



Relationships between biomass composition and liquid products formed via pyrolysis

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Thermal conversion of biomass is a rapid, low-cost way to produce a dense liquid product, known as bio-oil, that can be refined to transportation fuels. However, utilization of bio-oil is challenging due to its chemical complexity, acidity, and instability – all results of the intricate nature of biomass. A clear understanding of how biomass properties impact yield and composition of thermal products will provide guidance to optimize both biomass and conditions for thermal conversion. To aid elucidation of these associations, we first describe biomass polymers, including phenolics, polysaccharides, acetyl groups, and inorganic ions, and the chemical interactions among them. We then discuss evidence for three roles (i.e., models) for biomass components in the formation of liquid pyrolysis products: (1) as direct sources, (2) as catalysts, and (3) as indirect factors whereby chemical interactions among components and/or cell wall structural features impact thermal conversion products. We highlight associations that might be utilized to optimize biomass content prior to pyrolysis, though a more detailed characterization is required to understand indirect effects. In combination with high-throughput biomass characterization techniques, this knowledge will enable identification of biomass particularly suited for biofuel production and can also guide genetic engineering of bioenergy crops to improve biomass features.

Keywords: thermochemical conversion, plant biomass, bio-oil, lignin, polysaccharides, cell wall, fast pyrolysis, minerals

Biomass can be a renewable and sustainable source of transportation fuels not associated with fossil CO₂ release. Numerous studies highlight the advantages of displacing petroleum fuels with industrial production of liquid fuels from thermochemical conversion of biomass (Bridgwater et al., 1999; Perlack et al., 2005; Mohan et al., 2006; NSF, 2008). Thermochemical conversion entails heating of biomass in an anoxic environment; condensation of organic liquid products, known as bio-oil; and subsequent treatment of the products with catalysts to create liquid fuels, i.e., refined bio-oil, similar to petroleum-derived gasoline or diesel. This is in contrast to biochemical conversion, which utilizes enzymes to release sugars followed by microbial production of ethanol or other fuel molecules (Somerville, 2007; Youngs and Somerville, 2012). Relative to biochemical approaches, thermal conversion has the potential to make use of all carbon (C)-containing biomass components, would allow society to retain existing infrastructure associated with liquid hydrocarbon fuels, and, due to the rapidity of the process, may reduce production costs by permitting scalability and distribution of production (Huber et al., 2006; Mettler et al., 2012). For both

thermochemical and biochemical biofuels, lowering processing costs and improving fuel yields per hectare are major engineering challenges that hinder economic viability. Thermochemical fuel production also faces challenges related to maintaining a high C-yield while obtaining a fungible fuel. We posit that this latter challenge might be addressed by understanding the relationships between biomass composition and bio-oil components and using this information to alter biomass through genetic, chemical, or thermal means.

THERMAL CONVERSION CHALLENGES

Two types of pyrolysis have been developed: fast pyrolysis and slow pyrolysis. Slow pyrolysis is usually performed over several hours and has a high solid yield, and as such has little relevance for liquid fuels production. Fast pyrolysis, however, is typically performed quickly, in seconds, at temperatures between 400 and 600°C and decomposes most of the solid biomass into a volatile mixture of various organic molecules, water, and CO/CO₂. Pyrolysis oil or bio-oil constitutes the condensable portion of this vapor. Non-condensable components (primarily CO₂ and CO) and a mineral-rich solid (char) are other product classes that will not be addressed here, except in that they detract from the overall C-yield of raw and refined bio-oil. Bio-oil comprises water (15–30%) plus compounds from several chemical families including the following (Table 1): organic acids, light (C1–C3) oxygenates, furan and furan derivatives, phenolic species with various methyl and methoxy substituents, pyrones, and sugar derivatives like levoglucosan (Faix et al., 1991a,b). Bio-oil's chemically complex nature prohibits its direct use in combustion applications or petroleum refining. The reasons for this include low heating value; ignition difficulty; high chemical reactivity, which results in oligomerization and polymerization over time and upon heating, prohibiting distillative separation (Oasmaa and Czernik, 1999; Demirbas, 2011; Patwardhan et al., 2011a); immiscibility with petroleum; and high corrosivity (Oasmaa and Czernik, 1999). Many of these features are associated with the

high oxygen content of biomass and the resulting bio-oil, relative to fossil fuels.

In order to obtain desirable fuel properties and allow integration with the existing transportation fuels infrastructure (gasoline and diesel engines), the bio-oil must be chemically converted to reduce the undesirable characteristics mentioned above. Catalytic upgrading is typically used to refine bio-oil, improving its stability and making it an acceptable liquid fuel. The simplest method is hydrotreating or hydrodeoxygenation, which removes oxygen via catalytic hydrogenation (Furimsky, 2000), decreasing both the chemical reactivity and corrosivity. However, this process converts any C1–C5 oxygenates, representing as much as half of the carbon in bio-oil, to C1–C5 hydrocarbons that are too volatile for liquid fuels (Resasco, 2011). Another straightforward approach is to “crack” the pyrolysis vapors using acidic zeolite catalysts into light olefins and aromatic hydrocarbons (primarily benzene, toluene, and *o/m/p*-xylene) (Bridgwater, 1994; Carlson et al., 2008, 2009). This approach is appealing because of the lack of an external H₂ requirement and the simplicity of the product streams. Furthermore, since zeolite cracking is widely used in traditional petroleum refining/valorization (Wan et al., 2015), other advantages are the product compatibility with existing refinery infrastructure and the maturity of the process (Wan et al., 2015). However, zeolite cracking is crippled by poor usable carbon yield due to the high amounts of coke, CO, and CO₂ formed during the catalytic process (Carlson et al., 2008) and the concomitant rapid catalyst deactivation. Additionally, further catalytic oligomerization and reforming for olefins and aromatics, respectively, are needed to make these products suitable for addition to refinery fuel product streams, increasing the process costs and further reducing overall carbon yield.

More advanced strategies propose to use reactions such as ketonization, condensation, alkylation, and others to retain a higher fraction of the biomass carbon into liquid fuel-range molecules (Zhu et al., 2011; Zapata et al., 2012; Pham et al., 2013; Gonzalez-Borja and Resasco, 2015). However, catalytic upgrading of any one family of compounds (e.g., light oxygenates) typically requires a catalyst and reaction conditions different than those required for another family of compounds (e.g., substituted phenolics). Moreover, catalysts used for upgrading one family of compounds may be ill-suited for other families, either facilitating undesirable reactions (breaking C–C bonds unnecessarily or increasing H:C ratios above the 2:1 optimum) or undergoing rapid deactivation due to reactions with other non-targeted bio-oil oxygenates. These upgrading challenges suggest the desirability of thermal conversion producing more selective product streams, i.e., each stream comprising fewer families of chemical compounds. Developing such thermal conversion processes would be aided by clearer knowledge of the relationship between biomass composition and thermal conversion products.

BIOMASS COMPOSITION AND CHEMICAL STRUCTURES

Recent reviews have addressed the general relationships between biomass composition and thermal products, such as

TABLE 1 | The percentage ranges and categories of major bio-oil components.

Category	Major components	Wet weight (%)
Light oxygenates	Glycolaldehyde, acetol	3–26
Organic acids	Acetic acid, formic acid, propanoic acid	2–27
Aldehydes	Acetaldehyde, formaldehyde, ethanedial	3–18
Sugars	1,6-Anhydroglucose (levoglucosan)	5–14
Phenols	Phenol, catechol (di-OH benzene), methyl phenol, dimethyl phenol	3–13
Guaiacols	Isoeugenol, eugenol, 4-methylguaiacol	3–15
Furans	Furfural, hydroxymethyl furfural, furfural	2–11
Syringols	2,6-Dimethoxy phenol, syringaldehyde, propyl syringol	2–9
Ketones	Acetone	4–6
Alcohols	Methanol, ethylene glycol, ethanol	2–6
Esters	Methyl formate, butyrolactone, methylfuranone	<1–3

Source: Huber et al. (2006).

increasing the content of phenolics relative to carbohydrates to reduce the oxygen content of bio-oil (Tanger et al., 2013). Here, we provide a more detailed description of the chemical structure and interactions among major cell wall components to aid in understanding more subtle relationships between biomass and bio-oil content. Biomass consists of cell walls that establish the structure of the plant and, to a lesser extent, non-structural components (Table 2). Cell walls determine the shape of leaves and stems and the cells that compose them and consist of cellulose, hemicellulose, lignin, as well as structural proteins and wall-associated mineral components (O'Neill and York, 2009; Vogel et al., 2011; Tanger et al., 2013). Non-structural components include sugars, proteins, and additional minerals (O'Neill and York, 2009; Vogel et al., 2011; Tanger et al., 2013). For example, in switchgrass, an important potential bioenergy crop, dry biomass consists of ~70% cell walls, 9% intrinsic water, 8% minerals, 6% proteins, and 5% non-structural sugars (Vogel et al., 2011). The relative fractions of different components, chemical linkages within and between polymers, and cellular patterning vary among plant species, organs, developmental stages, and growth conditions (Adler et al., 2006; El-Nashaar et al., 2009; Singh et al., 2012; Zhao et al., 2012). Here, we review the components of secondary cell walls, which are formed as plant growth ceases, as they constitute the majority of plant biomass (Pauly and Keegstra, 2008), and then discuss evidence for interactions among components. Table 2 lists the different major and minor components of biomass and the broad ranges of their representation within biomass for biofuel conversion.

TABLE 2 | The variation of biomass components among vascular plants including grasses, softwoods, and hardwoods.

Biomass component	Dry weight (%) ^a
Cellulose	15–49 ^b
Hemicellulose	12–50 ^{b,c,d}
Xylan	5–50 ^e
Mixed-linkage glucan	0–5 ^{c,e}
Xyloglucan	Minor ^c
Mannan (and galactoglucomannan)	0–30 ^{c,f}
Soluble (mainly sucrose)	9–67 ^{b,g}
Pectin	<0.1 ^h
Lignin	6–28 ^b
Ferulic acid and <i>p</i> -coumaric acid	<1.5 ^h
Protein	4–5 ^b
Ash (mainly silicate)	0.4–14.4 ^b
Intrinsic moisture	11–34 ⁱ

^aPercent mass composition of secondary cell walls.

^bPauly and Keegstra (2008).

^cScheller and Ulvskov (2010).

^dAs the highest percentage of xylan in Scheller and Ulvskov (2010) is higher than the highest percentage of hemicellulose in Pauly and Keegstra (2008), the highest percentage of hemicellulose is set to the highest percentage of xylan.

^eMLG is only abundant in grasses. The maximum percentage of MLG we are aware of is that of the mature rice stem after flowering (Vega-Sanchez et al., 2012).

^fGalactoglucomannan is only abundant in gymnosperm woods. Dicots and grasses possess <8% of mannan and galactoglucomannan (Scheller and Ulvskov, 2010).

^gThe high abundance of solubles is only for sorghum biomass. Other plants usually have less than 15% soluble content (Pauly and Keegstra, 2008).

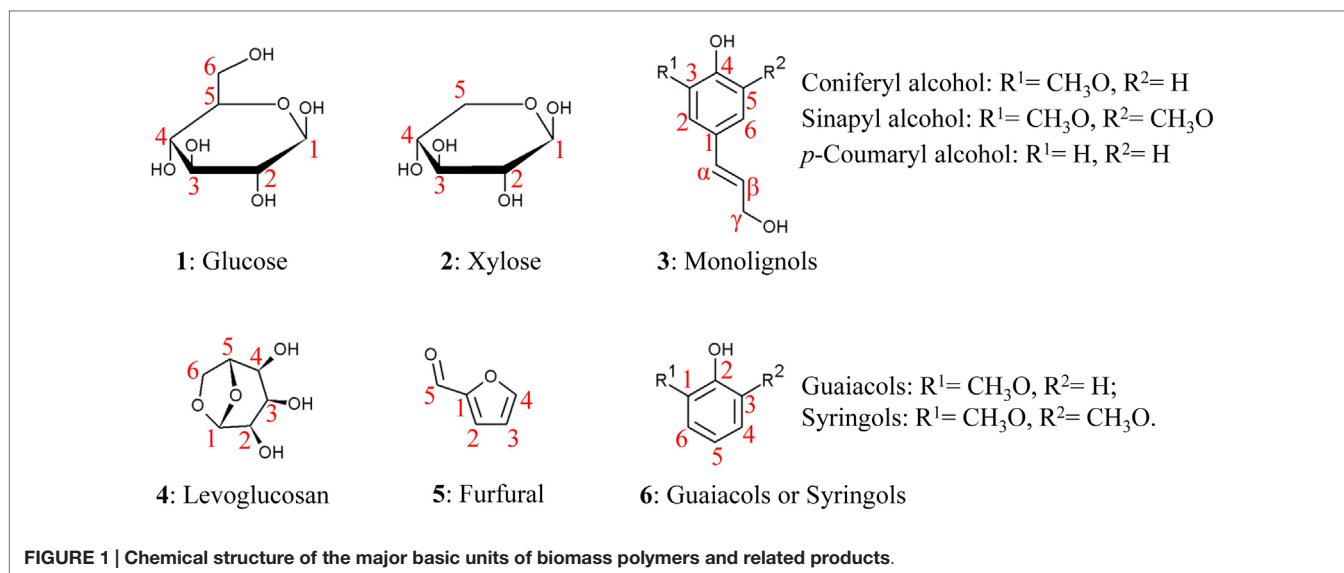
^hVogel (2008).

ⁱMcKendry (2002).

Figure 1(1–3) shows the chemical structures and atom numbering of the most abundant cell wall monomeric species.

Cellulose and hemicellulose represent 15–49% and 12–50% of biomass by dry weight, respectively (Pauly and Keegstra, 2008; Vogel, 2008; Zhao et al., 2012). Cellulose is an unbranched homopolymer of >500 β-(1,4)-linked glucose units. In plant cell walls, cellulose is primarily in the form of crystalline microfibrils consisting of approximately 36 hydrogen-bonded cellulose chains, but also has amorphous regions (Somerville, 2006; Newman et al., 2013).

Hemicelluloses are typically branched polysaccharides substituted with various sugars and acyl groups. As discussed further in the Section “Evidence Relating Biomass Content and Bio-oil Composition,” the different sugar composition and linkages of hemicelluloses influence thermal products (Shafizadeh et al., 1972; Mante et al., 2014). The structure and composition of hemicellulosic polysaccharides differ depending on plant species classification, i.e., taxonomy. Major taxonomic divisions with relevance to bioenergy production are grasses, such as switchgrass and wheat; woody dicots, i.e., hardwoods, such as poplar; and woody gymnosperms, i.e., softwoods, such as pine. The most abundant grass hemicelluloses are mixed-linkage glucan (MLG) and glucuronoarabinoxylan (GAX) (Scheller and Ulvskov, 2010; Vega-Sanchez et al., 2013); the hemicelluloses of hardwood are primarily composed of glucuronoxylans (GX) but also contain a small amount of galactomannans (GM) (Pauly and Keegstra, 2008); and softwood hemicelluloses are largely galactoglucomannan (GGM) and GAXs (Scheller and Ulvskov, 2010). MLG is an unbranched glucose polymer similar to cellulose but containing both β-(1-3)- and β-(1-4)-linkages (Vega-Sanchez et al., 2012). MLG is nearly unique to the order Poales, which includes the grasses, but has also been found in horsetail (*Equisetum*). Its abundance in mature tissues and secondary cell walls has recently been recognized (Vega-Sanchez et al., 2013). Xylans consist of a β-(1-4)-linked xylose backbone with various substitutions. GXs are xylans substituted mostly by glucuronic acid and 4-*O*-methyl glucuronic acid through α-(1-2)-linkages. GAXs are not only substituted by glucuronic acid but also substituted by arabinofuranoses at the O-3, which can be further substituted by the phenylpropanoid acids, to form feruloyl- and *p*-coumaroyl esters linked at the O-5 (Scheller and Ulvskov, 2010). Acetyl groups are often attached to the O-3 of backbone xyloses but also attach to the O-2. Unlike xylans, which mainly consist of pentoses, mannans consist of hexoses like mannose, glucose, and galactose. GM and GGM have a β-(1-4)-linked backbone with mannose or a combination of glucose and mannose, respectively. Both GM and GGM can be acetylated and substituted by α-(1-6)-linked galactoses (Scheller and Ulvskov, 2010; Rodriguez-Gacio Mdel et al., 2012; Pauly et al., 2013). Relatively depleted in secondary walls, but rich in growing primary walls of dicot species, xyloglucan and pectins are two other polysaccharides in cell walls. Xyloglucan consists of β-(1-4)-linked glucose residues, modified by xylose and other sugar residues; and pectin is another branched or unbranched polymer that is rich in galacturonic acid, rhamnose, galactose, and several other monosaccharide residues (Somerville et al., 2004; Scheller and Ulvskov, 2010).



Lignin is a cross-linked, heteropolyphenol mainly assembled from three monolignols – sinapyl (S), coniferyl (G), and *p*-coumaryl (H) alcohols. As waste products are often selected as biofuel feedstocks, it is also relevant to note that lignin derived from other monolignols such as caffeyl alcohol and 5-hydroxyconiferyl have been found in the seedcoat of both monocots and dicots (Chen et al., 2012, 2013). Lignin structural heterogeneity and various types of incorporated groups can lead to a variety of different depolymerization reactions during pyrolysis (Kawamoto et al., 2007). Often traceable to the corresponding bio-oil components, the three major lignin units differ in the degree of methoxylation of their carbon ring. S-units are methoxylated at both O-3 and O-5 ring positions; G-unit have one methoxy group at the O-3 position; and H-units lack ring methoxy groups (**3, Figure 1**) (Boerjan et al., 2003). Lignin units undergo oxidative coupling in the cell wall to form many types of dimers, including β -O-4, β -5, β - β , 5-5, 5-O-4, and β -1, leaving other atoms free to further polymerize, which significantly increases the structural heterogeneity of lignin. Lignin units can also be esterified with *p*-coumaryl, *p*-hydroxybenzoyl, and acetyl groups, primarily at the γ position of terminal units (Petrik et al., 2014; Lu et al., 2015). Lignin compositions and the acylation groups vary among plant clades (Boerjan et al., 2003). Woody dicot lignins have G- and S-units and trace amount of H-units. Poplar wood, for example, has a G:S:H ratio of 55:45:1 (Vanholme et al., 2013). The lignin of many hardwoods is acylated by *p*-hydroxybenzoates (Lu et al., 2015) and acetyl groups in low amounts (Sarkanen et al., 1967). Biomass from other species, such as palms and kenaf, possess a high degree of lignin acetylation (Lu and Ralph, 2002). Grass lignins also contain G- and S-units with slightly higher amount of H-units than woody dicots. Wheat straw, for example, has a G:S:H ratio of 64:30:6 (Bule et al., 2013). Grass lignin possesses high levels of *p*-coumarate esters (Hatfield et al., 2008) and can also be etherified by triclin and ferulic acid (Ralph et al., 1995; Lan et al., 2015), as discussed further below. Woody gymnosperm

lignins are different from angiosperm lignins, being primarily composed of G-units and a lower amount of H-units (Boerjan et al., 2003).

Biomass also contains inorganic elements including Ca, K, Si, Mg, Al, S, Fe, P, Cl, and Na and some trace elements (<0.1%) such as Mn and Ti, according to ash analysis, formed by oxidation of biomass at 575°C (Masia et al., 2007; Vassilev et al., 2010). As with other biomass components, the abundance of mineral elements varies among species. In general, compared with grass biomass, woody biomasses contain less ash, Cl, K, N, S, and Si, but more Ca (Vassilev et al., 2010).

Plant biomass components do not accumulate independently of each other, though their relationships are still an active area of research (Dick-Perez et al., 2011; Tan et al., 2013; Mikkelsen et al., 2015). Biomass component amounts can correlate because they are physically bound to each other through covalent and non-covalent bonds or because they accumulate in the same plant organ or stage of plant development, though a physical interaction may not exist. Because the abundance of some biomass components is correlated, the thermal products from one biomass component may also correlate with other components. For example, the abundance of cellulose correlates with the abundance of lignin in five different biomass sources (Pearson's correlation coefficient = 0.83) and lignin-derived thermal products correlate with cellulosic glucose (Mante et al., 2014). Many mineral elements are also correlated with each other, for example, N, S, and Cl; Si, Al, Fe, Na, and Ti; Ca, Mg, and Mn; K, P, S, and Cl (Vassilev et al., 2010). Numerous interactions between lignins and hemicelluloses and among hemicelluloses have been observed. Among the best-studied examples, GAXs of grasses and other recently evolved monocot species covalently link to lignin through ether bonds with ferulate esters on arabinose moieties of arabinoxylan (Bunzel et al., 2004). In poplar and spruce wood, NMR results indicate that lignin and carbohydrates are directly bonded through several types of ether linkages (Yuan et al., 2011; Du et al., 2014). The data provide evidence for ether

bonds between lignin and C1, C5, and C6 atoms of pentoses and hexoses (Yuan et al., 2011). Generally, xylan is the most closely associated polysaccharide to lignin, and NMR studies have also clearly identified lignin–glucuronic acid ester bonds (Yuan et al., 2011). Also, MLGs closely coat low-substituted xylan regions, likely via non-covalent interactions (Carpita et al., 2001; Kozlova et al., 2014). Furthermore, some components can also affect the distribution of other components. For example, rice plants that overexpress an enzyme that cleaves MLG exhibit reduced MLG and have an altered distribution profile of Si though maintain the same total amount of Si (Kido et al., 2015). In sum, mounting evidence supports covalent and non-covalent interactions among cell wall polymers and components; however, these connections have been difficult to study with questions persisting related to how different cell wall preparations and manipulation may alter observations.

MODELS FOR RELATIONSHIPS BETWEEN BIOMASS COMPONENTS AND BIO-OIL PRODUCT COMPOSITION

Reaction pathways of individual biomass components to formation of thermal products have been described (Collard and Blin, 2014). However, the pyrolysis literature suggests that biomass components tend to have more complex effects on bio-oil yield and product composition than simply their quantity. Here, we introduce three possible “models” of how biomass components may influence the yield or composition of thermal products, and in Section “Evidence Relating Biomass Content and Bio-oil Composition,” we discuss evidence supporting each of them. **Figure 2** provides schematic representations of the following models:

Model 1: Biomass components are the direct sources of thermal products. Components are converted to products through depolymerization and secondary reactions such as cracking, i.e., splitting, and recombination (**Figure 2A**).

Model 2: Components or their derived products act as catalysts that accelerate thermal reactions of other components, altering product yields and ratios (**Figure 2B**).

Model 3: Chemical interactions or structural relationships among cell wall components alter bio-oil composition and/or yield (**Figure 2C**). This “indirect” model applies when variation in a biomass component alters the yield of a chemically unrelated product in a manner not easily explained by a catalytic effect. Chemical interactions that alter products may either be covalent or non-covalent chemical bonds between cell wall components. Structural relationships refer to correlations between components, often minor ones, and physical features of the biomass. For example, the abundance of a cell wall component may be indicative of the structure of the plant material, such as biomass bulk density differences caused by different leaf to stem ratios, but do not reflect chemical bonding between components. As of the preparation of this review, very little evidence addresses how biological correlations effect bio-oil products, so the discussion focuses on potential chemical interactions.

EVIDENCE RELATING BIOMASS CONTENT AND BIO-OIL COMPOSITION

Evidence in the literature for the three models described above is presented in **Table 3** and discussed below. In the reviewed experiments, relationships between biomass components and pyrolysis products have been identified by varying the starting biomass, either through experimentation on purified components, via naturally occurring variation among different biomass sources, or via pretreatment of the biomass. Most studies included in this discussion report the chemical products derived from pyrolysis of biomass or biomass components. Studies that only reported weight losses or elemental balances were not considered. The two dominant techniques present in this corpus of literature are either pyrolysis-gas chromatography/mass spectroscopy, where pyrolysis vapors from microgram- to milligram-scale samples are directly transported to a GC for analysis, or pyrolysis in a gram- to kilogram-scale reactor system followed by condensation of the vapors and subsequent chromatographic analysis of the liquid.

Model 1: Direct Products of Cellulose, Hemicellulose, and Lignin

Thermal breakdown of purified cellulose, hemicellulose, and lignin has been relatively well studied. Levoglucosan, a six-carbon 1,6-anhyrosugar (see **Figure 1**), was identified as the main product of cellulose pyrolysis nearly a century ago (Pictet and Sarasin, 1918). Levoglucosan is formed alongside other smaller decomposition products, with maximum levoglucosan production occurring at 500°C (Shafizadeh et al., 1979). Minor products of cellulose pyrolysis are dominated by other anhydrosugars that retain all six carbons of glucose, such as 1,6-anhydroglucofuranose and 5-hydroxymethyl furfural, but also smaller molecules, like furfural (**5**, **Figure 1**), formic acid, and glycolaldehyde, among others (Patwardhan et al., 2011b).

As with cellulose, hemicellulose pyrolysis products depend mostly on the number of carbons in the monosaccharide residues of the starting polymer (Shafizadeh et al., 1972). Pentoses and hexoses produce similar light C1–C3 oxygenates but differ in the types and selectivities (i.e., relative ratios) of heavier C4–C6 products. Consistent with expectations, pyrolysis of monosaccharides reveals that hexoses can form more unique compounds than pentoses, including pyranic species; additionally, pentoses yield more lighter fragmentation products than hexoses and only trace amounts of C6 and higher products (Raisanen et al., 2003).

Lignin thermal degradation products generally retain the characteristic ring decoration of the monolignols from which they originate (**3**, **Figure 1**). For example, syringol derivatives are bio-oil products derived from S-lignin units and guaiacols are products derived from G-lignin units (**6**, **Figure 1**). The derivative groups possess 1–3 carbons and/or oxygenate moieties at the fourth position (**6**, **Figure 1**). Consistent with expectations, softwood lignins yield almost exclusively guaiacyl derivatives, while hardwood lignins yield both guaiacyl and syringyl derivatives. Grasses yield not only guaiacyl, syringyl, and *p*-hydroxyphenyl derivatives but also vinylphenol, propenyl-phenols, and *p*-hydroxybenzaldehyde that are not produced during pyrolysis of

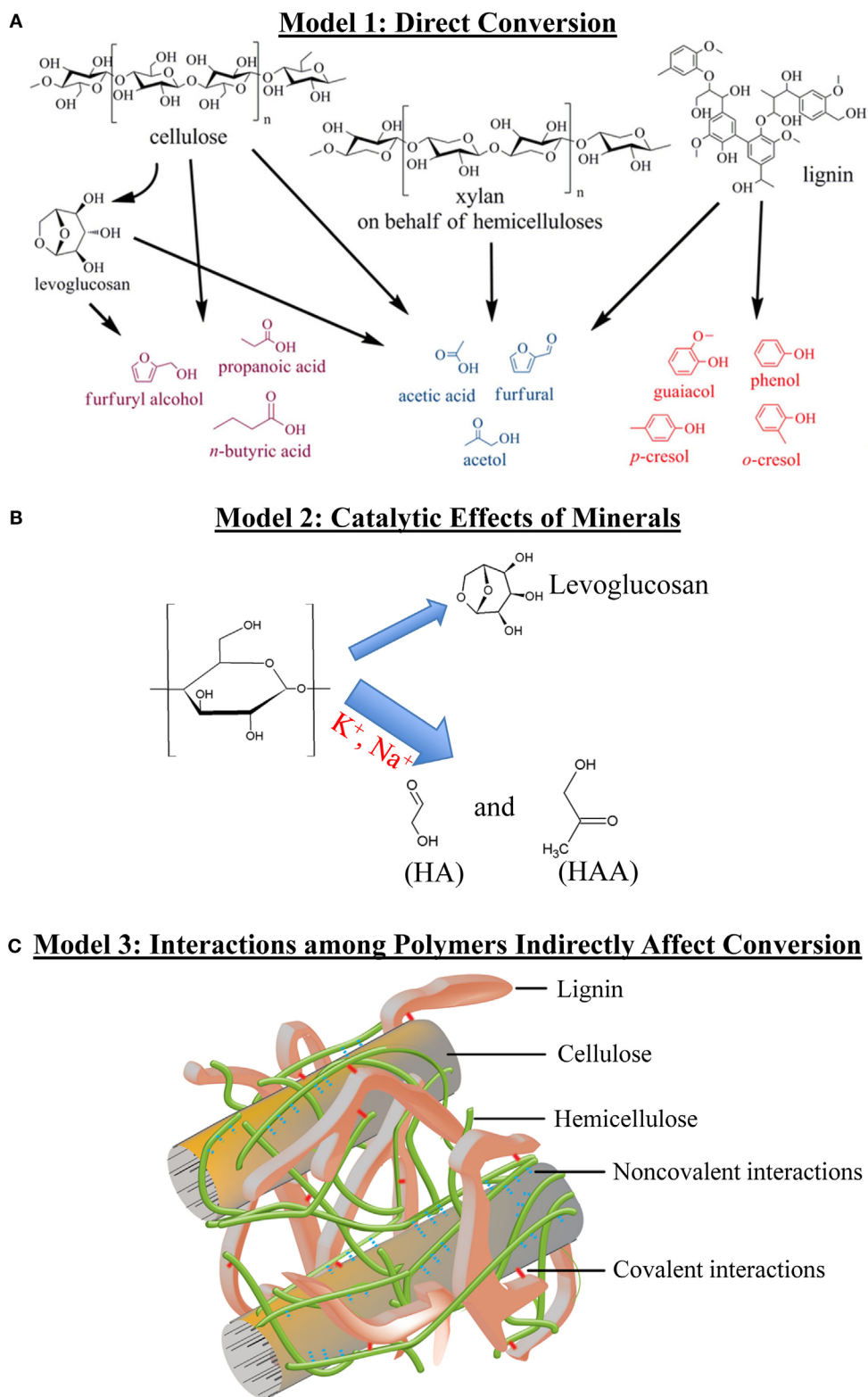


FIGURE 2 | Three models of how biomass components and their interactions affect the formation of thermal products. HA, hydroxyacetaldehyde; HAA, hydroxyacetaldehyde. **(A)** Direct conversion. **(B)** Catalytic effect of minerals. **(C)** Interactions among polymers indirectly affect conversion. **(A)** and **(C)** were adapted and modified with permission (Vanholme et al., 2010; Zhang et al., 2013).

TABLE 3 | Possible models of how biomass components affect the composition and yield of liquid thermal products.

Possible model	Biomass component	Variation of input material (independent variable)	Effect on products (dependent variable)	Sample type	Thermal conversion condition	Reference
1	Hemicellulose	Arabinose, xylose, mannose, arabinitol	Arabinose and xylose produce similar products but slightly different yields and product ratios. Mannose gives more decomposition products than arabinose and xylose and a unique product, 5-hydroxymethyl furfural	Powdered high-purity monosaccharides (>99%)	500 and 550°C, 10 s	Raisanen et al. (2003)
1	Hemicellulose or non-structural polysaccharides	Variation in sugar composition	Fermented grain samples produce less acetic acid, furfural, and acetone than hull and straw	Barley straw, hull and yeast-fermented grain	Fluidized bed, 500°C	Mullen et al. (2010)
1	Lignin	Lignin variation among hardwoods, softwoods, and grasses	Hardwood lignin produces guaiacyl and syringyl derivatives. Softwood lignin produces mostly guaiacyl derivatives but no hydroxyphenyl or syringyl compounds. Grass lignin uniquely produces vinylphenol, propenyl-phenols, and <i>p</i> -hydroxybenzaldehyde	Solvent extracted lignin from milled spruce, beech, aspen, and bamboo	510°C, 10 s	
1	Lignin	Natural variation and variation by hydrogen peroxide treatment in Klason lignin	Samples with high Klason lignin produce more 4-vinylguaiacol. Klason lignin positively correlates with 4-vinylguaiacol	Hybrid maize, <i>bm1</i> mutant, <i>bm3</i> mutant, and switchgrass biomass treated by different [H ₂ O ₂] to remove lignin	650°C, 20 s	Saizjimenez and Deleeuw (1986)
1	Lignin	Natural variation in lignin abundance	High-lignin endocarp biomasses produce more phenolic compounds, like phenol, 2-methoxyphenol, 2-methylphenol, 2-methoxy-4-methylphenol, and 4-ethyl-2-methoxyphenol, compared to switchgrass biomass	Walnut, olive, coconut husks, and peach drupe endocarp biomass and switchgrass biomass	650°C, 20 s	Li et al. (2012)
1	Lignin	Natural variation in lignin composition or structure	Compared with endocarp lignin, switchgrass lignin produces more acetic acid, toluene, furfural, and 4-methylphenol, and lower or undetectable amounts of 4-ethyl-2-methoxyphenol, 2-methoxy-4-vinylphenol and 2-methoxy-4-(2-propenyl)-phenol. Compared with walnut and olive endocarp lignin, coconut endocarp lignin produces strikingly more phenol and less 2-methoxy-4-methylphenol. Coconut shell lignin produces unique compounds among the analyzed feedstocks, such as 2,6-dimethoxyphenol, 2-methoxy-4-(2-propenyl)-phenol and vanillin, but less 2-methoxy-4-(1-propenyl)-phenol compared to walnut shell and olive lignin	Lignin extracted from various endocarps and switchgrass	650°C, 20 s	Mendu et al. (2011)
1	Lignin interunit linkages (lignin dimer)	Variation of lignin interunit linkages, including β-O-4' ethers, pinoresinols, phenylcoumaran, and dibenzodioxocins, among lignin-carbohydrate complexes with different compositions	Glucomanan-associated lignin produces more guaiacol than xylan-associated lignin and glucan-associated lignin	Lignin-carbohydrate complexes extracted from spruce wood	500°C, 1 min	Mendu et al. (2011)
2	Mineral content	Variation of K ⁺ , Mg ²⁺ , and Ca ²⁺ by demineralization and impregnation	Samples with more K ⁺ produce more glycolaldehyde, acetic acid, acetol, butanedial, guaiacol, syringol, and 4-vinylsyringol, but less levoglucosan, furans, and pyrans. Samples with more Mg ²⁺ produce less glycolaldehyde, levoglucosan, and 3-methoxycatechol. Samples with more Ca ²⁺ produce more pyrans and cyclopentenes but less levoglucosan and 3-methoxycatechol	Poplar wood powder demineralized with hydrofluoric acid and impregnated with KCl, MgCl ₂ , and CaCl ₂	550°C, 10 s	Eom et al. (2012)

(Continued)

TABLE 3 | Continued

Possible model	Biomass component	Variation of input material (independent variable)	Effect on products (dependent variable)	Sample type	Thermal conversion condition	Reference
2	Mineral content	Increase of minerals by adding 1% and 5% NaCl	Samples with more NaCl added produce more furans, acids, ketones, and phenols than the samples with no NaCl added	Rice straw and bamboo with NaCl	400–900°C, 4 min	Lou et al. (2013)
2	Mineral content	Decrease minerals by acid wash	Cellulose with the acid-washed char produces more levoglucosan but less formic acid, furane-type derivatives, and light oxygenates, than cellulose with unwashed char	Cellulose with acid-washed and unwashed red oak char	400°C, 15 s	Ronsse et al. (2012)
2	Mineral content	Decrease of K ⁺ and Na ⁺ by washing	Washed samples yield more levoglucosan, hydroxyacetaldehyde, and char than unwashed samples	Washed and unwashed lolium, festuca, willow, and switchgrass biomass	500°C, 10 s	Fahmi et al. (2007)
2	Mineral content	Increase mineral content by impregnation with NaCl, KCl, MgCl ₂ , CaCl ₂ , Ca(OH) ₂ , Ca(NO ₃) ₂ , CaCO ₃ , and CaHPO ₄	Impregnated samples produce less levoglucosan, but more glycolaldehyde and acetol, compared to untreated cellulose	Microcrystalline powdered cellulose impregnated with salt or switchgrass ash solution	500°C, 30 s and a range from 350 to 600°C with 50°C increments	Patwardhan et al. (2010)
2	Mineral content	Natural variation in ash	Ash negatively correlates with hydroxyacetaldehyde and phenolic compounds, such as trimethoxybenzene, syringol, 4-allyl-2,6-dimethoxyphenol, syringaldehyde, and 3,5-dimethoxy-4-hydroxycinnamaldehyde	Poplar, willow, switchgrass, hot-water extracted sugar maple, and debarked sugar maple	550°C, 20 s	Mante et al. (2014)
2	Mineral content	Increase mineral content by adding CaCl ₂ , NaCl, KCl, K ₂ SO ₄ , KHCO ₃ individually to washed wood	Washed wood with calcium salt added produces more C ₆ H ₈ O ₂ compound compared to washed wood with no additive. Samples with sodium salt and potassium salt added produce less 2-hydroxy-butanedial, 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one, and levoglucosan, but more tetrahydro-4-hydroxy-pyran-2-one, compared to washed samples	Hornbeam wood washed and mixed with salts	280°C, 20 min, 100–500°C	Muller-Hagedorn et al. (2003)
2	Mineral content	Increase mineral content by adding 1% NaCl	Xylans with NaCl added yield more glycolaldehyde but less 1,4-anhydro- α -D-xylopyranose, 1,5-anhydro-4-deoxypent-1-en-3-ulose and char	Synthesized xylan	280°C, 30 min	Ponder and Richards (1991)
2	Mineral content	Replace the cations in biomass with Na ⁺ by ion-exchange or increase mineral content by adding Na ₂ SO ₄ or NaHCO ₃	Sodium-containing pulps produce less polysaccharide-derived products and similar amounts of lignin-derived products compared to untreated pulps	Spruce pulp, treated with ion exchange and salt impregnation	620°C, 2 s	Kleen and Gellerstedt (1995)
3	Intercomponent linkages	Biomass with hemicellulose selectively removed, compared with a physical mixtures of lignin and cellulose, and separate pyrolysis of lignin and cellulose	The native grass cellulose–lignin samples produce more C1 to C3 products and furan, but less pyrans and levoglucosan	Corn stover, red oak, pine, and switchgrass depleted of hemicellulose and compared with different extracted component mixtures	500°C	Zhang et al. (2015)

(Continued)

TABLE 3 | Continued

Possible model	Biomass component	Variation of input material (independent variable)	Effect on products (dependent variable)	Sample type	Thermal conversion condition	Reference
1 and 2 or 3	Acetyl content	Natural variation in acetyl content among five species	Acetyl content positively correlates with acetic acid, but also methyl pyruvate and 2-furanone	Poplar, willow, switchgrass, hot-water extracted sugar maple, and debarked sugar maple	550°C, 20 s	Mante et al. (2014)
1 and 3	Acetyl content	Variation of acetylation between acetylxylan and xylan	The acetylxylan produces more acetic acid, furan, and acetone, but less 2-furfural and acetaldehyde, than xylan	Xylans extracted from cotton wood	500°C	Shafizadeh et al. (1972)
1 and 3	Cellulose	Natural variation in glucans, mostly cellulose, among five species	Glucans positively correlate with levoglucosan and hydroxymethyl furfural, but also phenolic compounds like syringaldehyde, vanillin, and 3,5-dimethoxy-4-hydroxycinnamaldehyde	Poplar, willow, switchgrass, hot-water extracted sugar maple, and debarked sugar maple	550°C, 20 s	Mante et al. (2014)
1 and 3	Lignin	Natural variation in lignin among five species	Lignin positively correlates with hydroxyacetaldehyde and phenolic compounds, trimethoxybenzene; syringol; 4-allyl-2,6-dimethoxyphenol; syringaldehyde; and 3,5-dimethoxy-4-hydroxycinnamaldehyde	Poplar, willow, switchgrass, hot-water extracted sugar maple, and debarked sugar maple	550°C, 20 s	Mante et al. (2014)
1 and 3	Xylan	Natural variation in xylan among five species	Xylan positively correlates with hydroxyacetone, but negatively correlates with hydroxymethyl furfural and syringaldehyde	Poplar, willow, switchgrass, hot-water extracted sugar maple, and debarked sugar maple	550°C, 20 s	Mante et al. (2014)
2 and 3	Mineral content or other structure	Variation in weakly associated and strongly associated K, Na, Mg, and Ca by washing with deionized water or nitric acid	Acid-washed samples with less mineral content produce bio-oil with a greater fraction of water-insoluble content and produce more levoglucosan and sugar compounds but less monophenols like phenol, 2-methyl-phenol, syringol compared to unwashed samples	Eucalyptus wood	Fluidized bed, 500°C	Mourant et al. (2011)
3	Water	Natural variation in moisture content (0–20%)	Samples with greater moisture content produce more char and gas but less water compared to lower moisture samples	Pine wood	Fluidized bed, 480°C, 2 s	Westerhof et al. (2007)
3	Water	Natural variation in moisture content (2–55%)	Samples with greater moisture content produce more condensable products, but less char than dry samples	Norway spruce	500°C, 30 min	Burhenne et al. (2013)
3	Water	Natural variation in moisture content (5–15%)	Samples with greater moisture content produce less levoglucosan at 450 and 500°C than samples with lower moisture content. Other products are also significantly affected by moisture content, but trends depend on pyrolysis temperature	Switchgrass	Fluidized bed, 450, 500, and 550°C	He et al. (2009)
3	Intercomponent linkages	Variation in polysaccharide amounts in lignin–carbohydrate complexes by enzyme treatment	Samples with lignin-associated polysaccharides removed produce more coniferyl alcohol than untreated samples	Lignin–carbohydrate complexes extracted from spruce wood	500°C, 1 min	Du et al. (2014)

softwood and hardwood (Saizjimenez and Deleeuw, 1986; Mante et al., 2014) and are likely derived from ferulate and coumarate esters (Penning et al., 2014b). Phenol derivatives are the large majority of the products formed from lignin pyrolysis; aromatic hydrocarbons and some furan derivatives are also detectable, but at very low amounts that might represent lignin sample contaminants (Saizjimenez and Deleeuw, 1986). Lignins from spruce wood with different dimer compositions also show different product distributions, including variations in the yield of major products like guaiacol (Du et al., 2014). This suggests that bonds between lignin units and the lignin structure determined by those bonds may impact pyrolysis as well.

Model 2: Secondary Reactions Catalyzed by Inorganic Components

The biopolymers that make up the majority of the biomass by weight are established as the primary source of bio-oil products formed during thermal degradation. However, secondary reactions occur during the pyrolysis process involving other components present within the biomass (Ponder and Richards, 1991; Kleen and Gellerstedt, 1995; Muller-Hagedorn et al., 2003; Fahmi et al., 2007; Patwardhan et al., 2010; Ronsse et al., 2012; Lou et al., 2013; Mante et al., 2014). As products form, they can interact with catalytic minerals in the residual solid. For example, levoglucosan has been shown to react on minerals present in the residual char from pyrolysis of biomass. The products formed include levoglucosenone, furan derivatives, and lighter oxygenates such as acetic acid, acetone, and acetol. Demineralization prohibits the formation of these products (Fahmi et al., 2007; Ronsse et al., 2012).

Different inorganics are responsible for different kinds of secondary reactions. In general, the presence of metal cations enhances the homolytic cleavage of pyranose ring bonds over the heterolytic cleavage of glycosidic linkages, leading to the increased formation of light oxygenate decomposition products at the expense of levoglucosan formation. While Na^+ , K^+ , Mg^{2+} , and Ca^{2+} all catalyze levoglucosan decomposition, the effects of group 1 (alkali metals) and group 2 (alkaline) elements differ. Increased Na^+ and K^+ alkali metal loading increased formic acid, glycolaldehyde, and acetol more than similar amounts of the alkaline metals, Mg^{2+} and Ca^{2+} , though more furfural is produced with increasing concentrations of Mg^{2+} and Ca^{2+} . Additionally, the alkali metals reduce levoglucosan production at very low thresholds. This suggests that Na^+ and K^+ ultimately promote cracking reactions while Mg^{2+} and Ca^{2+} promote dehydration reactions (Muller-Hagedorn et al., 2003; Patwardhan et al., 2010; Eom et al., 2012).

Model 3: Interactions and Linkages Between Primary Components

While the first two models address the direct conversion of biopolymer organic components to related bio-oil products and their further reaction catalyzed by biomass inorganics, the third addresses compositional and structural relationships among cell wall components and their impact on products. Interactions between polysaccharides and lignin have been shown to alter pyrolysis products (Du et al., 2014; Zhang et al., 2015). The cellulose–lignin interaction can lead to a decrease in levoglucosan

yield and an increase in light (C1–C3) compounds, especially glycolaldehyde and furans. Based on the nature of the small products, Zhang et al. (2015) hypothesized that the cellulose–lignin interaction occupies the C6 position, disfavoring glycosidic bond cleavage that is required for the formation of levoglucosan and favoring light compound and furan formation through ring scission, rearrangement, and dehydration reactions. The strength of this effect on pyrolysis products is most pronounced in grasses, followed by softwood and then hardwood, possibly due to the increased prevalence of covalent bonds between cellulose and lignin in grass cell walls (Jin et al., 2006; Zhou et al., 2010). Hemicellulose–lignin interactions, especially the xylan–lignin interaction revealed in NMR experiments (Yuan et al., 2011), may also affect pyrolysis. Indeed, enzymatic removal of hemicelluloses from lignin–carbohydrate complexes increased coniferyl alcohol yields (Du et al., 2014).

An example of a compositional feature that may impact product distribution is the degree of acetylation of the biopolymers. As mentioned, acetyl groups decorate hemicellulose side chains and are also present in the lignin. The increased abundance of these groups in biomass correlates with increasing yields of acetic acid, methyl pyruvate, acetone, and furan; additionally, this acetylation correlates with decreasing yields of furfural and acetaldehyde (Shafizadeh et al., 1972; Mante et al., 2014). While the acetic acid and perhaps the methyl pyruvate can be explained by the direct production of these compounds upon pyrolytic decomposition (Model 1), the nature of the relationship between acetate and the furanic and other 4-carbon species has not been clearly defined. The production of the 4-carbon species may be due to an indirect effect (Model 3) or may be the result of catalytic reaction of acetate with itself (Model 2).

Several investigations (Westerhof et al., 2007; He et al., 2009; Burhenne et al., 2013) suggest that feedstock moisture content can also play a role in the yield and product distribution of the organic fraction of the bio-oil. As previously discussed, the presence of water in bio-oil prohibits its direct use and creates challenges to catalytic valorization. For these reasons, biomass is typically subjected to drying prior to pyrolysis, which both reduces the required energy of the pyrolysis step and limits the water in the liquid condensate to water produced by decomposition reactions. However, the degree to which the feedstock moisture content should be eliminated is still under investigation. Burhenne et al. (2013) found that higher feedstock moisture content led to slightly lower char and gas yields upon pyrolysis with minimal changes to the elemental composition of the char. However, this is in disagreement with Westerhof et al. (2007) who observed slightly higher char yields with increasing moisture content. The water weight fraction distribution of the feedstocks in the two studies were quite different, 2.4–55.4% in Burhenne et al. versus 0–20% in Westerhof et al. Beyond impacts to the yields, He et al. (2009) studied the change in selectivity to the organic fraction produced upon pyrolysis of switchgrass with 5, 10, and 15% feedstock moisture contents. The authors found that at 500°C, the lowest moisture content feedstock produced the highest amounts of levoglucosan and acetic acid. The authors note that while significant differences in pyrolysis products were observed, they could not identify clear trends in their data. Among these

studies, the observable but sometimes contradictory or unclear trends suggest that the feedstock moisture content may have multiple impacts on the pyrolysis process, possibly related to the physical location of the water in biomass.

In addition to compositional factors, morphological factors also influence the bio-oil product distributions. Biomass undergoing thermal decomposition retains its morphology even in harsh thermal treatment regimes (Pohlmann et al., 2014). Biomass is a poor conductor of heat (conductivity <0.1 W/m K) (Bridgwater et al., 1999), and large temperature gradients occur in heated biomass particles (Bryden et al., 2002). Most reactor systems for thermal degradation require size reduction of biomass particles; as an example, fluidized beds require particle sizes no larger than 2 mm (Bridgwater et al., 1999) to ensure rapid reaction. These particle sizes are larger than the tissue structures present in biomass. While the overall tissue and cellular morphology remain intact, micropore formation and shrinkage during the reaction process can occur in a non-uniform manner throughout the biomass (Davidsson and Pettersson, 2002; Pohlmann et al., 2014). Piskorz and colleagues observed decreasing liquid yields with increasing particle size, attributed to increasing incidence of secondary reactions with in wood particles (Scott and Piskorz, 1984). The principles of internal and external diffusion and the impacts of tortuosity, surface area, and diffusion path lengths are all fundamental to catalytic reaction engineering, and in the case of thermal biomass conversion, these important parameters are all dictated by the reacting feedstock (Fogler, 2006). Some evidence supports the notion that different plant developmental stages, which are related to the ratio of leaves to stems and biomass density, result in different pyrolysis products. For example, switchgrass harvested at later times during the growing season produced increased yields of condensable products, relative to that from younger, leafier material (Boateng et al., 2006), though compositional and developmental differences of the starting material were not carefully assessed.

CONCLUSION

Years of research have led to understanding of the direct pyrolysis conversion pathways of the major monomeric and polymeric constituents of biomass (Model 1, **Table 2**). The observation that these constituents often represent minor components in raw bio-oil (**Table 1**) highlights the importance of catalytic degradation (Model 2) and possibly indirect effects (Model 3) on pyrolysis products. The latter model is only recently receiving attention as knowledge of cell wall structures and analytical repertoires blossom (Mante et al., 2014; Zhang et al., 2015). Detailed examination of the relationships between components and products is still sparse, with the biological literature providing detailed characterization of cell wall components, while the engineering literature analyzes the chemical components, or often just total yields, of different pyrolysis fractions. We would argue that further investigations on the relationships between biomass components and thermal products will allow improvement of thermal product “quality.” Short of attaining (or improving on) petroleum fuel-like properties, even the criteria for a high-quality thermal product remain unclear. As discussed, this is, in part, because methods

for upgrading are so dependent on bio-oil composition. Thus, methods that economically separate and/or simplify the different product streams, while still maintaining C–C bonds and overall C-content, are more likely to be amenable to catalytic upgrading.

Greater and more systematic analysis of biomass composition and pyrolysis products within species that show significant compositional variation will aid in better understanding biomass–bio-oil relationships. Much of the existing literature relies on comparisons of thermal degradation products across diverse taxonomic groups that vary greatly in cell wall composition beyond the biomass components measured (**Table 3**). An analysis of more subtle compositional differences, in which compositional factors are varied across different samples, may aid in refining biomass–bio-oil relationships. For example, genetic mutants that vary in only one component relative to near isogenic, unmutated “wild-type” plants can directly address relationships between starting components and products (Li et al., 2012). In addition to genetically determined compositional differences, biomass composition also depends on growth conditions and developmental stage, which relates to harvest time. Taken together, the scale of the problem points to the value of developing high-throughput methods to help identify species and genotypes that are most suitable for production of specific thermal products and to guide the optimization of genetic stocks and growth condition for bio-energy crops. Methods available to identify such “high-quality” biomass include near-infrared reflectance spectroscopy (Vogel et al., 2011), Fourier transform near-infrared spectroscopy (Liu et al., 2010), and pyrolysis molecular beam mass spectrometry, at least for lignin components (Sykes et al., 2009; Penning et al., 2014b). In general, these methods can be trained, either rationally or in a model-independent manner, to detect spectroscopic or molecular signatures in biological materials with linear or non-linear relationships to thermal products.

Besides selecting or breeding for natural variation in biomass composition (Wegrzyn et al., 2010; Penning et al., 2014a), it is also possible to genetically modify biomass composition (Bartley and Ronald, 2009). Most simply, genetic engineering of bioenergy plants can be achieved by modifying the plant’s genome to (1) express genes from other organisms, (2) increase expression of native genes, or (3) reduce expression of native genes. More complex schemes are also possible, in which expression patterns of genes are altered through synthetic biology approaches that recombine various genetic elements (Yang et al., 2013). The most common method for plant genetic engineering co-opts the molecular machinery of a bacterial pathogen that introduces genes into plant chromosomes to facilitate its pathogenesis.

Genetic engineering to improve bio-oil production would aim to increase biomass components that enhance the yield of favored products and/or to decrease components that produce disfavored products or interfere with upgrading strategies. Advances in understanding cell wall biosynthesis, including genes responsible for synthesizing the major polymer classes (Bonawitz and Chapple, 2010; Scheller and Ulvskov, 2010; Pauly et al., 2013) and covalent interactions among them (Chiniquy et al., 2012; Bartley et al., 2013; Schultink et al., 2015); regulation of expression of the cell wall biosynthesis genes (Zhao and Dixon, 2011); and metal ion transport proteins that determine the abundance and

distribution of plant mineral content (Ma et al., 2006; Yamaji and Ma, 2009; Zhong and Ye, 2015), lay the foundation for genetically engineering bioenergy crop cell wall content and structure. For example, lignin is an important target for genetic engineering for pyrolysis since the major lignin-derived products have a lower O:C ratio, a higher energy value, and are more stable than sugar-derived products (Tanger et al., 2013; Mante et al., 2014). Some important genes that participate in or regulate lignin synthesis have already been modified in energy crops without major interference with plant biomass yield (Baxter et al., 2014, 2015; reviewed in Bartley et al., 2014). However, current genetic engineering strategies are focused on developing low lignin biomass for saccharification and biochemical conversion to fuels. Therefore, more work is required to develop biomass with high-lignin content for thermal conversion. Producing corrosive acetic acid in bio-oil (Mante et al., 2014), acetyl groups on cell wall polymers are another potential target for genetic engineering of “pyrolysis crops.” Three enzyme classes, including the reduced wall acetylation (RWA) proteins, Trichome birefringence-like (TBL) and Altered Xyloglucan (AXY) proteins acetylate cell wall polysaccharides (Lee et al., 2011; Xiong et al., 2013; Schultink et al., 2015). A mutant of the dicot reference plant, *Arabidopsis thaliana*, which lacks expression of all four RWA genes, shows a 40% reduction in secondary wall-associated acetyl groups (Lee et al., 2011). Reducing expression of this family of genes in bioenergy crops may help to solve the problems caused by acetic acid in bio-oil produced from such plants.

Pretreatments such as washing/leaching and torrefaction are another class of strategies to improve biomass quality by changing biomass composition (Zheng et al., 2013; Banks et al., 2014).

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- For example, by washing biomass with detergent (Triton) or acid to remove minerals, the yield of bio-oil is increased and reaction water content is reduced (Banks et al., 2014). Coupling biochemical conversion of biomass, which depletes the polysaccharide fraction, with pyrolysis of the resulting residue, or bagasse, is another avenue to explore further (Islam et al., 2010; Cunha et al., 2011). Torrefaction is a low-temperature (200–400°C) thermal pretreatment that decomposes hemicellulose and may segregate disfavored products such as water and acid into intermediate streams before the next stage of pyrolysis (Zheng et al., 2013). More efficient torrefaction may be achieved by changing the composition or chemical structure of hemicellulose through genetic methods to further separate the decomposition temperatures of hemicellulose from lignin and cellulose. By identifying and studying the roles of key biomass components during thermal conversion, it will be possible to maximize the economic and environmental benefits of plant biomass-derived biofuels in the future.

AUTHOR CONTRIBUTIONS

FL and CW drafted and revised the manuscript. LB, LL, and RM revised the manuscript.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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