Chapter

Woody Feedstock Pretreatments to Enhance Pyrolysis Bio-oil Quality and Produce Transportation Fuel

Hamid Rezaei, Fahimeh Yazdanpanah, Jim Choon Lim,
Anthony Lau and Shahab Sokhansanj

Abstract

Lignocellulosic biomass as a potential renewable source of energy has a near-zero CO_2 emission. Pyrolysis converts biomass to a liquid fuel and increases the energy density and transportability. The pyrolysis bio-oil shows promising properties to substitute the conventional fossil fuels. But, unprocessed biomass is low in bulk and energy density; high in moisture; heterogeneous in physical and chemical properties, highly hygroscopic and difficult to handle. That is why the biomass needs mechanical, chemical and/or thermal pretreatments to turn into a more homogeneous feedstock and minimize the post-treatment fuel upgrading. This chapter explains the effects that various pretreatments such as size reduction, drying, washing and thermal pretreatments have on the quality and quantity of bio-oil. Washing with water or acid/alkali solutions extracts the minerals that consequently reduces the ash and shortens the reactor clean-out cycle. Torrefaction is gaining attention as an effective pretreatment to modify the quality of biomass in terms of physical and chemical properties. Torrefaction produces a uniform biomass with lower moisture, acidity and oxygen contents and higher energy density and grindability than raw biomass. Pyrolysis of torrefied biomass produces bio-oil with enhanced compositional and physical properties such as a higher heating value and increased C (lower O/C ratio).

Keywords: pyrolysis, pretreatment, torrefaction, washing, bio-oil, bio-fuel

1. Introduction

Crude oil and coal with high energy density and stable properties to store and transport are preferred fuels for industrial and home applications [1]. The recent reduction in affordable fossil fuels and environmental concerns increased greenhouse gas (GHG) emissions from these fuels that have motivated the public and private sectors to develop renewable energy sources. In recent years, the governments of Canada and the USA adopted regulations to phase out coal-fired power plants by 2030 and investigate other resources to reduce GHG emission. Biomass feedstocks are considered as the renewable resource with a near-zero CO_2 input-output balance [2–4]. Biomass is the only renewable energy source which may be used in all solid, liquid and gas phases [5]. But compared to fossil fuels, biomass is lower in energy (17–19 MJ/kg) and bulk density (60–100 kg/m^3) [6];

heterogeneous in physical, chemical and thermal properties; high in moisture [6], mineral [7] and oxygen contents [8]; highly hygroscopic [9] and difficult to handle [6]. Converting biomass to secondary liquid or gaseous fuels through thermal conversion processes is a way of increasing the energy density and transportability. Mechanical, chemical and thermal pretreatments are able to modify the biomass properties in order to produce a more homogeneous fuel and minimize the post-treatment fuel upgrading.

The current article reviews the feedstock properties that are important for the fast pyrolysis process and the potential pretreatments to modify the biomass properties are explained. Specifically, drying, grinding, washing and torrefaction processes and their influence on the final bio-oil product are thoroughly explained.

2. Pyrolysis

Pyrolysis is a thermal process to convert biomass particles to secondary solid, liquid and/or gaseous fuels [10]. The liquid bio-oil obtained from pyrolysis of biomass shows promising properties to substitute the conventional fossil fuels. The breakdown of biomass particles takes place in a pyrolysis reactor by exposing them to an oxygen-free or deficit environment. As the temperature of the particle increases, different stages of thermal treatment occur. Drying happens first when a moist particle is heated up to temperatures of about 150°C [11]. At temperatures of 200–300°C and in the absence of oxygen/air, various degrees of torrefaction happen and release volatile [12–14]. At temperatures higher than 300°C, more severe decomposition of biomass happens and structural changes such as a change in chemical composition and porosity of particles occur in the solid matrix.

Pyrolysis processes are generally categorized as "slow" and "fast" according to the time taken for processing the feed into pyrolysis products. Slow pyrolysis utilizes low temperatures of 300–400°C over a residence time of 30 minutes to hours to maximize char formation. Fast pyrolysis is a rapid thermal decomposition process to maximize the liquid fraction of products. In industrial fast pyrolysis, biomass particles would be exposed suddenly to an environment of 400–600°C to heat up rapidly. The combined effects of moisture content, particle size [15–17] and reactor temperature [18, 19] make a non-linear temperature profile inside the particle which affects the rate of conversion. The residence time of the volatile fraction in the pyrolysis reactor and its contact with solid particles should be less than 2–3 seconds to prevent the secondary reactions. Pyrolysis takes place in a complete absence of oxygen. The volatiles are quickly removed and quenched to maximize liquid yield. **Figure 1** displays a schematic diagram of an industrial pyrolysis process. In the following sections, a comprehensive literature review is presented to discuss the effects of various parameters related to feedstock and pre-treatments on the efficiency of the pyrolysis process.

2.1 Feedstock composition

A plant-based dry biomass has the main fractions of cellulose, hemicelluloses, lignin, extractives and minerals. Wood extractives, or wood extracts, are low molecular weight molecules that are extracted from wood using solvents or other extraction methods. The extractives are the waxes, fatty acids, resin acids and terpenes of a tree. **Table 1** lists the composition of a broad range of biomass species. The composition of biomass changes the chemical composition and heating value of pyrolysis products [33]. Higher lignin content reduces the bio-oil yield at

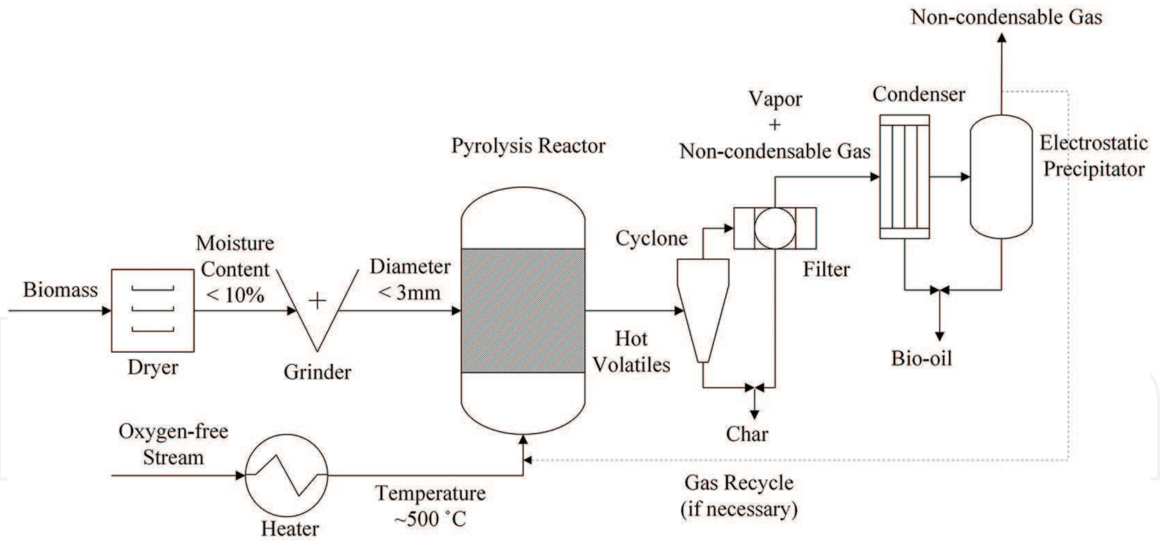

Figure 1.
Schematic diagram of the pyrolysis process, including drying, grinding, pyrolyzer, separation stages and condenser.

Biomass species	Composition (wt.%)			Refs.	Ultimate analysis (wt.%)			Ash (wt.%)	HHV (MJ/kg)	Refs.
	Cel.[1]	Hem.[2]	Lig.[3]		C	H	O			
Pine wood	42.1	27.7	25.0	[20]	45.9	5.3	48.2	0.35	18.98	[21]
Beech wood	41.7	37.1	18.9	[22]	46.7	5.7	47.6	1.04	–	[22]
Douglas fir	50.0	17.8	28.3	[23]	50.7	6.0	42.5	0.50	20.07	[24]
Spruce wood	41.1	20.9	28.0	[20]	48.9	6.0	44.6	0.30	19.26	[20]
Poplar aspen	49.9	22.4	18.1	[25]	–	–	–	–	–	–
Poplar wood	42.2	16.6	25.6	[26]	48.4	5.8	43.7	1.43	19.71	[26]
Birch wood	35.7	25.1	19.3	[20]	49.0	6.3	44.1	0.30	18.40	[27]
Corn stover	36.4	22.6	16.6	[28]	–	–	–	–	–	–
Corn cob	52.0	32.5	15.5	[29]	49.0	5.6	43.8	1.10	–	[29]
Wheat straw	38.2	24.7	23.4	[28]	40.7	5.8	52.9	10.58	16.24	[30]
Rice straw	34.2	24.5	23.4	[31]	36.9	5.0	37.9	11.70	16.78	[31]
Rice straw	32.1	26.5	12.5	[32]						
Olive husk	25.2	24.2	50.6	[29]	50.2	6.4	38.4	4.10	–	[29]
Tea waste	33.2	23.3	43.5	[29]	48.2	5.5	44.3	1.50	–	[29]

[1] *Cellulose.*

[2] *Hemicellulose.*

[3] *Lignin.*

Table 1.
Composition and ultimate analysis, ash content and calorific value of various biomass feedstock.

the expense of higher biochar yield in the pyrolysis process [29]. The extractives have the highest heating value in the woody biomass. The heating values of biomass components are 17–18, 16–17, 25–26 and 33–38 GJ/tonne for cellulose, hemicellulose, lignin and extractives, respectively [34].

Each sub-component of the biomass has a specific thermal reactivity. For example, cellulose decomposes at 300–400°C; hemicellulose decomposes at 200–300°C and lignin decompose continuously in the wide temperature range of

180–600°C [35]. This specification directly influences the temperature range at which the material thermally decomposes and consequently the optimum pyrolysis temperature at which the maximum bio-oil yield is obtained. **Table 2** lists pyrolysis liquid yield of various biomass species at tested temperatures and depicts the variability of produced bio-oil yield among the pyrolysis of different feedstocks. Apart from variability in conversion rate among species, the conversion rate increases with the reaction temperature.

In addition to the chemical composition, the elemental and proximate analysis of the biomass feedstock changes the properties of the produced fuel. From the elemental point of view, the biomass is mainly contained of carbon, hydrogen and oxygen (**Table 1**). The composition of elements affects the storage properties of the liquid fuel. Compared to conventional fossil fuels, biomass has a high amount of ~40–50% oxygen content. High oxygen content makes the produced liquid fuel unstable, corrosive and consequently not qualified for transportation and storage [16].

The minor elements present in the biomass material are minerals such as potassium, chlorine, sulfur, silicon, calcium and magnesium [45]. Minerals are present in all biomass species, in a much lower amount than carbon, hydrogen and oxygen elements. Agricultural biomass has much more mineral contents than woody biomass. In a thermal process, minerals turn to ash (**Table 1**). The pyrolysis biochar typically contains up to 90% of the biomass minerals [46]. Ash shifts the size distribution of the char to smaller sizes that make their recovery from the gas stream challenging. An incomplete separation of char and volatiles causes continuous secondary reactions in the liquid phase [16, 47, 48] that accelerates the aging phenomenon and contribute to its instability [49, 50]. Aging phenomena is defined as a slow increase in viscosity bio-oil resulting from secondary reactions [16]. Minerals have a catalytic effect on the rate of secondary reactions [51].

2.2 Pyrolysis products

Products of the pyrolytic reaction are biochar and hot volatile that need to be separated and cooled down quickly. The residence time of char and volatile in direct contact should be less than 2–3 seconds [5, 15, 52]. Char is greatly porous and has a catalytic effect on volatile cracking to non-condensable gases, more char and also non-desirable volatiles [1]. The main product of fast pyrolysis is liquid bio-oil that is obtained by condensation of volatiles, yielding up to 75 wt.% based on a dry feed

Biomass type	Pyrolysis temperature (°C)	Bio-oil yield (wt.%)	Refs.
Pine wood	450	55.0	[36]
Waste furniture sawdust	450	65.0	[37]
Wood sawdust	650	74.0	[38]
Corncob	550	56.8	[39]
Municipal, livestock and wood waste	500	39.7	[40]
Pine wood	450	50	[41]
Rice husks	450	60	[42]
Corn cobs and corn stover	650	61.6	[43]
Sugar cane waste	470	56.5	[44]

Table 2.
Bio-oil yield in fast pyrolysis of different biomass feedstocks.

basis [15]. **Table 3** lists a few key properties of bio-oil and the properties of petroleum grade fuel (Fuel No. 6). Bio-oil has a heating value of about half of conventional fossil fuel oil, 17–19 MJ/kg for bio-oil versus 35–40 MJ/kg for petroleum fossil fuel [52].

The final application of produced bio-oil depends on its quality and properties such as solid content, stability during storage and transportation, oxygen and water contents and its pH value [54]. High oxygen and water content make the bio-oil less stable and less competitive with conventional fossil fuels. Low stabilization, including phase separation and polymerization, and acidic and corrosive properties of bio-oil make its storage and transportation difficult [39, 55]. Based on National Renewable Energy Laboratory's (NREL) recommendation, Multi-Year Program Plan (MYPP 2011), the bio-oil must maintain its consistency for at least 6 months of storage. Based on the published studies, a drastic reduction in water content of bio-oil, insoluble solids and oxygen content and a substantial increase in the calorific value of bio-oil are needed for upgrading to fuel grade.

Gas and biochar are generated as by-products of the pyrolysis process. Optimizing their properties helps to find an application for by-products to make the overall process more economically feasible. They have the potential to provide the heat required for the pyrolysis process. The non-condensable gases of the pyrolysis process have a substantial amount of CO_2 and CH_4. Combustion of these permanent gases makes heat for the pyrolysis process. Biochar has various interesting properties. First one is that the biochar also has a high calorific value. The energy density for charcoal is 9–11 GJ/m^3, while energy density for wood and coal are 8–10 and 25–40 GJ/m^3, respectively [1]. Second, biochar is enriched with carbon that is a good soil amendment. In addition, adding char to soil moves the carbon from atmosphere to soil [56]. Third but not last, pyrolysis biochar has promising adsorption properties for heavy metals [57], dyes [58, 59] and aromatics [60] in agricultural and industrial effluents. The biomass properties influence the biochar properties to be used for adsorption purposes. For example, woody biomass contains more lignin content than agricultural biomass and its biochar has higher surface area than other biomass-derived biochars. Then, it is speculated to have better adsorptivity properties [61].

Characteristics	**Fast pyrolysis bio-oil**		**Heavy petroleum fuel**
	Wet	**Dry**	
Water content (wt.%)	15–25		0.1
Insoluble solids (%)	0.5–0.8		0.01
Carbon (%)	39.5	55.8	85.2
Hydrogen (%)	7.5	6.1	11.1
Oxygen (%)	52.6	37.9	1.0
Nitrogen (%)	<0.1		0.3
Sulfur (%)	<0.05		2.3
Ash (%)	0.2–0.3		<0.1
Heating value (MJ/kg)	17		40
Density (g/ml)	1.23		0.94
Viscosity (cp) @ 50°C	10–150		180

Table 3.
Properties of wood-derived bio-oil and heavy petroleum fuel [53].

3. Feedstock pretreatment

Physical properties like particle size, particle shape and density influence the material handling and flowability of particles that are leading properties for an uninterrupted feeding system [62]. Chemical properties like elemental and proximate analyses influence the pyrolysis products' distribution and properties. Although biomass has inherent heterogeneous properties [1], various physical, chemical and thermal pretreatments contribute to achieving homogeneity in properties of biomass. Homogeneous feedstock with uniform physical and chemical properties plays a key role in a pyrolysis process and quality of its products. Although pretreatments create an additional feedstock cost, they facilitate feeding a wide range of biomass species with broad properties and are beneficial due to producing uniform and homogeneous feedstock for power plants.

3.1 Moisture reduction

Biomass particles are dried for a more-efficient thermal combustion in pyrolysis reactors to produce bio-oil [63, 64]. A fresh biomass has a high moisture content of up to 80% [34]. High moisture content reduces the heating value of the fuel and shifts the ignition point to higher temperatures [6], and inhibits the rise of temperature inside the particles and conversion reactor [65, 66]. Reduced particle and reactor temperatures diminish the liquid yield at the expense of a larger fraction of biochar and non-condensable gases [22, 66]. Water has a catalytic effect on volatile cracking. Di Blasi [67] showed that moisture content conducts the pyrolysis reaction to a low activation energy path that promotes the formation of char, non-condensable gases and more water. Biomass should be dried down to less than 10% moisture content to improve the quality of produced fuel [15]. Pyrolysis of dry material produces less water compared to wet biomass. Bio-oil with a lower amount of water has higher heating value, a lower ignition point, higher combustion rate and a lower potential of phase separation [6].

Rezaei [68] stated that size of particles [69], initial moisture content [70], drying temperature [69, 71], relative humidity of drying gas [72, 73] and particle heating rate [74] influence the rate of moisture loss. Rezaei et al. [75] showed that biomass shrinks during the moisture loss that influences the drying rate. Dehydration of fresh wood causes a reduction in the dimension of wood in a direction normal to the microfibril orientation, whereas the longitudinal shrinkage is usually negligible [76]. Mazzanti et al. [77] showed that the longitudinal shrinkage for poplar wood is negligible. Taylor et al. [78] showed that the radial shrinkage of beech wood is about 70 times of longitudinal shrinkage.

3.2 Size reduction

Grinding reduces the dimensions of a particle and increases the particle's specific surface area (ratio of the particle's surface area to its mass). The same relationship holds for a bulk of particles where the surface area of the solids increases in a given volume of bulk particles. Therefore, the smaller particles have a more exposed surface to the raised-temperature environment to boost the rate of heat and mass transfer between the particles and surrounding. Rezaei et al. [79, 80] showed that larger particles (from 1 to 5 mm) have a delay in heat and mass transfer and reduced rate of pyrolysis (**Figure 2**). On the other hand, grinding the biomass to smaller particles requires more energy input. Rezaei et al. [81] reported that grinding wood chips to produce particles with average sizes of 1, 1.8, 3 and 5 mm requires about 124.0, 85.7, 52.6 and 28.2 kJ/kg, respectively. Van Der Stelt et al. [82] measured

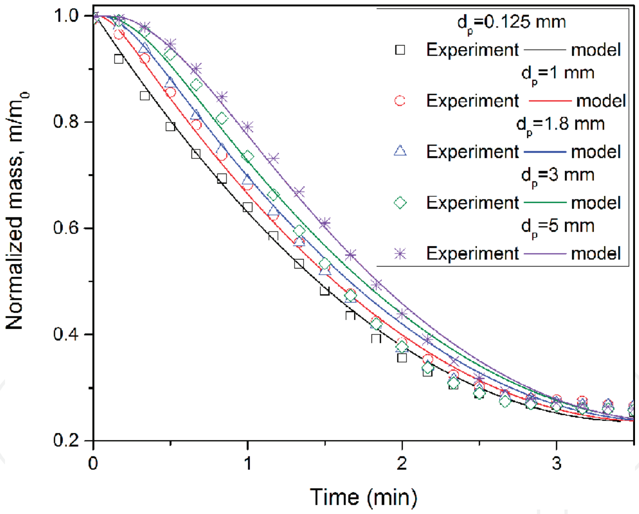

Figure 2.
Effect of particle size on the pyrolysis rate of ground wood particles at 500°C [80].

the power required for size reduction of coal, torrefied woodcutting, willow and demolition wood. He showed that to have particles smaller than 0.6 mm, the grinding power consumption increases sharply. The balance of the conversion rate and energy consumption identifies the optimum particle size appropriate for a fast pyrolysis process.

Figure 3 shows the published data on yields of three phases of solid, liquid and gas in pyrolysis of a range of particle size. In the range of particle size up to 2 mm, only the apricot stone pyrolyzed at 800°C showed a yield that was sensitive to particles size. An increase in particle size increased the char yield at the expense of less liquid yield [15, 22, 26, 83]. Some researchers did not observe any effect of particle size on the yield of products. For example, Şensöz et al. [84, 85] did not observe any meaningful influence of particle size on the pyrolysis products of rapeseed (*Brassica napus* L.) in the range of 0.22–0.85 mm [84] and of debarked pine in the range of 2–5 mm [85]. Encinar et al. [86] reported that liquid yield was independent of biomass particle size during pyrolysis of 0.4–2.0 mm grape residue and olive residue particles pyrolyzed at 500°C. On the other hand, some researchers showed that larger particles in pyrolysis decrease liquid yield and increase biochar yield [22, 83, 87]. NikAzar et al. [22] found out that size increase from 53 to 63 μm to 270–500 μm declined liquid yield from 53 to 38%. He claimed the particle's core temperature diminished by particle size and caused the change in the yield of products. This result was confirmed by some other researchers [15–17, 26, 29, 88].

Most of the published data recommend that particles in the range of 1–2 mm are appropriate for fast pyrolysis [17, 52, 82, 89]. However, the effect of particle size on the pyrolysis process needs more work. The range of particle sizes tested in various studies is seldom comparable and a study on a wider range of particle size seems necessary. In addition, the challenges associated with commercial grinding and feeding the bulky lightweight biomass in the reactor should be taken into account that is out of the scope of the current chapter.

3.3 De-mineralization

The mineral elements in biomass may be listed mostly as potassium, chlorine, sulfur, silicon, calcium and magnesium [45]. The mineral content of biomass exists on the particle surface because of contact with soil during harvest and/or transportation, or within the material as biogenic characteristics.

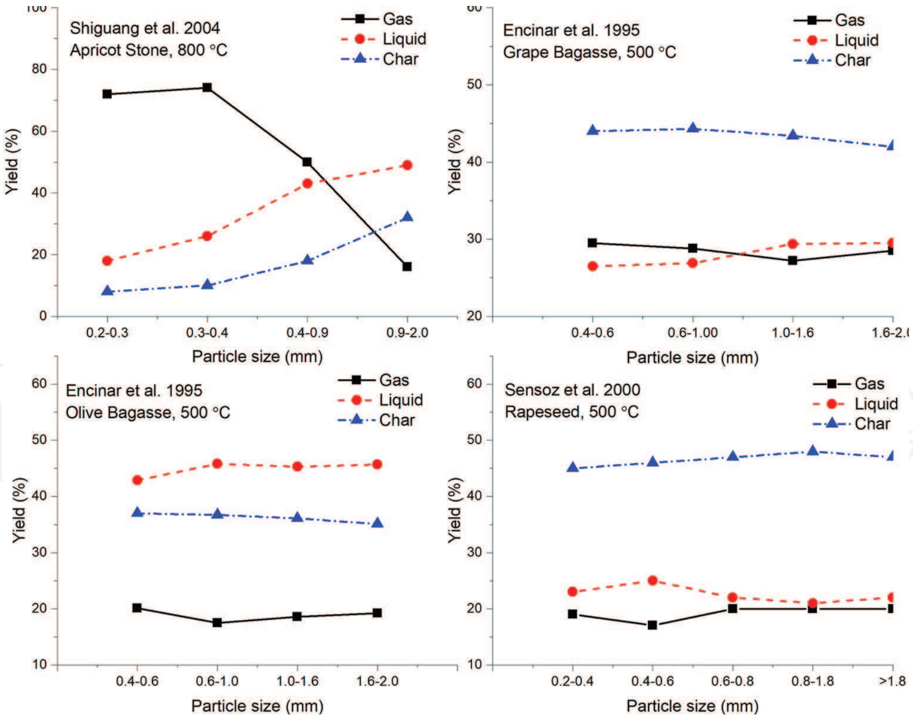

Figure 3.
Effect of biomass particle size on the yield of products in a fast pyrolysis process.

The minerals of the biomass present as ash or fouling in conversion vessels. In a pyrolysis process, the biochar typically contains up to 90% of the biomass minerals [46] that changes the physical properties of char. Ash shifts the size distribution of the char to smaller sizes that hardens its full separation from produced volatile. A partial char separation results in a high solid content bio-oil that cannot be used as turbine fuel [49]. Furthermore, minerals act as a catalyst and cause continuous secondary reactions in liquid phase [16, 47, 48] at the expense of char formation [51, 90]. More secondary reactions promote an increases in bio-oil viscosity with time and accelerate aging phenomenon [50]. Mineral contamination accelerates the catalytic breaking of levoglucosan into unwanted hydroxyl acetaldehyde compounds [51, 91]. Former is desired part of volatiles and latter is an undesirable portion of volatiles. Addition of 0.05 wt.% NaCl to an ash-free cellulose decreases the levoglucosan formation yield by a factor of 6 [92].

One efficient pretreatment to reduce the mineral content is washing the biomass with water, acidic and/or alkaline solutions. Washing with dilute acid and hot water results in a slight decomposition of hemicellulose [93]. Washing with dilute alkali disrupts the lignin structure and solubilize the hemicellulose [94]. Washing biomass prior to pyrolysis takes away a huge amount of minerals from the biomass, up to 70% of the initial minerals [1, 17].

Das et al. [95] studied the effect of various washing solutions, concentrations and the time of washing on ash content and products' yields of sugarcane bagasse pyrolysis (**Figure 4**). The ash content decreased from 1.83% before washing to 0.03%. The only washing solution that had a reverse effect was 5 M HCl. It must have been due to the adding chlorine element into the biomass. The important point is the effect of washing on yield of total liquid versus the bio-oil. The total liquid contains bio-oil and aqueous solutions. All washing solutions reduced the total liquid yield but boosted the bio-oil yield.

Table 4 lists different washing solutions based on demineralization yield, ash content, char and liquid yield and maximum decomposition rate [96]. Washing demineralized the biomass up to 98%, enhanced liquid yield, lowered the char yield, shifted up the decomposition rate and reduced the low molecular weight compounds

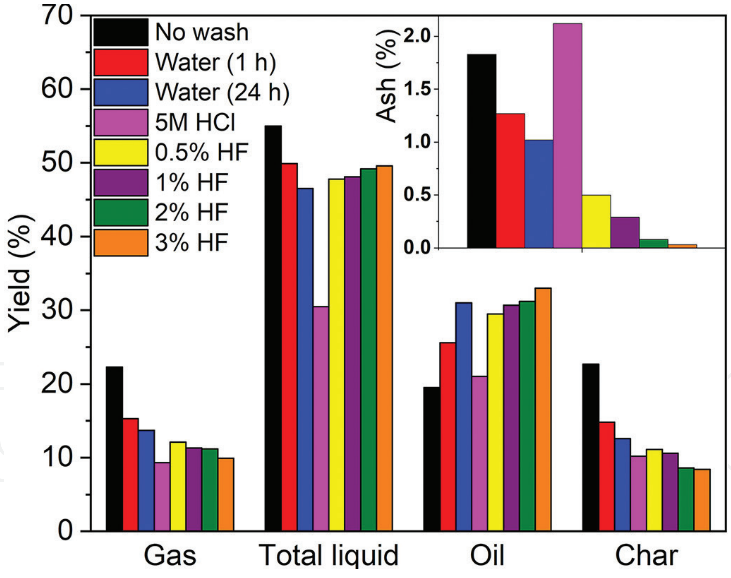

Figure 4.
Effect of de-mineralization pretreatment on biomass ash content and products' yield of sugarcane bagasse pyrolysis [95].

Washing solution	Demineralization yield (%)	Char yield (%)	Volatiles yield (wt.%)	Max. decomposition rate (wt.%/°C)	Tp[3] (°C)
No washing	–	14.9	85.1	0.96	362
HCl[1]	69.3	11.8	88.2	1.55	366
HF[2]	97.3	10.2	89.8	1.15	368
Deionized water	97.7	11.0	89.0	1.23	372
Tap water	98.2	11.4	88.6	1.19	376

[1] *Hydrochloric acid.*

[2] *Hydrofluoric acid.*

[3] *Temperature at which maximum decomposition rate happens.*

Table 4.
Specifications for pyrolysis of demineralized poplar wood at 550 °C [96].

in pyrolysis products. Solution temperature also influences the demineralization yield. Deng et al. [7] showed that demineralization of candlenut wood raised from 8% at 30°C to 35% to 90°C. Mineral removal increased the higher heating value from 16.53 to 17.82 MJ/kg and the rate of devolatilization increased too. Natural rain and season of raining change the composition of minerals in biomass [97].

3.4 Torrefaction

Torrefaction is a mild thermal treatment that modifies the structure and chemical composition of biomass by removing hemicelluloses [98], dehydrating and partially reducing cellulose and lignin [99]. Li et al. [13] described torrefaction as a mild heat treatment of biomass at a temperature range of 200–300°C, prolonging 15–30 minutes. Westover et al. [6] divided torrefaction into three stages of non-reactive drying (50–150°C), reactive drying (150–200°C) and destructive stage (200–300°C). During thermal treatment, biomass releases moisture up to the temperature of 150–170°C [11]. In 180–270°C, exothermic hemicellulose degradation happens and biomass turns to brown color. At this stage, torrefaction reaction produces more water, CO_2, acetic acid and phenols [12–14, 35]. The released gases are combustible and may be used to provide a portion of process energy. Beyond 270°C, the reactions are more exothermic and produce CO and some other heavier products such as CH_4 and C_2H_6. Torrefaction continues to a temperature of 300°C, where pyrolysis starts.

Torrefied biomass contains about 80% of the mass and 90% of the energy of the initial biomass [82, 99]. Similar to other thermal processes, mass and energy yield of torrefaction depends on biomass species [99], particle size [14, 26], operating temperature [6, 13, 33, 100, 101] and residence time [13, 33, 101]. Biomass torrefaction has been recognized as a feasible technique to convert raw biomass to a high energy density, hydrophobic, grindable, homogeneous, low moisture content (<5%) [6], better storage stability [34] and low-oxygen-content fuel that is a suitable feedstock for pyrolysis [102].

Torrefaction changes the stiffness and glass transition temperature (T_g) of biomass [6] that contributes to the grindability of the material. Ground torrefied biomass particles are smaller, drier and more uniform in size and physical and chemical properties [13, 14]. **Table 5** lists the specific grinding energy of raw and torrefied pine and logging residue. Higher torrefaction temperature makes the biomass structure more brittle and reduces the specific grinding energy. Specific grinding energy consumption reduced by 90% from 240 kWh/t for raw pine chips to 24 kWh/t for torrefied pine chips at 300°C.

Using the torrefied biomass as a feedstock for fast pyrolysis has various benefits. The level of these modifications depends on torrefaction temperature and residence time. First of all, torrefaction removes the hemicellulose and enriches the biomass into the cellulose and lignin (**Figure 5**). Presence of hemicellulose intensively decreases the yield of levoglucosan and promotes the formation of hydroxyl acetaldehyde. The torrefied feedstock may eliminate or reduce this interaction as it removes hemicelluloses.

Bio-oil of torrefied biomass has a lower water content that increases bio-oil's stability (less phase separation) [100, 104, 105], lower oxygen/carbon ratio and higher calorific value [104] compared to the bio-oil produced from non-torrefied biomass [5, 89, 99, 101]. Because torrefaction extracts contain acidic condensable volatiles such as acetic acid, furfural, formic acid, methanol, lactic acid and phenol from the biomass [106], the bio-oil has a lower acidity and aldehydes content [17, 105].

Sample	Specific grinding energy (kWh/t)	Hemicel. (wt.%)	Sample	Specific grinding energy (kWh/t)	Hemicel. (wt.%)
Untreated-PC[1]	237.7	15.19	Untreated-LR[3]	236.7	14.77
TPC[2]-225°C	102.6	12.87	TLR[4]-225°C	113.8	13.26
TPC-250°C	71.4	6.94	TLR-250°C	110.4	5.87
TPC-275°C	52.0	0.99	TLR-275°C	78.0	5.23
TPC-300°C	23.9	0.56	TLR-300°C	37.6	1.04

[1] *Pine chips.*

[2] *Torrefied pine chips.*

[3] *Logging residues.*

[4] *Torrefied logging residues.*

Table 5.
Specific energy consumption for grinding of untreated and torrefied biomass with a residence time of 30 minutes [98].

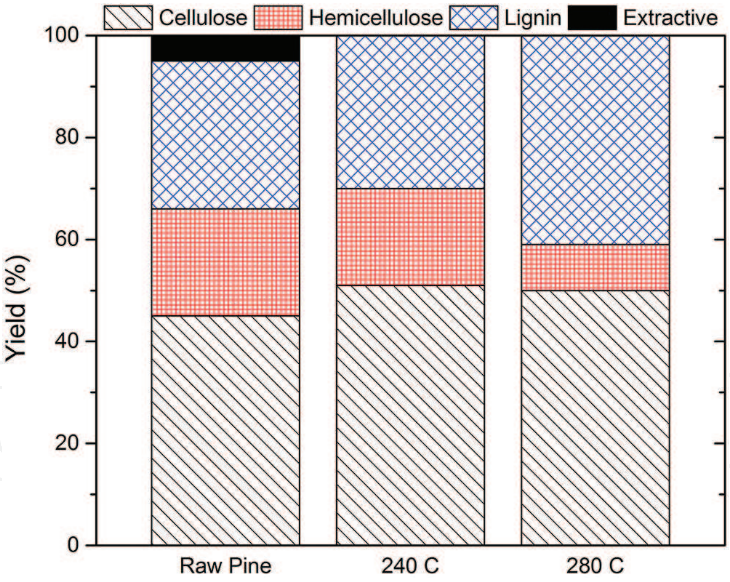

Figure 5.
Composition of raw and torrefied pine at 240 and 280°C [103].

Klinger [105] pyrolyzed the torrefied material and observed 27% water reduction, 36% CO reduction, 55% CO_2 reduction and 67% acetic acid reduction in the produced volatiles compared to volatiles obtained from non-torrefied biomass.

Despite all benefits, pyrolysis of torrefied biomass has a lower yield of total liquid. Liaw et al. [100] reported that pyrolysis total liquid yields of raw Douglas fir and torrefied Douglas fir at 280, 320 and 370°C was 59, 55, 48 and 30%, respectively [100]. Boateng [99] and Zheng [5, 104] reported that more sever torrefaction decreases the total liquid yield and increases the yield of biochar and permanent gases. **Tables 6** and **7** list the results of Zheng's work for pyrolysis of raw and torrefied corncob.

Water content reduced from 35% in bio-oil produced from raw corncob to 21% in bio-oil produced from torrefied corncob at 300°C. The pH increased in the bio-oil prepared from torrefied corncob. The viscosity of bio-oil also increased probably due to a reduction in water content. The acetic acid content decreased moderately with increasing torrefaction temperature and residence time. The furfural content also decreased gradually with torrefaction temperature and residence time. Acetic acid and furfural are mainly derived from hemicellulose and cellulose. Ren et al. [101, 107] conducted a research on Douglas fir in two sequent

Properties and compounds	Raw corncob	Torrefied (240°C)	Torrefied (300°C)
Water content (wt.%)	35.00	30.00	21.00
High heating value (MJ/kg)	14.85	16.49	17.21
pH	2.68	3.30	3.34
Kinematic viscosity @ 20°C (cSt)	3.42	7.27	12.62
Acids (95% acetic acid) (%wb)	7.16	5.65	4.75
Ketones (wt.%)	8.16	7.42	6.02
Furans (wt.%)	0.98	0.8	0.76
Phenols (wt.%)	2.45	4.51	5.27

Table 6.
Physical properties and a few main chemical contents of bio-oil produced from pyrolysis (at 500°C) of raw and torrefied corncob at 240 and 300°C for 20 minutes [104].

Properties	Raw corncob	Residence time: 20 minutes			Temperature: 275°C	
		250°C	275°C	300°C	10 minutes	60 minutes
Ultimate analysis of torrefied corncob (wt.%)						
C	43.87	45.10	48.54	57.86	47.64	57.33
H	6.06	6.20	6.65	6.75	6.10	5.93
O	49.50	48.01	44.06	34.43	45.61	35.92
N	0.53	0.61	0.70	0.86	0.60	0.75
S	0.04	0.08	0.05	0.11	0.04	0.06
O/C	1.13	1.06	0.91	0.60	0.96	0.63
Yield of pyrolysis products (wt.%)						
Bio-oil	57.20	55.15	47.60	40.74	50.36	39.35
Biochar	21.14	24.57	30.21	38.19	26.31	40.70
Non-condensable gas	21.66	20.28	22.19	21.07	23.33	19.95
Physical properties of bio-oil						
Water content	35.0	33.0	25.0	21.0	30.0	22.0
Higher heating value (MJ/kg)	14.85	15.12	16.49	17.21	15.58	17.09
pH	2.68	2.97	3.30	3.34	2.88	3.35
Kinematic viscosity @ 20°C (cSt)	3.42	3.96	7.27	12.62	4.23	12.48
Crystallinity (%)	20.06	25.74	34.82	27.35	23.26	22.83

Table 7.
Effect of temperature and residence time of corncob torrefaction on ultimate analysis of feedstock, the yield of pyrolysis products (at 500°C) and physical properties of bio-oil [5].

articles. They determined the effects of pyrolysis temperature and torrefaction time, as a pretreatment, on the characterization of produced total bio-oil and syngas. Total bio-oil is the sum of condensed liquids from torrefaction and pyrolysis. **Figure 6** shows that bio-oil yield from raw (untreated) biomass ranged from 31 [107] to 53% [101] for pyrolysis at 400 and 450°C, respectively. The bio-oil yield from a 450°C pyrolysis decreased to 51 and 46% for 8 and 15 minutes torrefaction pretreatment at 275°C was carried out. Longer torrefaction reduced slightly the yield of bio-oil. Torrefaction also altered the compositions of syngas by reducing CO_2 and increasing H_2 and CH_4. The syngas produced from pyrolysis step was rich in H_2, CH_4 and CO implying that the syngas quality was significantly improved by torrefaction process [105]. The quantity of syngas increased with the severity of the torrefaction.

Table 8 summarizes a qualitative analysis of benefits of feedstock thermal pretreatment on logistical and quality of bio-oil properties. Column 1 lists major properties that a feedstock would gain as a result of thermal pretreatment. The degree of change in properties depends upon the severity of thermal treatment. Column 2 lists the benefits of these properties on improving conversion efficiency or the quality of produced bio-oil when the pretreated feedstock is pyrolyzed. Column 3 outlines the benefits of feedstock properties from a logistical perspective, that is, handling, transport, storage, unit operations like blending and feeding the feedstock to the pyrolysis reactor. Finally, column 4 lists the potential monetary benefits of thermal pretreatments mostly due to improvements in logistics.

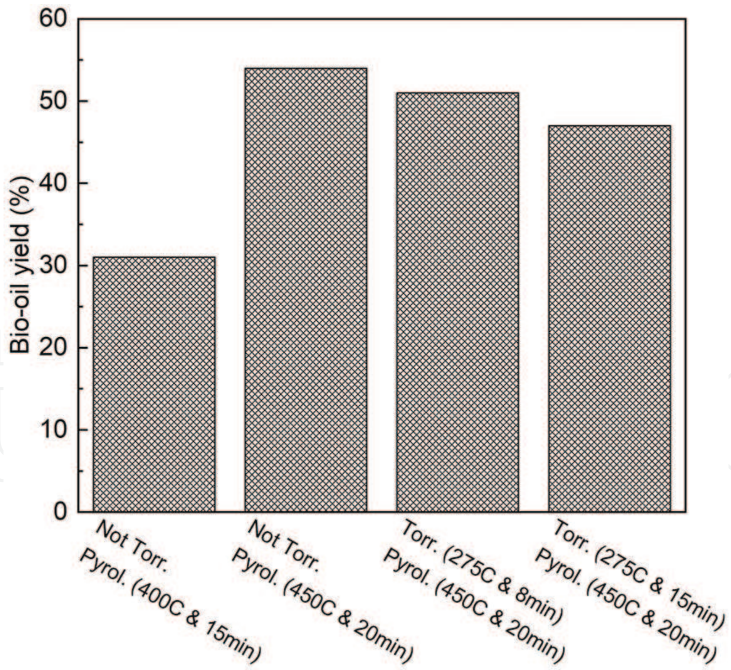

Figure 6.
Bio-oil yield from raw and torrefied Douglas fir at the various duration and temperature [101, 107].

Feedstock properties	Conversion and quality of bio-oil benefit	Logistics benefit	Economic benefit
Grindability	Uniform small size particles for high heat transfer in the reactor	Torrefied particles are dry and a lower tendency for electrostatic charged	Lower investment and operating cost in grinder and grinder operation
Hydrophobicity	Less water content due to a decrease in OH and COOH groups	Store unprotected, exposure to rain, long shelf life	Lower storage cost, lower transport cost
Low moisture content	Reduced water in the bio-oil	Reduced mass to handle, stable in storage	Expensive drying is not required
High heat value	Bio-oil will have a higher heat value due to increased C and low O/C ratio	Can be blended with coal and other high heat value products	Lower cost ($/GJ) No need to design a new combustion chamber
Homogeneity	Predictable conversion performance in the pyrolysis reactor	Reduced quality control, may easily become a commodity	Lower management cost
High density (after grinding)	Can be controlled to a precise particle size and density	Improved flowability, low off-gas emissions	Reduced cost of shipping and storage
Thermal degradation	Lower acidity	Higher energy density (GJ/m^3)	Higher $/GJ
Wet fractionation (wet torrefaction)	Less chlorine and ash	Access to low-quality feedstock (e.g. bark)	Reduced overall feedstock cost ($/t)

These improvements are in comparison with the untreated feedstock.

Table 8.
Overview of benefits of torrefied feedstock for bio-oil production.

4. Conclusions

The energy produced from lignocellulosic biomass is renewable, environmentally friendly and carbon-neutral. Characteristics of bio-oil produced in fast pyrolysis showed that it is capable to substitute conventional petroleum-based fuels. This chapter explained the fast pyrolysis process and the pretreatments that contribute to acquiring a transportation bio-oil with enhanced physical and chemical properties. The modification of biomass feedstock properties through available pretreatment techniques plays a key role in the pyrolysis process. Pretreatments change the biomass feedstock's size, shape, mineral content, composition, hygroscopic properties, homogeneity, grindability, stability and transportability.

Torrefaction as a mild pyrolysis of biomass feedstock is a promising pretreatment that modifies the structure and chemical composition of biomass by removing hemicelluloses, dehydrating and enriching biomass in cellulose and lignin. Torrefaction makes the structure of biomass more brittle that make it more grindable. Grinding torrefied biomass produces more uniform particles with smaller and narrower particle size distribution. Pyrolysis of torrefied material enhances the properties of produced bio-oil. This enhancement is consistent with the DOE MYPP's target that "additional processing of the bio-oil is required to enable it to become a feedstock suitable for use in a petroleum refinery at several entry points." However, this is penalized with a liquid yield reduction.

With all the opportunities of renewable biomass energy, some important issues are still needed to be solved to commercialize the process. To find the least-cost combination of torrefaction along with biomass fast pyrolysis, further testing of the two along with economic analysis are required.

Author details

Hamid Rezaei[1]*, Fahimeh Yazdanpanah[1], Jim Choon Lim[1], Anthony Lau[1]
and Shahab Sokhansanj[1,2]

1 Chemical and Biological Engineering Department, University of British Columbia, Vancouver, BC, Canada

2 Agricultural and Bioresource Engineering, University of Saskatchewan, Saskatoon, Canada

*Address all correspondence to: hamidrezaei@chbe.ubc.ca

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