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Biomass Compositional Analysis for Conversion to Renewable Fuels and Chemicals

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Abstract

As the world continues to deplete its nonrenewable resources, there has begun a shift toward using renewable materials for the production of fuels and chemicals. Terrestrial biomass, as well as municipal solid wastes, provides renewable feedstocks for fuel and chemical production. However, one of the major challenges to using biomass as a feedstock for fuel and chemical production is the great amount of innate variability between different biomass types and within individual biomass species. This inconsistency arises from varied growth and harvesting conditions and presents challenges for conversion processes, which frequently require physically and chemically uniform materials. This chapter will examine intrinsic biomass compositional characteristics including cellulose, hemicellulose, lignin, extractives/volatiles, and ash for a wide array of biomass types. Additionally, extrinsic properties, such as moisture content and particle grind size, will be examined for their effect on biomass conversion to fuels using four major conversion processes: direct combustion, pyrolysis, hydrothermal liquefaction, and fermentation. A brief discussion on recent research for the production of building block chemicals from biomass will also be presented.

Keywords: biomass, composition, variability, renewable, fuels, chemicals

1. Introduction

CO₂ and other greenhouse gases are contributing to increased concerns about global warming. Biomass growth and utilization provides one solution to reduce greenhouse gas emissions and balance the ecosystem. For instance, carbon sequestered by the world's forests accounts for about 77% of terrestrial ecosystem [1]. In concert with fears about CO₂ production and global warming, concerns over dwindling and limited petroleum resources have

given momentum to the production of renewable fuels, chemicals, and other materials from biomass [2]. In addition to providing carbon sequestration benefits for the world, biomass is also positioned to have a large impact on the domestic production of fuels and chemicals in the United States. According to the “Billion-Ton” Study [3] and its update [4] by the US Department of Energy (USDOE) and US Department of Agriculture (USDA), biomass has the potential to sustainably supply one third of the nation’s petroleum consumption. This large available supply makes biomass one of the most abundant, inexpensive, and currently underutilized products from the agricultural and biorefinery industries [5]. While the first generation of biofuels is being produced using sugarcane in places such as Brazil, the second generation of biofuels will likely be derived from the over 1 billion tons of lignocellulosic biomass that is produced annually in the United States or from the estimated 10 to 50 billion tons of waste lignocellulose that is produced worldwide [3, 6]. The beginning of the second-generation enzymatic conversion of lignocellulosic material to fermentable sugars for fuel ethanol is becoming more economically viable in the United States [7] with companies such as DuPont [8] and POET [9] making gains in the production of second-generation cellulosic ethanol using agricultural wastes such as corn stover. In fact, to meet the US congressional mandate to manufacture 36 billion gallons of biofuels per year by 2022, several new types of biomass including energy crops, forest residues, and municipal wastes will have to be processed through modern conversion systems.

Besides just the production of fuel petroleum also produces a significant portion (basically all) of our plastics and other materials. The use of petroleum to produce chemical building blocks and materials has resulted in a global interest in using renewable bio-based polymers and composites derived from biomass to reduce our environmental impact [10, 11]. Additionally, from a broad energy standpoint, biomass has a significant advantage over renewable energy sources such as hydropower, wind, geothermal, and solar in that biomass is the only renewable energy source that can be turned directly into fuels and chemicals, as opposed to just generate electricity.

The output of these conversion systems, whether it is fuels or chemicals, is highly dependent on the quality of biomass input to the system. The quality of the biomass is dependent on inherent species variability, production conditions, and differing harvest, collection, and storage practices. Some of the most important parameters related to the biomass composition, in regard to the impact on biofuels production, are moisture content, ash content and speciation, carbohydrate distribution, and higher heating value. For example, moisture content impacts the storage, supply, and transportation of feedstock to biorefineries, and ash content often reduces oil yields in thermochemical conversion processes and, to a lesser extent, reduces the effectiveness of dilute alkali pretreatment in biochemical processes. Commercialization of biorefineries in the United States has resulted in an understanding of the importance of biomass quality (moisture, ash, and sugar content) and physical properties (particle size and shape), especially in regard to feed and handling issues. The overall objective of the present research is to understand the impact of the chemical and physical composition of various biomass feedstocks on the production of fuels and chemicals through a variety of conversion pathways. This work will focus on everything from the feeding and handling of biomass all the way through the effect of feedstock variability on the final oil product. Specific objectives

seek to understand chemical composition of woody and herbaceous crops, agricultural residues, and municipal solid wastes and suggest their suitability for different biofuel production conversion pathways. This research will also briefly touch on platform chemical production from biomass and consider methods for mitigating the problems associated with feedstock variability while converting biomass to fuels and chemicals.

2. Biomass compositional analysis

To effectively produce fuels and chemicals from biomass, it is critical to understand the composition of the feedstock material. The chemical composition of biomass, whether it is lignocellulosic or herbaceous, can be characterized by five primary components: cellulose, hemicellulose, lignin, extractives/volatiles, and ash. The most abundant biopolymer on earth, cellulose, is a polysaccharide of glucose monomers held together by $\beta(1\rightarrow4)$ linkages. These $\beta(1\rightarrow4)$ linkages are what make cellulose resistant to hydrolysis. The second major component of biomass, hemicellulose, is an amorphous heteropolymer comprised of several different carbohydrates including xylose, mannose, and glucose, among others. Due to its amorphous structure, hemicellulose is significantly more susceptible to hydrolysis than crystalline cellulose. Cellulose and hemicellulose, combined with the third major component of biomass, lignin, make up over 90% of lignocellulosic biomass and 80% of herbaceous biomass. Lignin is an intricate array of aromatic alcohols and is intertwined with the cellulose and hemicellulose fraction of the biomass structure. This interwoven nature of the lignin helps provide rigidity to lignocellulosic materials, such as trees.

The other minor components of biomass are extractives/volatiles and ash. While these components make up a smaller portion of the biomass composition, they can still have a major influence on what ends up being the optimal conversion process. The components comprising the extractives/volatiles include both water and ethanol solubles. Water-soluble compounds include nonstructural sugars and proteins, and ethanol-soluble components are typically represented by chlorophyll and waxes. Ash, which comprises the inorganic content in biomass, can be intrinsic to the biomass or added anthropogenically. Intrinsic ash includes material-like calcium and potassium ions, while anthropogenic ash is mostly silica (dirt) collected during harvest.

There is obviously significant compositional variation between different biomass types, but there is also a lot of variation within a single feedstock. This variation, while substantial across terrestrial feedstocks, varies even more widely when municipal solid wastes are included as renewable energy feedstocks. **Table 1** illustrates the large difference in composition across three broad categories of renewable feedstocks including lignocellulosic, herbaceous biomass, as well as municipal solid wastes. Algal biomass was not included in this study due to a lack of available data and the difficulty in obtaining consistent analysis methods across institutions [12].

As seen in **Table 1**, there exists a significant amount of variability in overall composition (i.e., cellulose, hemicellulose, and lignin) between different types of feedstocks. These

Feedstock composition	Woody	Herbaceous	Wastes
<i>Proximate</i>			
Volatiles (%)	84.0 (2.1) ¹⁹³	79.1 (5.8) ²⁸⁴	76.7 (5.5) ²¹
Ash (%)	1.3 (0.9) ¹⁹³	5.5 (3.2) ²⁸⁴	6.6 (6.7) ²¹
Fixed carbon (%)	14.7 (1.6) ¹⁹³	15.4 (4.0) ²⁸⁴	14.8 (5.0) ²¹
<i>Ultimate</i>			
Hydrogen (%)	6.0 (0.1) ¹⁹²	5.8 (0.3) ²⁷⁶	5.9 (0.4) ²¹
Carbon (%)	50.7 (4.71) ¹⁹²	47.4 (1.9) ²⁷⁶	46.0 (4.0) ²¹
Nitrogen (%)	0.32 (0.01) ¹⁹²	0.75 (0.49) ²⁷⁶	1.3 (1.6) ²¹
Oxygen (%)	41.9 (1.4) ¹³⁴	41.0 (2.4) ¹⁰⁷	38.3 (4.2) ⁷
Sulfur (%)	0.03 (0.01) ¹³⁵	0.10 (0.32) ¹⁰⁷	0.15 (0.16) ⁷
<i>Structural</i>			
Cellulose (%)	51.2 (8.7) ²⁴¹	32.1 (4.5) ²⁴²⁵	28.4 (13.2) ²⁷
Hemicellulose (%)	21.0 (8.7) ²⁴¹	18.6 (3.4) ²⁴²⁵	16.4 (5.5) ²⁷
Lignin (%)	26.1 (5.3) ²⁴¹	16.3 (3.3) ²⁴²⁵	12.5 (2.7) ¹⁵

Table 1. Feedstock compositions for woody, herbaceous, and waste materials; average (standard deviation)^{number of samples}.

differences are large enough that conversion reactors have to be operated under different conditions based on the type of material supplied to the conversion facility (such as lower pyrolysis temperatures for herbaceous feedstocks). Also, herbaceous feedstocks, in addition to having higher ash content, exhibit more variability in their composition of volatiles (and ash) than woody biomass.

While a high degree of variability is expected across broad categories such as lignocellulosic material and municipal solid waste (MSW), there also exists significant variability within individual feedstock categories. **Tables 2–4** highlight the differences within an individual feedstock category for lignocellulosic material, herbaceous material, and municipal solid waste, respectively.

While it is obvious that compositional differences can be stark between different biomass types, there is also a substantial compositional variability between different anatomical fractions of the same type of biomass. **Table 5** compiles information on the chemical composition of different plant fractions for woody biomass, corn, and wheat.

It can be seen that lignocellulosic biomass contains a large fraction of cellulose in the heartwood (shown by *whole tree*), while the *bark* contains a high percent lignin. In woody biomass, the extractives are fairly evenly distributed. Conversely, corn stover contains a majority of the extractives in the leaves and internodes (the links between different stalk segments). Taking advantage of processing a specific anatomical fraction could allow for greater control over product output by tailoring the composition of the reactor feed. Additionally, utilizing anatomical fractionation separation could increase the economic viability of a process by

Feedstock composition	Shrub willow	Hybrid poplar	Pine	Other softwoods	Other hardwoods
<i>Proximate</i>					
Volatiles (%)	84.7 (0.8) ⁷⁶	84.0 (1.3) ⁴¹	83.5 (2.5) ⁴⁶	81.3 (2.9) ¹⁸	85.1 (3.0) ¹¹
Ash (%)	1.5 (0.4) ⁷⁶	1.3 (0.5) ⁴¹	0.7 (0.6) ⁴⁶	2.1 (2.0) ¹⁸	1.8 (1.2) ¹¹
Fixed carbon (%)	13.8 (0.7) ⁷⁶	14.6 (0.1) ⁴¹	15.7 (1.9) ⁴⁶	16.5 (1.6) ¹⁸	13.1 (1.8) ¹¹
<i>Ultimate</i>					
Hydrogen (%)	6.0 (0.2) ⁷⁶	6.0 (0.1) ⁴¹	6.1 (0.1) ⁴⁵	6.1 (0.1) ¹⁸	6.1 (0.1) ¹¹
Carbon (%)	50.3 (0.9) ⁷⁶	50.0 (1.1) ⁴¹	51.5 (1.0) ⁴⁵	51.8 (0.9) ¹⁸	50.2 (0.5) ¹¹
Nitrogen (%)	0.36 (0.10) ⁷⁶	0.35 (0.17) ⁴¹	0.17 (0.12) ⁴⁵	0.27 (0.21) ¹⁸	0.55 (0.49) ¹¹
Oxygen (%)	42.6 (0.4) ⁴⁴	42.8 (1.2) ²⁸	41.4 (1.0) ³⁸	39.7 (1.8) ¹⁴	41.1 (1.6) ¹⁰
Sulfur (%)	0.04(0.01) ⁴⁴	0.03 (0.01) ²⁸	0.02 (0.01) ³⁹	0.03 (0.01) ¹⁴	0.05 (0.05) ¹⁰
<i>Structural</i>					
Cellulose (%)	–	43.8 (1.2) ⁴³	47.4 (2.2) ⁵⁵	42.1 (7.1) ²⁶	50.8 (6.9) ²⁴
Hemicellulose (%)	–	14.7 (0.1) ⁴³	21.9 (4.9) ⁵⁵	25.1 (5.2) ²⁶	29.7 (4.3) ²⁴
Lignin (%)	–	25.7 (0.3) ⁴³	28.6 (0.7) ⁵⁵	29.1 (1.7) ²⁶	19.5 (4.1) ²⁴

Table 2. Feedstock compositions for specific woody feedstocks; average (standard deviation)^{number of samples}.

Feedstock composition	Corn stover	Switchgrass	Sorghum	Energy cane (bagasse)	Mixed grasses	Miscanthus
<i>Proximate</i>						
Volatiles (%)	78.1 (5.0) ⁵⁰	82.4 (4.1) ⁴³	77.0 (3.7) ⁴⁴	82.2 (1.9) ⁴⁸	78.6 (2.8) ⁴⁷	82.5 (3.5) ³⁵
Ash (%)	6.3 (3.5) ⁵⁰	4.0 (2.0) ⁴³	7.2 (2.6) ⁴⁴	3.4 (1.6) ⁴⁸	6.6 (1.7) ⁴⁷	2.6 (1.3) ³⁵
Fixed carbon (%)	15.6 (4.4) ⁵⁰	13.6 (3.0) ⁴³	15.7 (2.3) ⁴⁴	14.4 (1.0) ⁴⁸	14.8 (2.4) ⁴⁷	14.8 (2.9) ³⁵
<i>Ultimate</i>						
Hydrogen (%)	5.7 (0.3) ⁴⁰	5.9 (0.2) ⁴³	5.7 (0.2) ⁴⁴	6.1 (0.1) ⁴⁸	5.8 (0.3) ⁴⁷	5.8 (0.1) ³⁵
Carbon (%)	47.1 (2.3) ⁴⁰	47.1 (1.1) ⁴³	46.4 (1.3) ⁴⁴	48.8 (0.9) ⁴⁸	47.6 (1.1) ⁴⁷	48.9 (1.5) ³⁵
Nitrogen (%)	0.63 (0.32) ⁴⁰	0.60 (0.26) ⁴³	1.04 (0.38) ⁴⁴	0.43 (0.20) ⁴⁸	1.38 (0.54) ⁴⁷	0.35 (0.17) ³⁵
Oxygen (%)	40.3 (2.2) ³⁹	42.4 (2.3) ⁴²	40.3 (0.6) ³	–	39.5 (0.7) ²	42.3 (1.1) ⁴
Sulfur (%)	0.14 (0.53) ³⁹	0.06 (0.03) ⁴²	0.11 (0.01) ³	–	0.12 (0.02) ²	0.04 (0.02) ⁴
<i>Structural</i>						20.1 (1.4) ²⁷⁴
Cellulose (%)	34.3 (2.5) ²⁵¹	34.2 (2.7) ³⁴⁸	28.6 (2.6) ⁴⁸⁸	32.1 (3.2) ⁴⁷⁹	28.9 (2.9) ⁴⁶⁵	38.9 (3.2) ²⁷⁴
Hemicellulose (%)	20.7 (2.0) ²⁵¹	21.9 (2.6) ³⁴⁸	15.4 (1.6) ⁴⁸⁸	19.5 (1.9) ⁴⁷⁹	16.7 (3.9) ⁴⁶⁵	20.1 (1.4) ²⁷⁴
Lignin (%)	15.2 (1.6) ²⁵¹	19.2 (1.4) ³⁴⁸	12.2 (1.9) ⁴⁸⁸	16.3 (1.8) ⁴⁷⁹	15.7 (1.7) ⁴⁶⁵	21.1 (1.6) ²⁷⁴

Table 3. Feedstock compositions for specific herbaceous feedstocks; average (standard deviation)^{number of samples}.

Feedstock composition	MSW	C&D waste	Woody residues
<i>Proximate</i>			
Volatiles (%)	76.5 (1.1) ¹¹	76.5 (3.7) ⁹	81.1 (2.4) ²
Ash (%)	11.8 (5.2) ¹¹	0.8 (0.4) ⁹	1.2 (0.3) ²
Fixed carbon (%)	11.2 (5.2) ¹¹	18.9 (2.1) ⁹	17.8 (2.0) ²
<i>Ultimate</i>			
Hydrogen (%)	5.6 (0.4) ¹¹	6.2 (0.2) ⁹	6.0 (0.0) ²
Carbon (%)	43.3 (3.3) ¹¹	48.3 (1.2) ⁹	52.5 (0.2) ²
Nitrogen (%)	1.52 (1.72) ¹¹	1.09 (1.47) ⁹	0.22 (0.06) ²
Oxygen (%)	36.3 (4.8) ⁴	42.4 (0.1) ²	40.1 (0.6) ²
Sulfur (%)	0.25 (0.14) ⁴	0.02 (0.01) ²	0.01 (0.01) ²
<i>Structural</i>			
Cellulose (%)	28.4 (13.2) ¹⁵	—	—
Hemicellulose (%)	16.4 (5.5) ¹⁵	—	—
Lignin (%)	12.5 (2.7) ¹⁵	—	—

Table 4. Feedstock compositions for specific waste feedstocks; average (standard deviation)^{number of samples}.

Structural component	Cellulose	Hemicellulose	Lignin	Extractives
Woody biomass (wt%–daf)^a				
Whole tree	51.2	23.4	25.4	3.0
Bark	22.0	47.0	31.0	3.3
Twigs	15.4	62.3	22.3	1.6
Leaves	26.5	47.2	26.3	3.7
Corn (wt%–db)^b				
Corn cobs	35.92	30.7	16.44	5.89
Corn leaves	34.33	22.77	13.99	10.54
Corn husk	37.73	31.18	10.52	5.80
Corn internodes	40.21	20.03	17.24	12.29
Wheat (wt%–db)^b				
Internode 1	34.34	21.30	16.36	16.24
Internode 2	39.04	21.07	18.58	10.98
Internodes 3/4/5	38.92	21.56	19.50	9.67

Source: ^aVassilev et al. [13]; ^bINL Library [14]; daf—dry ash-free, db—dry basis.

Table 5. Compositional variation with anatomical fraction for woody biomass, corn, and wheat.

extricating high value components. Profitable use of a coproduct is exemplified by the use of distiller's dried grains with solubles (DDGS) in ethanol production for high-protein animal feed [15, 16].

The majority of the data included in **Tables 1–5** can be found in Idaho National Laboratory's (INL) Bioenergy Feedstock Library. The woody materials in **Table 1** include a wide variety of softwoods, hardwoods, and other wood varieties making up around 23 different woody species. The herbaceous materials include those listed in **Table 3** along with sugarcane, sugarcane bagasse, and wheat. The waste materials from **Table 1** are all represented in **Table 4**. In **Table 4** municipal solid waste (MSW) includes fractions of paper, cardboard, and grass clippings. No food-based waste is currently accounted for by this data. The construction and demolition (C&D) waste included oriented strand board, particle board, and a variety of lumber conditions. Woody residues included forest thinning and logging residues.

All of the values reported for proximate and ultimate (reported on a dry basis) for **Tables 1–5** were collected at INL [17] and stored in the Bioenergy Feedstock Library [14]. The reported cellulose, hemicellulose, and lignin values were a combination of glucose (representing the cellulose fraction) and xylose, galactose, and arabinose (representing the hemicellulose) values measured using NREL's LAP determination of structural carbohydrates and lignin in biomass [18], glucose, and xylose values predicted using an NIR-based predictive models developed at NREL [19], and cellulose and hemicellulose values reported in literature are all reported on a dry basis. It should be noted that the value for volatiles in the previous tables is determined by heating samples to 950°C in an inert atmosphere. This value for volatile will therefore include all thermal decomposition products, in addition to molecules that could be removed without thermal decomposition.

Understanding the degree of biomass compositional variability is crucial to developing a robust conversion process. However, in addition to understanding compositional variability, it is useful to know where this variability originates. Kenney et al. have produced a thorough review discussing several sources of biomass variability [20]. Briefly, some of the major sources of biomass compositional variation derive from local agronomic conditions [21], drought [22], harvest season and year [23], and harvest method [24]. A further analysis of the sources of biomass variability and its impact on conversion processes has been compiled by Williams et al. [25].

3. Biomass conversion to renewable fuels and chemicals

As can be seen in **Tables 1–5**, biomass has a broad range of compositional variability, even within an individual feedstock. This variation has a substantial impact on biomass conversion to fuels and value-added chemicals that varies depending on the chosen conversion process. The following section investigates how feedstock quality impacts four common conversion processes: biochemical fermentation, direct combustion, pyrolysis, and hydrothermal liquefaction (HTL). General impacts of feedstock physical and chemical properties will be discussed before a more in-depth look at each conversion process.

The physical properties of biomass have a myriad of effects on its conversion to fuels and chemicals. Arguably, the two most important physical properties of biomass, regardless of conversion process, are particle size and moisture content. Practically all conversion methods require some degree of size reduction. Biochemical conversion processes can accept a greater range of particle sizes, and the final size needed tends to be dependent on the processing system utilized [26, 27]. On the thermochemical side, hydrothermal liquefaction is much more insensitive to particle size due to high heating rates in the liquid media [28], but a significant amount of size reduction is needed to pump biomass sludges in a continuous system [29]. Pyrolysis uses particles smaller than 0.5 mm because small particles decrease char yields and have higher heating rates [30]. Optimal combustion particle size is often larger and varies for different biomass types at approximately 6 mm for straw, 4 mm for *Miscanthus*, and 2–4 mm for wood [31]. While particle size is obviously important, others have argued that moisture content is likely the single most problematic property affecting feedstock supply and biorefining operations [20]. Moisture increases heating rates during steam pretreatment for biological conversion [32], reduces bio-oil quality and thermochemical conversion [33], and causes low thermal efficiency in combustion processes [34]. Aside from particle size and moisture content, other physical properties of interest include bulk density, elastic properties, and microstructure. Bulk density has a strong effect on transportation and handling costs (lower densities greatly increase transportation costs), and the elastic properties/microstructure can increase compressibility and interparticle interactions at constricted flow points such as hopper openings.

Biomass chemical properties also have a large influence on best conversion process and the quality of the final product. The three primary chemical components of interest in biomass conversion are ash content, volatiles, and lignin. High ash content generally has a negative effect on biomass conversion across the board by reducing the effectiveness of dilute acid pretreatment for biological processes [35] and increasing char yields and fouling in thermochemical processes such as HTL [36], pyrolysis [37], and combustion [38]. However, there exist several strategies for ash removal including leaching and air classification [39]. Volatiles are generally represented by light organic acids (such as acetic acid) and furans. The furan fraction of the volatiles can reduce fermentation efficiency in biological processes [40] and lower energy content and stability in bio-oils produced by thermochemical processes [41]. Lignin, on the other hand, can have a variety of effects on biomass conversion depending on the process chosen. Lignin generally has a negative effect on ethanol production by blocking enzyme access to cellulose [42] but can increase oil yields for pyrolysis [43] and heating values for combustion [34] during thermochemical conversion.

3.1. Biochemical conversion—fermentation

Ethanol production from biomass occurs via two primary steps: depolymerization of the cellulose and hemicellulose to fermentable sugars and fermentation of these sugars to ethanol. Biomass conversion to ethanol has been evaluated in many reviews [42–45] which vary focuses from pretreatment and enzymatic hydrolysis [42] to optimization of the cellulase enzyme for improving sugar conversion to ethanol [44] and evaluation of current and future economic aspects of fuel ethanol production [46]. This work will build upon these previous

reviews to explain how biomass compositional variability can influence fermentation processes for fuel production.

Mixed rangeland grasses are a prime example of a feedstock with high compositional variability. These grasses are an emerging alternative to traditional energy crops. Mixed rangeland grasses also preserve natural habitat and typically require less maintenance than traditional energy crops. However, the naturally high variability of these grasses can lead to reduced product yields in biochemical conversion processes. Adler et al. have shown that ethanol yield per unit area decreases as plant species diversity increases. Ethanol yields are maximized when there is increased targeted coverage of C_4 prairie grass energy crops, such as switchgrass, which sequester more carbon than typical C_3 conservation grassland varieties [47]. This preference for C_4 grasses illustrates how the production of ethanol using fermentation is typically much more dependent on biomass carbohydrate content. In fact, techno-economic analysis has indicated that adjusting total carbohydrate content by 1% of total dry matter can change the minimum ethanol selling price (MESP) by \$0.018/gal [46]. Given the compositional data above, fermentation is better matched to herbaceous crops than lignocellulosic material due to the higher carbohydrate content of grasses. Additionally, fermentation processes are typically more tolerant of the higher ash contents of herbaceous feedstocks [48]. However, it should be repeated that high alkali metal content from excess soil collected during harvest can increase acid neutralization during pretreatment and lower the xylan digestibility for corn stover, consequently lowering ethanol yields [35].

Despite compositional variability generally being a disadvantage in feedstock processing, there exists at least one aspect to variability that could be advantageous. Changes in structural carbohydrate content with anatomical fraction in corn stover significantly affect glucose yield. After hydrolysis, glucose concentration can be three times greater in the cobs, leaves, and husks than stalks [49]. Additionally, the corn cobs, leaves, and husks respond better than stalks to simultaneous saccharification and fermentation (SSF) despite having similar glucan levels [50]. Therefore, selective fermentation of specific anatomical fractions could increase process efficiency if a cost-effective separation process could be devised and there is a value-added coproduct that could be produced from the stalks. The advantage of separating biomass by anatomical fraction extends to other biomass types as well. For example, different fractions within wheat stover exhibit an almost 10% difference in glucan content, and some parts are much more susceptible to chemical saccharification [51].

3.2. Thermochemical conversion—general

While biomass as a feedstock exhibits a significant amount of compositional variability, illustrated in the tables above, the different options for thermochemical conversion are almost diverse. Thermochemical conversion operations utilize reactions using both solids (pyrolysis and combustion) and liquids (hydrothermal liquefaction). Products from thermochemical processes also span a wide range of states from solid (biochar), through liquid (bio-oil), all the way to gas (syngas). The wide variety of processing options and product outputs, along with short reaction times (on the order of seconds), allows thermochemical conversion operations to utilize a wide array of diverse process inputs.

3.3. Thermochemical conversion—combustion

The combustion of biomass, which is still common in developing countries, has been used for thousands of years to do everything from managing agricultural lands to producing heat and energy for industrial processes [52]. Currently, developed countries use nonrenewable fossil fuels such as oil, coal, and natural gas as a primary source of energy; however, these energy supplies could be depleted in the next 40–50 years [53]. In an effort to reduce the rate at which these nonrenewable resources are being depleted and reduce environmental impact, there is a shift toward the combustion of renewable biomass and other waste products (such as paper and plastics). Literature reviews focus on the combustion of biomass as an energy source both with [54–56] and without [30, 53, 57, 58] torrefaction as a pretreatment to improve combustion efficiencies and material grinding and storage properties. One of the major problems with combusting biomass in a traditional coal plant is slagging, a mineral buildup due to the higher ash content in biomass than in coal. This problem means that low-ash content biomass, such as woody feedstocks, is better to use than herbaceous materials (which have intrinsic ash contents about five times greater than woody materials) in combustion applications. While biomass combustion does present problems with slagging, it does have the benefit of reducing harmful greenhouse gas emissions as compared to coal [59], and the energy produced can be incorporated directly into the current energy grid without infrastructure changes.

3.4. Thermochemical conversion—pyrolysis

Pyrolysis is a thermochemical process that starts with a solid and can be tuned to produce either a solid (biochar) or a liquid (bio-oil). However, this chapter will focus on the production of bio-oil and the effects of biomass composition on the resulting oil yields and quality. Pyrolysis is performed at temperatures from 400 to 600°C [60] and often includes a catalyst with the aim of increasing the energy density of the product by removing oxygen (as water and volatiles) [61]. Pyrolysis of biomass to produce fuels has been thoroughly reviewed in the academic literature [33, 61–64].

The pyrolysis process is well suited for low-moisture-content material with low ash and high lignin content, meaning that pyrolysis processes favor lignocellulosic feedstocks. For example, lignin content increases the average molecular weight of resulting pyrolysis oil by 100 Da as lignin content rises from 5 to 15% [43]. The high ash content of herbaceous feedstock can decrease oil yields by 1–5% for every 1% increase in ash over an ash range of 1.5–7.5% [43]. In addition to decreasing oil yields, the alkali metals common in herbaceous crops can also have damaging effects on reactors and reduce catalyst lifetimes [65]. However, more recent studies have taken into account not only the production of pyrolysis oil but also the upgrading of that oil to the final fuel for a range of feedstocks including pines, poplars, switchgrass, and corn stover. In these integrated fast pyrolysis/hydrotreating studies, the effects of ash content on oil and upgraded fuel yields were relatively insignificant over a narrow ash range of 0.7–1.6% [66] (an ash range common for woody materials but low for grasses).

3.5. Thermochemical conversion—hydrothermal liquefaction (HTL)

Hydrothermal liquefaction (HTL) is a unique thermal conversion process that utilizes biomass and water slurries. This makes HTL particularly well suited to turning high water content material, such as algae, municipal solid wastes, or grasses into bio-based oils. Additionally, HTL bio-oils tend to be higher quality than pyrolysis oils because they have less oxygen. However, the oil yields for HTL are lower than pyrolysis and the oxygen content is still higher than crude oil [67]. Performing the dissolution of biomass in a water media also saves energy on drying the feedstock, and the high heat transfer rates in a liquid media reduce particle size reduction requirements [36]. HTL can operate over a wide range of temperatures (200–600°C) to create products that range from solid biochars to gases. Reaction temperatures from 200 to 275°C are suitable for solid production [68], while temperatures from 275 to 350°C produce liquid products, and temperatures above 400°C are suitable for gas production [36]. Due to the liquid nature of the reaction media and the high temperatures, these reactors often operate at high pressures (5–40 MPa) to keep the reaction media as a liquid or supercritical fluid. Since the operating conditions and products of hydrothermal reactors are so diverse, the reviews of this material span a wide range. Some reviews cover both sub- and supercritical temperature regimes, with an array of model compounds and biomass feedstocks, and product arrays including liquid bio-oils and gases [67]. Other reviews focus on narrower operating regimes and liquid products from a variety of feedstocks with both high and low ash content [28, 36] or simply the processing of lignin (which is usually considered a waste product) [69]. While the hydrothermal processing of biomass offers advantages in being more feedstock agnostic, it has drawbacks in high capital equipment cost due to the extreme operating conditions, high energy input to heat the water, and lower yields (even though the oil quality is generally high).

3.6. Chemical production

Aside from the production of biochar and bio-oil, hot liquid water can also be used to convert biomass into value-added chemicals. Luterbacher et al. have achieved a 65% yield of sugars from woody biomass and a 55% yield from switchgrass using a biphasic CO₂/H₂O system. This biphasic system improves process separations and can use larger particles (~1 cm) at a high solids loading (40 wt%) [70]. The targeted production of sugars from biomass, instead of a bio-oil destined for fuel blending, could facilitate the production of high-value chemicals and materials. For instance, biomass-derived sugars can be used to make renewable plastics by producing *p*-xylene [71–73]. The conversion of biomass-derived cellulose to *p*-xylene could take place using a scheme such as the one in **Figure 1**. In this scheme cellulose is converted to *p*-xylene in a four-step process: step one uses a biphasic CO₂/H₂O system to convert biomass into sugars [70], step two isomerizes glucose to fructose [74], step three converts fructose to 2,5-dimethylfuran (DMF) [75], and step four converts DMF to *p*-xylene [71]. The final step of converting *p*-xylene to polyethylene terephthalate (PET) would take place in a typical refinery because this renewable *p*-xylene would act as a standard drop in feedstock.

The production of chemicals from biomass has the potential to produce a wide array of drop in building blocks. The top twelve most promising drop in chemical building blocks can be

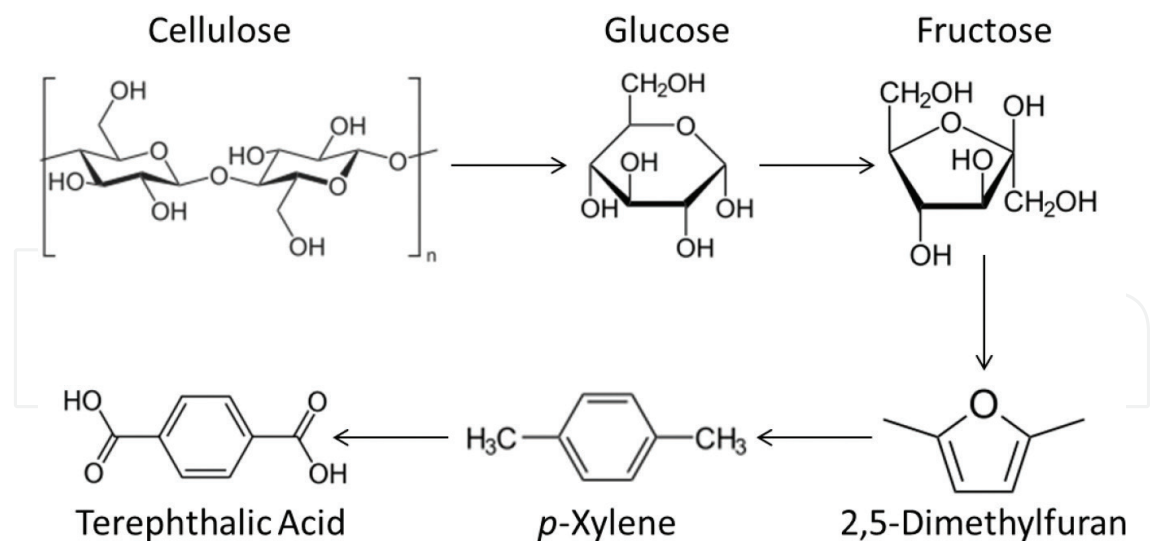


Figure 1. A representative pathway for conversion of cellulose to terephthalic acid through the transformation of cellulose-derived sugars to furans.

found in the Department of Energy's report on Top Value-Added Chemicals from Biomass [76]. This report lists several chemicals that could be made from biomass with an emphasis on the conversion of sugars to building block chemicals and the conversion of these building block chemicals to intermediates. After examining both biochemical and thermochemical pathways, it was noted that biochemical pathways focused on the conversion of sugars to building block chemicals, and thermochemical pathways dominated the conversion of building block chemicals to final products.

4. Pretreatments to improve biomass feedstock chemical composition and suggestions for optimal biomass conversion pathways

Raw herbaceous biomass has a chemical composition which is low in carbon content and high in oxygen, volatiles, and ash; is high in moisture; and has low energy content. This combination of properties does not make herbaceous crops suitable for thermochemical applications such as gasification, pyrolysis, and co-firing [77]. The shortcoming of many types of raw biomass, in terms of chemical and physical properties, can be overcome by pretreatment to produce a conversion-ready feedstock. Currently, there exist a variety of pretreatment methods including pelletization, air classification, dry torrefaction, hydrothermal carbonization, steam explosion, ionic liquid dissolution, acid and alkali leaching, and ammonia fiber expansion (AFEX). These pretreatment techniques are being looked at to improve biomass quality to produce a conversion-ready feedstock for both thermochemical and biochemical applications [25, 78]. Pretreatment can reduce biomass chemical and physical heterogeneity and lessen problems in (a) conversion applications (removing using air classification to remove ash prior to co-firing biomass could reduce slagging), (b) supply chain logistics (pelletizing biomass reduces transportation costs), (c) operational constraints (certain forms of pretreatment allow for utilization of coal infrastructure for feeding, milling, etc. of biomass, without

costly modifications or installation of separate processing lines), and (d) technical constraints (e.g., reduction of corrosion due to biomass washing).

Pretreatment for the optimization of chemical production from biomass is very much in its infancy. However, it is a safe bet that pretreatment will be required to get a consistent product, given that specialty chemicals require a much higher purity than the fuels currently being produced. Current research is ongoing for the production of many different value-added chemicals such as *p*-xylene [71], dimethylfuran [75], and levulinic acid [79] to name just a few, but at this point, all of these studies start with pure feedstocks, such as cellulose, and not biomass. To move the industry, past fuels to value-added chemicals will require a greater understanding of how biomass composition effects its conversion to fuels and chemicals.

As the previous pages have illustrated, the transformation of biomass to fuels and chemicals can take place over a wide variety of pathways with numerous influences from the biomass composition. These conversion pathways can be generally grouped as either biochemical or thermochemical. A greatly simplified process diagram for the production of renewable liquid fuels and chemicals from biomass can be seen in **Figure 2**. This figure groups feedstocks with their most likely conversion pathway based on the previous discussion regarding biomass composition.

Given the current variability in biomass resources, it is apparent that conversion technology will have to be tailored to regional renewable supply, be it lignocellulosic, herbaceous, a municipal solid waste stream, or algae. Given the high ash content of herbaceous biomass and the high water content of some municipal solid wastes, it is likely that these streams will be destined for use in biochemical pathways to produce sugars through enzymatic hydrolysis or methane using anaerobic digestion. However, there is also a chance that these materials could be passed through the thermochemical process of hydrothermal liquefaction to produce oils or undergo a more mild hydrothermal treatment to produce a platform chemical stream based on biomass-derived sugars. The abundant lignocellulosic biomass will likely be converted to bio-oil or energy using a thermochemical process such as pyrolysis or combustion, respectively. Thermochemical processes make use of lignocellulosic feedstocks in part due to their low ash content and because a high lignin content is unsuitable for enzymatic digestion in biochemical fermentation.

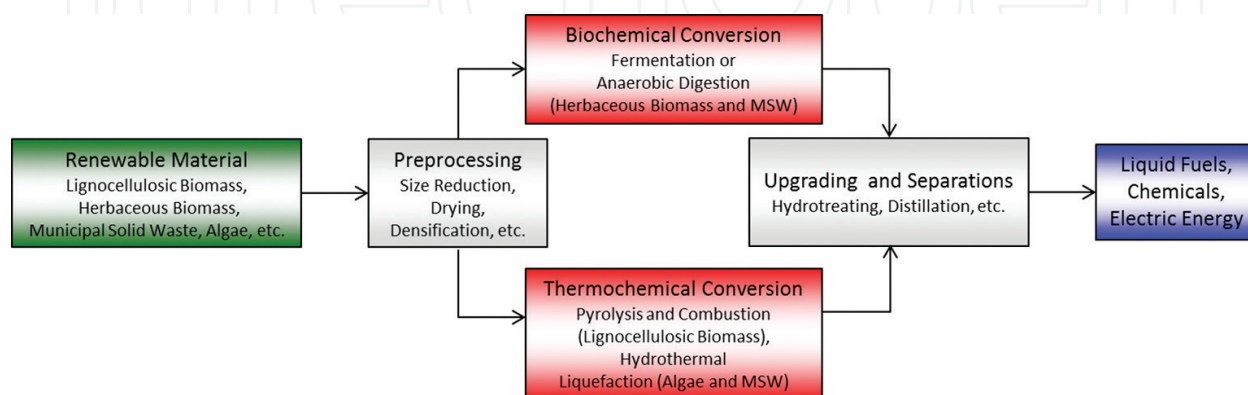


Figure 2. Broad scheme for conversion of renewable material to fuels, chemicals, and energy.

5. Conclusions

The large degree of variability between biomass resources, both currently available and emerging, is a significant barrier to the utilization of biomass as a feedstock for fuel and chemical production. The impacts of physical characteristics such as moisture content and particle size, as well as chemical characteristics such as ash content, extractives/volatiles, and lignin, all play varying, and intricate, roles during biomass conversion. Adding to the complexity of this system is the fact that, in addition to a myriad of compositionally diverse feedstocks, there also exist numerous conversion pathways to the final fuel or chemical products. To alleviate this problem, it will be necessary to develop techniques to reduce biomass variability and develop a consistent, conversion-ready feedstock for biorenewable fuel and chemical production.

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