das, K.C., Garcia-Perez, M., Bibens, B., and Melear, N., "Slow Pyrolysis of Poultry Litter and Pine Woody Biomass: Impact of Chars and Bio-Oils on Microbial Growth", *Journal of Environmental Science and Health, Part A*, 43:714-724 (2008).
 41. Kumar, R. and Wyman, C.E., "Effects of Cellulase and Xylanase Enzymes on the Deconstruction of Solids from Pretreatment of Poplar by Leading Technologies", *Biotechnology Progress*, 25:302-314 (2009).
 42. Azargohar, R., Jacobson, K.L., Powell, E.E., and Dalai, A.K., "Evaluation of Properties of Fast Pyrolysis Products Obtained from Canadian Waste Biomass", *Journal of Analytical and Applied Pyrolysis*, 104:330-340 (2013).
 43. Lu, C., Dong, J., and Yang, S.T., "Butanol Production from Wood Pulping Hydrolysate in an Integrated Fermentation-Gas Stripping Process", *Bioresource Technology*, 143:467-475 (2013).
 44. Maschio, G., Koufopoulos, C., and Lucchesi, A., "Pyrolysis, A Promising Route for Biomass Utilization" *Bioresource Technology*, 42:219-231 (1992).
 45. Mohanty, P., Nanda, S., Pant, K.K., Naik, S., Kozinski, J.A., and Dalai, A.K., "Evaluation of the Physicochemical Development of Biochars Obtained from Pyrolysis of Wheat Straw, Timothy Grass, and Pinewood: Effects of Heating Rate", *Journal of Analytical and Applied Pyrolysis*, 104:485-493 (2013).
 46. Scott, D.S. and Piskorz, J., "The Continuous flash Pyrolysis of Biomass", *Canadian Journal of Chemical Engineering*, 62:404-412 (1984).
 47. Scott, D.S. and Piskorz, J., "The Flash Pyrolysis of Aspen-Poplar Wood", *Canadian Journal of Chemical Engineering*, 60:666-674 (1982).
 48. Luo, Z., Wang, S., Liao, Y., Zhou, J., Gu, Y., and Cen, K., "Research on Biomass Fast Pyrolysis for Liquid Fuel", *Biomass and Bioenergy*, 26:455-462 (2004).

49. Kucuk, M.M. and Demirbas, A., "Bio-mass Conversion Processes", *Energy Conversion and Management*, 38:151-165 (1997).
50. Shen, J., Wang, X.S., Garcia-Perez, M., Mourant, D., Rhodes, M.J., and Li, C.Z., "Effects of Particle Size on the Fast Pyrolysis of Oil Mallee Woody Biomass", *Fuel*, 88:1810-1817 (2009).
51. Aho, A., Kumar, N., Eranena, K., Salmi, T., Hupa, M., and Murzin, D.Y., "Catalytic Pyrolysis of Woody Biomass in a Fluidized Bed Reactor: Influence of the Zeolite Structure", *Fuel*, 87: 2493-2501 (2008).
52. Horne, P.A. and Williams, P.T., "Influence of Temperature on the Products from the Flash Pyrolysis of Biomass", *Fuel*, 75:1051-1059 (1996).
53. Joshi, J. and Lawal, A., "Hydrodeoxygenation of Pyrolysis Oil in a Microreactor", *Chemical Engineering Science*, 74:1-8 (2012).
54. Ba, T.A., Chaala, M., Garcia-Perez, D., and Rodrigue, R.C., "Colloidal Properties of Bio-Oils Obtained by Vacuum Pyrolysis of Softwood Bark: Characterization of Water-Soluble and Water-Insoluble Fractions", *Energy and Fuels*, 18:704-712 (2004).
55. Zhang, L., Xu, C.C., and Champagne, P., "Overview of Recent Advances in Thermo-Chemical Conversion of Biomass", *Energy Conversion and Management*, 51:969-982 (2010).
56. Balat, M., "Mechanisms of Thermo-chemical Biomass Conversion Processes, Part 3: Reactions of Liquefaction," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 30:649-659 (2008).
57. Qian, Y., Zuo, C., Tan, J., and He, J., "Structural Analysis of Bio-Oils from Sub- and Supercritical Water Liquefaction of Woody Biomass", *Energy*, 32:196-202 (2007).
58. Zhong, C. and Wei, X., "A Comparative Experimental Study on the Liquefaction of Wood", *Energy*, 29:1731-1741 (2004).
59. Xu, J., Jiang, J., Dai, W., and Xu, Y., "Liquefaction of Sawdust in Hot Compressed Ethanol for the Production of Bio-Oils", *Process Safety and Environmental Protection*, 90:333-338 (2012).
60. Mun, S.P. and Hassan, E.M., "Liquefaction of Lignocellulosic Biomass with Mixtures of Ethanol and Small Amounts of Phenol in the Presence of Methanesulfonic Acid Catalyst", *Journal of Industrial and Engineering Chemistry*, 10:722-727 (2004).
61. Chiamonti, D., Bonini, M., Fratini, E., Tondi, G., Gartner, K., Bridgwater, A.V., Grimm, H.P., Soldaini, I., Webster, A., and Baglioni, P., "Development of Emulsions from Biomass Pyrolysis Liquid and Diesel and their Use in Engines—Part 2: Tests in Diesel Engines", *Biomass and Bioenergy* 25:101-111 (2003).
62. Tomishige, K., Asadullah, A., and Kunitomori, K., "Syngas Production by Biomass Gasification Using Rh/CeO₂/SiO₂ Catalysts and Fluidized Bed Reactor", *Catalysis Today*, 89:389-403 (2004).
63. Mosier, N.S., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., and Ladisch, R., "Features of Promising Technologies for Pretreatment of Lignocellulosic Biomass", *Bioresource Technology*, 96:673-686 (2005).
64. Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., Lee, Y.Y., Mitchinson, C., and Saddler, J.N., "Comparative Sugar Recovery and Fermentation Data Following Pretreatment of Poplar Wood by Leading Technologies", *Biotechnology Progress*, 25:333-339 (2009).
65. Zhu, S., Wu, Y., Yu, Z., Wang, C., Yu, F., Jin, S., Ding, Y., Chi, R., Liao, J., and Zhang, Y., "Comparison of Three Microwave/Chemical Pretreatment Processes for Enzymatic Hydrolysis of Rice Straw", *Biosystems Engineering*, 93:279-283 (2006).
66. Biely, P. and Kremnicky, L., "Yeasts and their Enzyme Systems Degrading Cellulose, Hemicelluloses, and Pectin", *Food Technology and Biotechnology*, 36:305-312 (1998).
67. Boominathan, K. and Reddy, C.A., "cAMP-Mediated Differential Regulation of Lignin Peroxidase and Manganese-Dependent Peroxidase Production in the White-Rot Basidiomycete *Phanerochaete chrysosporium*", *Proceedings of the National Academy of Sciences*, 89:5586-5590 (1992).
68. Azzam, A.M., "Pretreatment of Cane Bagasse with Alkaline Hydrogen Peroxide for Enzymatic Hydrolysis of Cellulose and Ethanol Fermentation", *Journal of Environmental Science and Health, Part B*, 24:421-433 (1989).
69. Saddler, J.N. and Mes-Hartree, M., "The Enzymatic Hydrolysis and Fermentation of Pretreated Wood Substrates", *Biotechnology Advances*, 2:161-181 (1984).
70. Yu, E.K.C., Deschatelets, L., and Saddler, J.N., "The Bioconversion of Wood Hydrolyzates to Butanol and Butanediol", *Biotechnology Letters*, 6:327-332 (1984).
71. Itoh, H., Wada, M., Honda, Y., Kuwahara, M., and Watanabe, T., "Bioorganosolve Pretreatments for Simultaneous Saccharification and Fermentation of Beech Wood by Ethanolysis and White Rot Fungi", *Journal of Biotechnology*, 103:273-280 (2003).
72. Heinonen, J., Tamminen, A., Uusitalo, J., and Sainio, T., "Ethanol Production from Wood via Concentrated Acid Hydrolysis, Chromatographic Separation, and Fermentation", *Journal of Chemical Technology and Biotechnology*, 87:689-696 (2012).
73. Baba, Y., Tanabe, T., Shirai, N., Watanabe, T., Honda, Y., and Watanabe, T., "Pretreatment of Japanese Cedar Wood by White Rot Fungi and Ethanolysis for Bioethanol Production", *Biomass and Bioenergy*, 35:320-324 (2011).
74. Maddox, I.S. and Murray, A.E., "Production of n-Butanol by Fermentation of Wood Hydrolyzate", *Biotechnology Letters*, 5:175-178 (1983).
75. Frazer, F.R. and McCaskey, T.A., "Wood Hydrolyzate Treatments for Improved Fermentation of Wood Sugars to 2,3-Butanediol", *Biomass*, 18:31-42 (1989).
76. Nanda, S., Dalai, A.K., and Kozinski, J.A., "Butanol and Ethanol Production from Lignocellulosic Feedstock: Biomass Pretreatment and Bioconversion", *Energy Science and Engineering*, 2:138-148 (2014).
77. Lu, Y., Ryan, W., Sedlak, M., Ho, N., and Mosier, N.S., "Comparison of Glucose/Xylose Cofermentation of Poplar Hydrolysates Processed by Different Pretreatment Technologies", *Biotechnology Progress*, 25:349-356 (2009).
78. Sukumaran, R.K., Surender, V.J., Sindhu, R., Binod, P., Janu, K.U., Sajna, K.V., Rajasree, K.P., and Pandey, A., "Lignocellulosic Ethanol in India: Prospects, Challenges, and Feedstock Availability",

- Bioresource Technology, 101:4826-4833 (2010).
79. Hahn-Hagerdal, B., Jeppsson, H., Skoog, K., and Prior, B.A., "Biochemistry and Physiology of Xylose Fermentation by Yeasts", *Enzyme and Microbial Technology*, 16:933-943 (1994).
 80. Palnitkar, S.S. and Lachke, A.H., "Efficient Simultaneous Saccharification and Fermentation of Agricultural Residues by *Saccharomyces cerevisiae* and *Candida shehatae*", *Applied Biochemistry and Biotechnology*, 26:151-158 (1990).
 81. Pasha, C., Kuhad, R.C., and Rao, L.V., "Strain Improvement of Thermotolerant *Saccharomyces cerevisiae* VS Strain for Better Utilization of Lignocellulosic Substrates", *Journal of Applied Microbiology*, 103:1480-1489 (2007).
 82. Madhavan, A., Tamalampudi, S., Ushida, K., Kanai, D., Katahira, S., Srivastava, A., Fukuda, H., Bisaria, V.S., and Kondo, A., "Xylose Isomerase from Polycentric Fungus *Orpinomyces*: Gene Sequencing, Cloning, and Expression in *Saccharomyces cerevisiae* for Bioconversion of Xylose to Ethanol", *Applied Microbiology and Biotechnology*, 82:1067-1078 (2009).
 83. Jones, D.T. and Woods, D.R., "Acetone-Butanol Fermentation Revisited", *Microbiology Reviews*, 50:484-524 (1986).



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