ANNUAL REVIEWS

Annual Review of Chemical and Biomolecular Engineering

Engineering Innovations, Challenges, and Opportunities for Lignocellulosic Biorefineries: Leveraging Biobased Polymer Production

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Annu. Rev. Chem. Biomol. Eng. 2023. 14:109–40

First published as a Review in Advance on April 11, 2023

The *Annual Review of Chemical and Biomolecular Engineering* is online at chembioeng.annualreviews.org

https://doi.org/10.1146/annurev-chembioeng-101121-084152

Keywords

lignocellulosic biomass, valorization, biorefinery, biobased polymers, life-cycle management, sustainability

Abstract

Alternative polymer feedstocks are highly desirable to address environmental, social, and security concerns associated with petrochemical-based materials. Lignocellulosic biomass (LCB) has emerged as one critical feedstock in this regard because it is an abundant and ubiquitous renewable resource. LCB can be deconstructed to generate valuable fuels, chemicals, and small molecules/oligomers that are amenable to modification and polymerization. However, the diversity of LCB complicates the evaluation of biorefinery concepts in areas including process scale-up, production outputs, plant economics, and life-cycle management. We discuss aspects of current LCB biorefinery research with a focus on the major process stages, including feedstock selection, fractionation/deconstruction, and characterization, along with product purification, functionalization, and polymerization to manufacture valuable macromolecular materials. We highlight opportunities to valorize underutilized and complex feedstocks, leverage advanced characterization techniques to predict and manage biorefinery outputs, and increase the fraction of biomass converted into valuable products.

1. INTRODUCTION

Synthetic polymers are ubiquitous in modern life, comprising everything from packaging to consumer electronics to clothing to medical devices (1, 2). However, most commercial polymers are derived from petroleum and contribute significantly to anthropogenic (i.e., human-generated) climate change (3). In 2018, plastics accounted for an estimated 6 wt.% of global oil consumption and were associated with the emission of 118 million metric tons of CO_2 equivalents (3). With more than 380 million metric tons of plastics and other synthetic polymers generated each year and accelerating production projected for the foreseeable future, more environmentally friendly polymer feedstocks must be identified and translated to application (1).

Lignocellulosic biomass (LCB) is a particularly promising alternative feedstock because it constitutes the most abundant bulk material on the planet, contains diverse chemical compositions, and offers renewably sourced monomers and monomer precursors (4). However, LCB-derived fuels, chemicals, and materials must compete with petroleum products currently on the market. These incumbent petrochemicals have a significant advantage in that oil refinery infrastructure is globally prevalent and optimized, whereas lignocellulosic biorefineries still require significant advances and investment to establish the necessary infrastructure and optimization systems. Thus, it is essential to evaluate the economic situations under which biofuels and biobased chemicals/materials can compete with their petroleum-derived analogs and determine the key factors that facilitate biobased materials adoption. Based on process and economic analyses of cellulosic biorefineries, the US Department of Energy (DOE) has set a target minimum biofuel selling price of \$2.50/gallon gasoline equivalent and recommended that integrated biorefineries manufacture an array of fuels, chemicals, and materials to reach this goal (5, 6). Lignin valorization is essential in realizing this selling price as it can reduce the effective biofuel cost by more than \$2/gallon gasoline equivalent (5). In particular, polymers are value-added materials that can enable the economic success of the collective LCB biorefinery, and we limit the scope of this review to the production of polymers from LCB. Polymers can be synthesized from small-molecule, dimeric, oligomeric, and macromolecular deconstruction products (7–13). These polymers can be direct substitutes for those made from petrochemicals, or ideally, they can be structurally unique and offer advantages in environmental, economic, processing, and/or performance properties to incentivize their translation into commercial markets.

Derived: obtained from a particular feedstock or class of feedstocks (e.g., bio- or lignin-derived)

LCB: lignocellulosic biomass

Biobased: prepared fully or partially from a bio-derived resource

DOE: Department of Energy

Valorization: process of controlling or increasing the value of a commodity through innovation, technology, or policy

Deconstruction: breakdown of a material/polymer into smaller fragments

LCB consists of three major components: cellulose (40–60 wt.%), hemicellulose (10–40 wt.%), and lignin (15–30 wt.%) (14). Substantial amounts of LCB have been processed in paper and pulping mills since the fourteenth century, and currently, more than 40 million tons/year of chemical pulp is produced in the United States alone (15, 16). Recently, cellulosic ethanol biorefineries have gained momentum, with three full-scale plants built in the United States in 2015, but these facilities have suffered technical and financial setbacks that have led to reduced/paused production or complete shutdowns (17, 18). In both pulp mills and cellulosic biorefineries, the lignin is extracted and often treated as a waste stream, and the valorization of cellulose and hemicellulose is prioritized. Pulp mills convert cellulose fibers to pulp and paper, and cellulosic biorefineries convert polysaccharides to ethanol through enzymatic hydrolysis, fermentation, and distillation (19). Because lignin valorization is neglected, only a fraction of the LCB feedstock is converted into valuable goods. Globally, lignin extraction generates an estimated 100 million tons/year of separated lignin, up to 98 wt.% of which is landfilled or burned in the form of black liquor for onsite energy generation and chemical recovery (20, 21). The small fraction of lignin that is isolated and available for commercial uses is generally employed in low-value applications such as adhesives, binders, dust suppressants, and cement admixtures (20–23).

Recent research efforts have suggested that lignin deconstruction could generate value-added products (6, 7, 24–26). However, lignin valorization is considered challenging because current industrial biorefineries produce technical lignins that are more recalcitrant [i.e., resistant to (bio)chemical conversion] than native lignin due to condensation from the harsh extractive conditions (21, 27). As such, innovative fractionation methods that reduce lignin recalcitrance have become a major research focus (19, 25–36). For example, less severe pretreatment procedures have been investigated to mitigate the formation of condensed lignin and thus improve sugar yields, lignin purity, and downstream processability (33–36). These fractionation approaches include the use of γ-valerolactone, ionic liquids (ILs), deep eutectic solvents, and molten salt hydrates (19, 29–32, 37); however, these milder pretreatment strategies often achieve lower isolated lignin yields than those obtained using the relatively harsher conditions employed in current LCB biorefineries and pulp mills (26, 27, 38). To avoid this trade-off between recalcitrance and yield, lignin-first processes have been developed to actively stabilize the lignin during fractionation, enabling the generation of high-quality cellulosic products in addition to less recalcitrant lignin (25, 26). Some approaches use a protecting agent during pretreatment [e.g., formaldehyde (27)], though the most common lignin-first strategy is reductive catalytic fractionation (RCF), a solvothermal extraction method with a transition metal catalyst and hydrogen donor (28).

These milder conditions and lignin-first strategies enable the manufacture of a wide variety of fuels, chemicals, and materials, but to transform LCB into valuable polymers, lignocellulosic biorefineries would benefit from several additional upstream and downstream processing considerations encompassing feedstock selection to polymerization (**Figure 1**). Feedstock selection is an especially important step, as it informs and affects every stage of the biorefinery. Lignocellulosic biorefineries must be amenable to a diverse set of feedstocks to avoid competition with food sources and land-use concerns and to mitigate issues stemming from geographical/seasonal variation in biomass availability (39, 40). Underutilized feedstocks that are available in bulk and at low costs are especially promising candidates, but a major barrier to their implementation is high heterogeneity because cellulose, hemicellulose, and lignin content vary in quantity and chemical composition due to factors such as species, age, and plant tissue (e.g., leaves versus bark) (41–43). Although petroleum feedstocks also are heterogeneous, oil refineries have had more than a hundred years to thoroughly optimize their processes to handle such variability (44). LCB biorefineries require similar optimization to embrace the inherent biomass heterogeneity and achieve favorable economics. Advanced characterization techniques are an important element in this optimization to predict and manage outputs throughout the biorefinery. Furthermore, biomass has a much higher oxygen content than fossil fuels, resulting in challenges for biofuel applications, such as decreased energy density or the need for additional refining steps. The high oxygen content does, however, provide opportunities to synthesize chemicals and polymeric precursors that cannot be made as easily from fossil fuel feedstocks. For example, producing oxygenated compounds, such as adipic acid and 1,4-butanediol, from petroleum feedstocks requires the addition of oxygen through expensive, energy-intensive synthetic steps, whereas these chemicals can be readily prepared from biomass (5). Finally, process design and intensification, life-cycle management, and scale-up are important areas for innovation in LCB biorefineries, and process modeling for technoeconomic analysis (TEA) and life-cycle assessment (LCA) is critical to evaluate any innovation's economic and environmental feasibility in a full-scale LCB biorefinery (24, 45). These analyses also can play a role in decision-making frameworks to assess current strategies and direct future research thrusts.

Fractionation: partial or full separation of mixture constituents into individual components or submixtures

IL: ionic liquid

RCF: reductive catalytic fractionation

Life-cycle management: development, manufacture, and processing of new and/or existing materials with a strong consideration of sustainability and/or circularity

TEA: technoeconomic analysis

LCA: life-cycle assessment

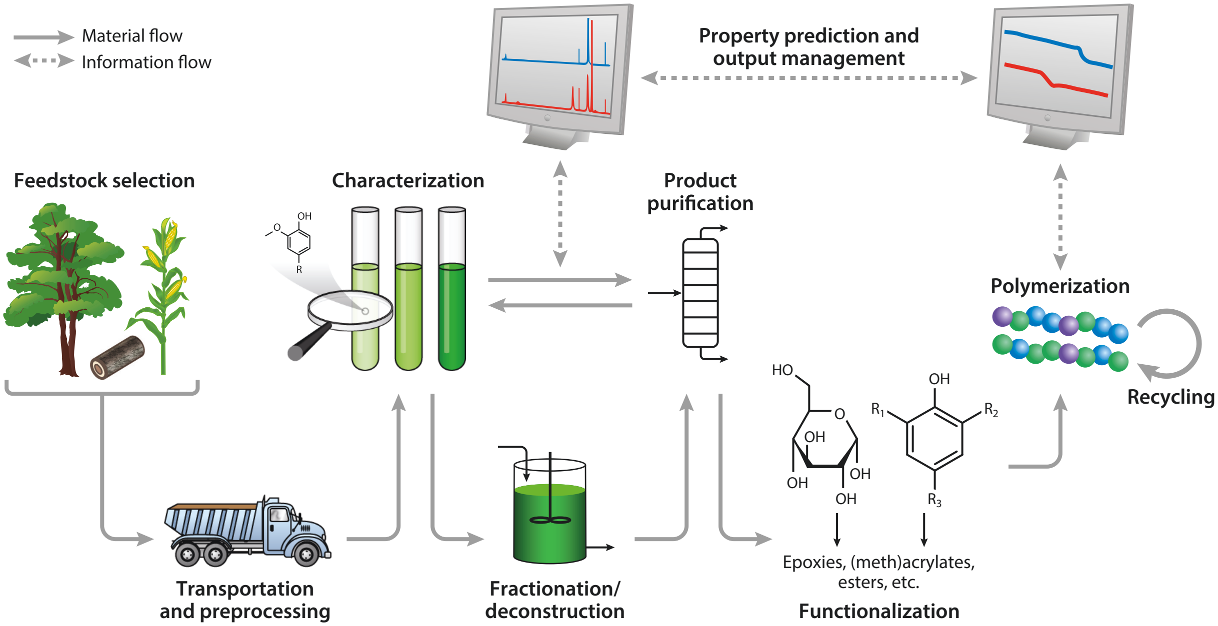

Figure 1

Overview of the major process stages associated with lignocellulosic biomass biorefineries for polymer production: feedstock selection, transportation and preprocessing, characterization, fractionation/deconstruction, product purification, functionalization, and polymerization. The importance of polymer property prediction and biorefinery output management enabled by advanced characterization techniques is highlighted. The solid arrows represent flows of materials, and the dashed arrows indicate flows of information throughout the biorefinery.

In this review, we describe recent innovations, current challenges, and future opportunities for the growth of lignocellulosic biorefineries to manufacture biobased polymers. We first discuss the variability of LCB feedstocks and emphasize the economic and environmental savings enabled by the use of underutilized LCB waste feedstocks. We then briefly summarize current advances in fractionation/deconstruction process engineering and highlight the power of advanced upstream and downstream biomass characterization techniques to predict and manage biorefinery outputs. Subsequently, we evaluate product purification, functionalization, and polymerization approaches to maximize the fraction of LCB that is converted to valuable products. We focus on major engineering challenges throughout the biorefinery, such as feedstock variability, process scale-up, and life-cycle management, to emphasize future directions that can optimize lignocellulosic biorefinery outputs.

2. FEEDSTOCK SELECTION

LCB biorefineries have enormous potential to manufacture next-generation fuels, chemicals, and materials, but the economic and life-cycle impacts of production, collection, transportation, and preprocessing of each feedstock must be considered to optimize productivity and mitigate social and environmental harms. For instance, the use of edible crops or unsustainable forestry practices to generate biorefinery feedstocks can result in food/resource competition, arable land-use concerns, deforestation, and biodiversity loss (39). Fortunately, many underutilized sources of waste LCB are available as feedstocks that are currently either landfilled, left to rot, or burned for energy (46, 47). Biomass in landfills adds to the volume of waste and emits greenhouse gases (GHGs) as it

GHG: greenhouse gas

decomposes. Specifically, landfills are the third-largest source of methane emissions in the United States, and because methane is a potent GHG with a 100-year global warming potential ∼27–30× that of CO_2, landfilling biomass can lead to significant environmental harm (48). Residues that are left in the field or composted add nutrients back to the soil, reduce fertilizer requirements, and mitigate soil erosion in future growing seasons, although not all the crop residues produced are required to achieve these benefits (39, 49). Incineration of biomass can be used to generate energy, but the process emits both GHGs and particulate matter that can contribute to global climate change and reduce local air quality (50). Thus, the use of these underutilized LCB wastes as feedstocks to generate value-added products is an opportunity to provide a more environmentally friendly and economically valuable end of life.

For an LCB feedstock to be both economical and sustainable, large volumes must be accessible to biorefineries at low costs and with minimal environmental harm. Regulatory measures can incentivize value-added uses for LCB wastes, such as laws in some US states that limit or ban incineration or landfill disposal of specific agricultural residues or yard wastes (51, 52). However, the sustainability of any biomass source depends on its collection method and the effect of its removal on the local ecosystem. LCB waste feedstocks, such as agricultural and forestry residues, food waste, municipal yard waste, and mixed plastics waste, are particularly promising because they are low cost and abundant, though each have their own advantages and limitations (39).

2.1. Agricultural Residues

Geographic variation is a key consideration for agricultural residues as each region and country has its own major crops. However, only a portion of any crop typically is used for food or industry, with the remainder typically burned, discarded, or left to decompose in the field (46). One of the most prevalent agricultural crops in the United States is corn, with ∼12 billion bushels/year produced, resulting in up to 100 million dry tons of corn stover available for collection (53); thus, many studies have focused on the generation of value-added materials from corn stover (46, 54, 55). **Table 1** provides additional agricultural waste projections in the United States for 2022. Globally, many other agricultural residues are generated in abundance from crops such as sugarcane (56, 57). Brazil is the global leader in its cultivation, and each ton of sugarcane processed results in 0.14 dry tons of sugarcane bagasse, nearly all of which is burned at sugar manufacturing facilities for heat (46). Incineration of bagasse yields just $15/ton in heat value but emits 0.75 tons

Table 1 Current availability and fate of lignocellulosic biomass waste streams in the United States

Waste stream	Volume available (dry tons/year)[a]	Price ($/dry ton)[a]	Current common end of life[a]
Corn stover	30–120 million	$40–80	Biofuels, left in field, or livestock feed
Sugar bagasse	4 million	$40–50	Burned at sugar manufacturing facility
Rice hulls	1.5 million	$40	Burned, landfilled, or used as a filter product
Wheat straw	8–17 million	$40–80	Left in field or bedding for livestock
Soybean hulls	3 million	$128	Livestock feed
Orchard and vineyard prunings	5–6 million	$20–30	Burned or left in field
Forestry residues	68 million	$30–50	Burned for energy generation or left in forest
Sawmill residues	4 million	$20–60	Burned for energy generation
Urban wood waste	6 million	$40–60	Burned or landfilled
Yard trimmings	3 million	$50–60	Landfilled or composted

[a] Agricultural residue and mixed waste stream information from Reference 46; forestry residue information from Reference 47.

of CO_2/ton of bagasse (58, 59). Other major globally produced agricultural residues include wheat straw (350 million tons/year) (56) and rice husks (600–900 million tons/year) (57). An additional underutilized agricultural residue is the inedible parts of drupes (e.g., endocarp and/or exocarp), such as nuts or coffee. These residues tend to have high lignin contents (above 40 wt.%) and significant valorization potential, but typically, they are either burned for energy or otherwise disposed (60, 61). Thus, there is significant opportunity to increase the value of these agricultural residues beyond their common uses (or nonuses).

MSW: municipal solid waste

2.2. Forestry Residues

Forestry residues are produced at each stage of processing in the lumber industry and include tree tops, branches, foliage, and understory brush left in the forest during logging, in addition to bark, wood cuttings, and sawdust burned for energy at sawmills (46, 62). These residues account for a significant portion of the total biomass: ~60% of the total felled tree mass is left in the forest, and ~50% of wood input to a sawmill becomes waste, meaning that <30 dry wt.% of felled tree mass is used to produce valuable goods (63, 64). Another source of forestry residues is forest thinning, a common practice employed to improve forest health in overstocked woodlands and reduce fire hazards in fire-prone locations like the western United States (65). The DOE funded the Waste to Wisdom project to address barriers in the generation of biofuels and biochar from the ~68 million dry tons/year of forest-thinning products available in the United States (47). The project's findings highlighted the negative consequences associated with the open burning of forest residues (e.g., reduced local air quality, increased forest management costs) and the importance of processing prior to transportation—key insights that can be applied beyond forest residues and biofuels to a broad range of LCB wastes and applications (47).

2.3. Mixed Waste Streams

Mixed waste streams [e.g., municipal solid waste (MSW)] are heterogeneous sources that include plastics, glass, metals, and LCB. Globally, ~2.01 billion tons of MSW were produced in 2018, and waste generation is projected to grow to ~3.4 billion tons/year by 2050 (66). With respect to the United States, MSW generally has a well-established collection system, and with the average landfill tipping fee estimated at $55.36/ton in 2019, MSW could be nearly universally available at a low cost for biorefineries (67). Differences in MSW composition are a function of local natural resources, culture, and social/economic development (68), but LCB-rich components, such as paper and paperboards, yard trimmings, natural textiles, food, and wood, make up ~63 wt.% of MSW, both in the United States and globally (66, 69). These mixed waste streams are currently underutilized, with only ~32.1 wt.% of the total MSW either recycled or composted in the United States in 2018 (69). Additionally, some LCB-rich MSW streams are collected separately and in bulk. For instance, yard wastes are generated at a rate of >20 million tons/year in the United States (69). Postconsumer or urban wood waste (e.g., old furniture) is another growing feedstock, with more than 6 million tons/year available in the United States; however, this feedstock would require additional pretreatment to remove coatings (i.e., paint and varnish), metal (i.e., nails and screws), and binders (i.e., in composite furniture) prior to valorization (46, 70). Some food waste also can be rich in LCB but is high in water content and has a relatively short lifetime in comparison to agricultural or forest residues (71). To incentivize the use of these underutilized wastes as biorefinery feedstocks, government policies can facilitate the transition away from landfilling or burning waste. For example, nine US states have implemented laws aimed at diverting food waste from landfills to mitigate groundwater contamination and reduce GHG emissions (71, 72). Similarly, 26 states have banned yard wastes from landfills to reduce landfill methane emissions (73).

2.4. LCB Feedstock Supply Variability

The lack of continuous supply is a major concern for waste LCB feedstock streams owing to seasonal availability. Agricultural residue supplies are impacted by harvest schedules, and forestry residue collection can depend on site access (39, 40). To further compound these issues, pricing and availability also are subject to factors such as extreme weather and disease (33). However, the price and availability of current feedstocks (i.e., petroleum and natural gas) are not immune to volatility and depend on factors such as global supply chains and regional instabilities. Proper inventory management is vital to petrochemical manufacturing, and biorefineries could adapt the optimization strategies employed in oil refineries to blend and schedule operations to ensure product quality and reduce costs year-round (74, 75). Improvements in long-term feedstock storage and flexibility in handling multiple feedstocks also could alleviate scarcity issues and maximize uptime (75, 76). Furthermore, LCB-based biorefineries could reduce our reliance on petroleum and enable a more distributed state of chemicals and materials manufacturing, resulting in a global market that is potentially less sensitive to supply/demand shocks, such as those resulting from war [e.g., the Ukraine conflict (77)] or pandemics [e.g., COVID-19 (78)].

Renewable: capable of being replenished by nature faster than consumed

3. TRANSPORTATION AND PREPROCESSING

The steps prior to LCB fractionation/deconstruction, such as collection, transportation, preprocessing, and storage, can contribute significantly to the ultimate price and environmental impact of the final products. TEA and LCA are essential tools to assess the impacts of transportation and preprocessing steps on the economic and environmental viability of waste feedstocks (40, 47, 64, 79). For instance, transportation costs were identified as the greatest obstacle in the use of uncollected forestry residues as fuel—a small, local electricity generation operation had 2.4-fold-lower GHG emissions than a larger station that required the forestry residues to be transported ∼4 h by truck (47). Moisture content is also a critical factor, as it adds weight in transport, shortens storage lifetimes, and requires an energy-intensive drying step prior to valorization (79). Drying forest residue prior to transport led to a 25–35% reduction in transportation costs via increased shipment throughput and storage lifetimes (40). However, the most energy-intensive step in a sawmill is kiln drying, which accounts for 27% of total sawmill GHG emissions, even when renewable energy is used (64). As such, air drying prior to transport is preferred, and once at a biorefinery or pulp/sawmill, air drying should still be prioritized over kiln drying to reduce energy use. The LCB must also be milled to improve yields, as higher surface areas increase heat and mass transfer (80). Small particle size is particularly important for the lignin fractions, as lignin is not readily soluble in water or most common organic solvents, and thus, particle size can be a limiting factor in the success of the subsequent valorization steps (81). Washing is another critical preprocessing step, as biomass contains dirt and rocks that can accumulate and obstruct industrial systems, such as in the Beta Renewables cellulosic ethanol biorefinery, where pretreatment issues resulted in a years-long complete processing overhaul (82). Together, these examples highlight the significant effect of the transportation and preprocessing steps on overall biorefinery environmental and economic performance, along with the utility of TEA/LCA for guiding decision making in biorefinery design.

4. FRACTIONATION AND DECONSTRUCTION

The fractionation and deconstruction methods used in a biorefinery significantly influence product distributions, required purification steps, and subsequent polymerization processes. As discussed above, there are numerous extractive pretreatment and active-stabilization methods to fractionate and deconstruct LCB (26, 28, 83, 84) (**Figure 2**). In addition to the primarily

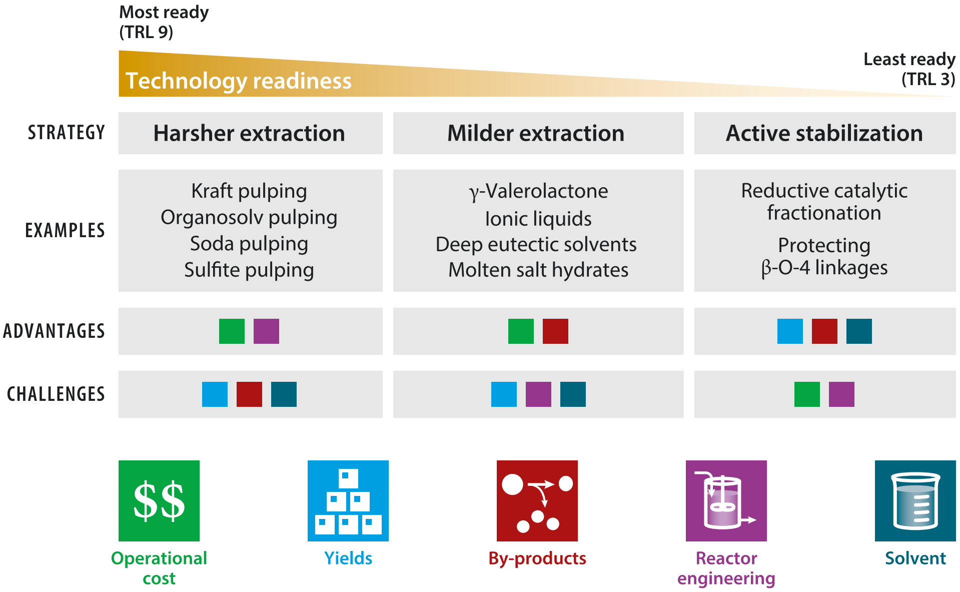

Figure 2

Comparison of historically harsher, industrial extraction; milder extraction; and active stabilization strategies for lignocellulosic biomass fractionation/deconstruction. The strategies are ranked based on the technological readiness scale (technology readiness level, TRL), in which TRL 9 indicates that the process has been proven effective in application, and TRL 3 indicates that the system is under active research and development (88). The major advantages and challenges of each method are indicated by colored squares. These are generic assessments, and individual readiness and pros/cons can vary within a given setup or process portfolio. Capital costs were not included in this analysis because they are highly variable and depend on plant-specific design considerations.

catalytic strategies highlighted herein, biological fractionation and deconstruction pathways are described elsewhere (85). Maximum conversion of all three major structural components to valuable products is key to the economic and environmental viability of lignocellulosic biorefineries, but the primary objective of the biorefinery (e.g., whether to manufacture specific materials/fuels/chemicals, use a particular feedstock, maximize profits, or minimize GHG emissions) will inform the choice of approaches (6, 24–26). Extractive pretreatment methods have been implemented historically when carbohydrates are the target for synthesizing valuable goods, but they struggle to balance lignin monomer yields and recalcitrance (26, 83, 84). Conversely, active stabilization procedures have been developed with lignin as a primary target along with the carbohydrates (7, 27), but the ultimate effect of such methods on the upgradability of the carbohydrate pulps is less understood. For example, RCF pulp was found to have higher apparent degrees of polymerization and higher xylan retentions than organosolv pulp, but additional work noted that RCF oil residue remaining in the pulp inhibited many of the industrially relevant microbes for enzymatic bioethanol production (86, 87). Thus, further research is needed to fully understand the impacts of active stabilization on the subsequent use of the carbohydrate pulp.

Regardless of the ultimate fractionation and deconstruction methods used in a biorefinery, numerous process design and scale-up considerations can affect the products, yields, economics, and sustainability of each approach. At laboratory scales, batch fractionation and deconstruction work well, but adaptation of these techniques to continuous or semicontinuous modes [i.e., flow-through (FT) strategies] enables time-resolved data collection, facile control of catalyst contact

FT: flow-through

time, and minimization of condensation and other side reactions (33–35). Additionally, increasing throughput (i.e., reducing the solvent-to-biomass ratio) and reducing solvent consumption in batch systems introduces mixing and mass transport challenges owing to the increased viscosity of the reaction mixtures. On the other hand, FT reactors can be more easily scaled for higher throughput and can minimize solvent consumption through more straightforward solvent recovery (25). One such advance is a multi-pass FT-RCF system to reduce the solvent loading relative to traditional FT-RCF from 48 to 1.9 L/kg—a 96% solvent reduction—without impacting lignin deconstruction yields (89). Mass and heat transport effects, reaction kinetics, and thermodynamics also have been evaluated with respect to LCB biorefinery scale-up (25, 80, 90). As one example, a kinetic investigation of batch and FT-RCF setups found both the activation barriers and the mass-transfer limitations, which are critical reaction engineering parameters for process design and scale-up, to identify the limiting step of the reaction (91). Further considerations include impurities, by-products, and processing solids that can poison catalysts, damage pumps, and clog pipes/filters. For instance, sulfur will poison metal catalysts like those used in RCF, and furfural, a common derivative of sugar degradation, can shorten catalyst lifetimes; thus, robust and reusable catalysts (e.g., those with more stable supports or improved chemical stability at reactor operating conditions) can minimize both catalyst costs and reactor downtime (80, 92). Finally, the generation of recalcitrant by-products (i.e., condensed lignin fractions and humins) can be mitigated through active stabilization or milder reaction conditions (26, 93). Dimeric, oligomeric, and macromolecular residues are also by-products (as the monomeric compounds are the desired products for polymerization), but these by-products can be converted to valuable materials, as discussed in Section 7.2. Although by-product formation is unavoidable (i.e., the theoretical yield of monophenolics is ∼20–60 mol.%, depending on the feedstock) (25, 27, 94), process decisions should target the theoretical yield to maximize the generation of the most valuable products, mitigate the formation of unwanted by-products, reduce costs, and minimize environmental impacts.

S: syringyl

G: guaiacyl

H: *p*-hydroxyphenyl

HT: high-throughput

5. CHARACTERIZATION

Rapid and reliable characterization is critical to LCB biorefineries because of the significant compositional variations among feedstocks and their subsequent deconstruction products. LCB is composed of cellulose, hemicellulose, and lignin that are composed primarily of glucose units; pentose and hexose units; and the aromatic syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) subunits, respectively (**Figure 3**). The quantity of these components and their subunits can vary by species [e.g., softwoods are dominated by G units; hardwoods contain S and G units; and herbaceous biomass contains S, G, and H units (28, 95)] and the plant's age [e.g., juvenile Chinese pines have a 4 wt.% higher cellulose content and a 2 wt.% lower lignin content than adult Chinese pines (42)]. The plant tissue also can significantly affect the LCB composition. For instance, yellow poplar bark, twigs/branchlets, and leaves contain 57.8, 28.6, and 25.7 wt.% of lignin, respectively (43). The fractionation/deconstruction method and reaction conditions add further variability to the subsequent product distributions and yields (7, 27, 33). As biorefineries aim to handle multiple feedstocks, each with their own compositional variability, the need for accurate, consistent, low-cost, and high-throughput (HT) (i.e., capable of quickly screening large numbers of samples) characterization is paramount to ensure maximum uptime, optimized economics, and quality assurance (96).

5.1. LCB Composition Characterization

Complete characterization of LCB requires complementary strategies that can provide detailed structural and/or chemical information on all LCB components. The current standard for lignin

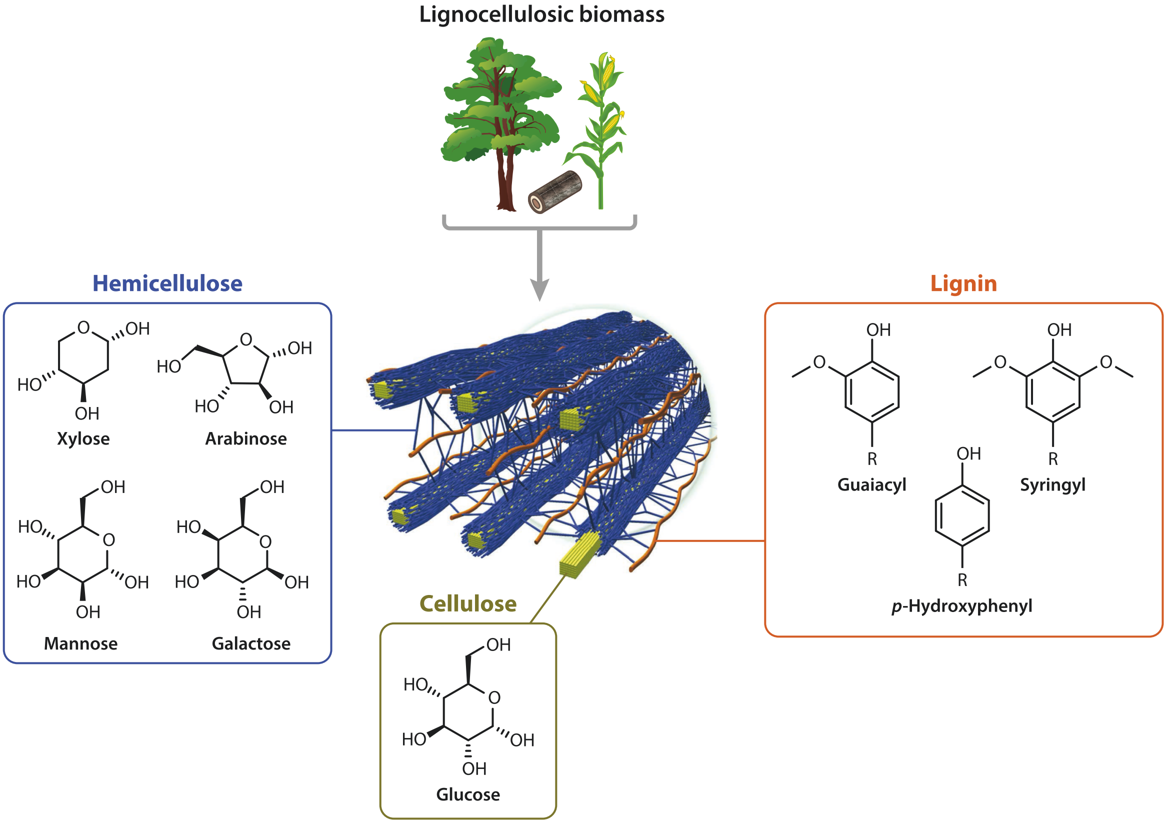

Figure 3

Lignocellulosic biomass is composed of three main components: cellulose, hemicellulose, and lignin. The primary components of lignin are guaiacyl, syringyl, and *p*-hydroxyphenyl units. The major constituents of hemicellulose are pentoses and hexoses, including xylose, arabinose, mannose, and galactose. The monomeric units of cellulose are glucose. The quantities of each component and their respective subunits are influenced by numerous factors. Middle image adapted from the US Department of Energy Genomic Science Program (**http://genomics.energy.gov**).

and carbohydrate quantification is a summative method published by the National Renewable Energy Laboratory (NREL) in a lab analytical procedure (LAP) (97). The LAP includes sample drying, moisture analysis, and extractive removal prior to a two-step sulfuric acid hydrolysis to fractionate carbohydrates and lignin (97). Lignin is analyzed via the Klason method, in which it is separated into acid-soluble and acid-insoluble fractions that are measured by UV-vis spectroscopy and gravimetric analysis, respectively. Cellulose and hemicellulose are hydrolyzed into monomeric sugars and characterized by high-performance liquid chromatography (HPLC) to determine the relative amounts of glucans (i.e., cellulose) and other sugars (i.e., hemicellulose). The NREL LAP provides excellent repeatability and accuracy across a wide range of woody biomass sources, but it has increased error in samples with higher amounts of nonstructural components (e.g., proteins and extractives in agricultural residues and foliage), requires higher sample volumes, generates significant amounts of chemical waste, and is time-consuming relative to other characterization methods (97, 98). Despite its limitations, the NREL LAP is the "gold standard" for LCB characterization (25), and as these measurements are used as a benchmark across feedstock options and fractionation/deconstruction strategies, alternative characterization approaches must maintain similar levels of accuracy and reliability (**Table 2**).

NREL: National Renewable Energy Laboratory

LAP: lab analytical procedure

HPLC: high-performance liquid chromatography

Table 2 Overview of common feedstock characterization approaches

Characterization method	Pros	Cons	Reference
NREL LAP	- Accurate, consistent, and reproducible for woody biomass - Widely used as a benchmark - Most comprehensive characterization of lignocellulosic biomass	- Increased error for nonwoody biomass - High sample volumes - Time consuming - Large amounts of chemical waste	97
Modified NREL LAP	- Improved accuracy and consistency for a range of feedstocks	- Increased error for nonwoody biomass - High sample volumes - Time consuming - Large amounts of chemical waste	99–100
Thermogravimetric analysis	- Accurate and consistent for carbohydrate contents - Small sample size - Automated - Minimal waste generated	- Limited accuracy and consistency for lignin contents - Limited structural information beyond component contents - Degradative method, increasing error - Limited range of biomass - Relies upon quality and breadth of calibration model	102–104
Analytical pyrolysis	- Detailed structural information - Small sample size - High throughput - Minimal waste generated	- Degradative method, increasing error - Limited range of biomass - Limited structural information beyond component contents - Relies upon quality and breadth of calibration model	106
Heteronuclear single-quantum coherence NMR spectroscopy	- Detailed structural information - Small sample volume - Accurate and consistent - Small sample size - Minimal waste generated	- Cannot provide absolute quantifications (except for isolated lignins)	109, 112
^{31}P NMR spectroscopy	- S/G/H ratio quantification - Accurate and consistent - Small sample size - Minimal waste generated	- Time consuming (due to the required phosphitylation prior to experiments) - Prior fractionation increases error	113, 114
Infrared spectroscopy	- Detailed structural information and component quantification - Small sample size - High throughput - No waste generated	- Relies upon quality and breadth of calibration model	115, 116

Abbreviations: LAP, lab analytical procedure; NMR, nuclear magnetic resonance; NREL, National Renewable Energy Laboratory; S/G/H, syringyl/guaiacyl/*p*-hydroxyphenyl.

Modifications to the NREL LAP have been proposed to improve accuracy and consistency for a range of feedstocks. For instance, an alternative to the Klason lignin method is an acetyl bromide route that is faster and provides improved reproducibility in low-lignin-content samples (99). Additionally, a cysteine-assisted sulfuric acid procedure adds cysteine to the Klason hydrolysis mixture to improve lignin solubility and the accuracy of total lignin quantification (100). Gas chromatography (GC) also can be substituted for HPLC to identify and quantify sugars quickly, but an

GC: gas chromatography

extra reduction and acetylation step is required prior to analysis, leading to reduced throughput and increased labor intensity (101). Each of these modifications is beneficial for particular aspects of LCB characterization, but all are constrained by the same limitations associated with the unmodified LAP. Hence, equally reliable methods with improved throughput and efficiency must be developed for LCB biorefinery optimization.

TGA: thermogravimetric analysis

py-MBMS: pyrolysis–molecular beam mass spectroscopy

HSQC: heteronuclear single-quantum coherence

NMR: nuclear magnetic resonance

FTIR: Fourier transform infrared

NIR: near-infrared

Indirect methods are promising to screen and characterize LCB samples quickly. For example, thermogravimetric analysis (TGA) is commonly used to investigate the kinetics of biomass pyrolysis and gasification, and recent work has expanded its scope to quantify cellulose, hemicellulose, and lignin in LCB (102–105). These efforts have successfully determined absolute cellulose and hemicellulose content, but they have either provided only relative amounts of lignin between samples, overestimated lignin quantities, or applied only to specific biomass types (103–105). Additionally, component quantifications using TGA-based methods rely on kinetic models in which the parameters (e.g., activation energies) can vary significantly, particularly for lignin, and often provide variable results (102). Analytical pyrolysis [e.g., pyrolysis–molecular beam mass spectroscopy (py-MBMS)] strategies are similar to TGA-based methods, but py-MBMS can characterize lignin and carbohydrate structures rapidly by directly identifying their pyrolysis products (106). Yet, both TGA and analytical pyrolysis approaches are degradative and therefore result in chemical alteration of biomass structural components (25). Specifically, thermal decomposition can lead to the formation of recalcitrant components and not release all polymeric subunits equally, resulting in increased compositional error or biased results for certain types of biomass (e.g., softwoods versus hardwoods) (94, 96). TGA and analytical pyrolysis are straightforward techniques that require little sample preparation and generate minimal waste. However, because they are indirect methods, further refinement of the underlying models or modification of the methods to incorporate reactive intermediate stabilization strategies [e.g., formaldehyde-assisted stabilization, catalytic analytical pyrolysis (107, 108)] could improve accuracy and repeatability and could significantly expand their applicability to additional biorefinery-relevant inputs.

5.2. Detailed Structural Information of Lignocellulosic Biomass

Spectroscopic approaches can elucidate structural information beyond the quantification of cellulose, hemicellulose, and lignin. Heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR) spectroscopy measures correlations between ^{1}H and ^{13}C spectra and provides qualitative information about biomass structure and composition, such as relative amounts of lignin interunit linkages (109, 110). HSQC NMR spectroscopy experiments are noninvasive (i.e., no fractionation and/or deconstruction is necessary) and thus can be employed to probe native LCB structures. However, a major limitation is that absolute quantification of lignin composition (i.e., S/G/H ratios) is challenging because differences in relaxation times cause end and pendant groups to be overcounted and backbone units to be undercounted (111). Use of gradient-selective HSQC$_0$ NMR spectroscopy could eliminate relaxation time errors, although further research is needed to apply this technique to whole biomass samples in addition to isolated lignins (112). A quantitative alternative to HSQC NMR spectroscopy that can determine lignin composition is ^{31}P NMR spectroscopy; however, this approach requires fractionation and lignin phosphitylation prior to the experiment, increasing time and labor intensity, and risking structural alterations during fractionation (113, 114). Other common methods to elucidate LCB structural information are Fourier transform infrared (FTIR) and near-infrared (NIR) spectroscopy. For example, FTIR spectroscopy has been employed to estimate both interunit linkage abundance and molecular weight in technical lignins (115), and NIR spectroscopy has been used to measure lignin, glucan, xylan, and ash composition (116). IR spectroscopic measurements are fast and require only several milligrams of sample, and they can discern detailed structural information through identification of key functional groups. IR spectroscopy methods rely on models built with data collected via other techniques; thus, their predictive capabilities rely upon the quality and breadth of these models (116). For instance, a multi-feedstock NIR spectroscopy model provided similar or improved accuracy in the determination of glucan, xylan, and lignin content for a broader range of feedstocks in comparison to an analogous single-feedstock model (116). Together with the methods described in the previous subsection to quantify the high-level composition of LCB, these strategies to elucidate finer structural details of lignin fractions, such as interunit linkage distributions or S/G/H ratios, can provide invaluable information for biorefinery operations. Although future work should focus on increasing consistency and throughput for a diverse set of LCB feedstocks, these spectroscopic approaches could inform decisions around feedstock selection and blending, biorefinery operating parameters, and output management.

MS: mass spectrometry

LC: liquid chromatography

FID: flame ionization detector

5.3. Characterization of Deconstruction Products

Despite significant overlap between the methods used to characterize biomass feedstocks before and after deconstruction, additional obstacles arise in the complete characterization of complex and heterogeneous LCB deconstruction product mixtures. In the lignin bio-oil, the liberated monophenolics can be identified via GC-mass spectrometry (MS) or liquid chromatography (LC) and then quantified via a GC-flame ionization detector (FID) (25). Some dimers can be identified/quantified with GC-MS/FID, but other techniques are needed to analyze larger dimers and oligomers. For instance, more than 50 dimers and trimers in RCF bio-oil were identified through a high-temperature 2D-GC × GC-MS/FID system (117). This approach can be applied to other fractionation products and expanded to identify more small oligomers, but in general, trimers and larger oligomers in the bio-oils are more challenging to conclusively identify and quantify (118). These oligomeric or macromolecular products instead can be analyzed like synthetic polymers or technical lignins—gel permeation chromatography can determine molecular weight distributions, and NMR spectroscopy can identify the types of interunit linkages remaining in these fractions to elucidate the effects of deconstruction on their chemical structures (13, 117).

Characterization of deconstruction products should account for intended downstream use cases. For example, the carbohydrate pulps and hydrolyzed sugars from deconstruction processes can be identified and quantified using the same HPLC or GC techniques employed for whole LCB characterization (119), but residual lignin-derived monophenolics, dimers, and oligomers can add complexity for downstream uses. The presence of these lignin deconstruction products may not be captured by using standard carbohydrate characterization strategies, and biorefineries that intend to generate biofuels from cellulosic pulps would need to conduct additional digestibility studies with commercial cellulase cocktails to determine if residual deconstruction products interfere with the generation of ethanol or other fermentation-based targets from the pulp (120). Significant developments have been made in the characterization of heterogeneous LCB deconstruction mixtures, especially with respect to small-molecule components; however, efforts to better characterize macromolecular deconstruction residues and leverage that information to translate these products to high-value applications could significantly improve biorefinery economics.

5.4. High-Throughput and Inline Characterization Opportunities

As biorefineries scale up, HT characterization approaches are needed to quickly evaluate new feedstocks and ensure batch-to-batch consistency (98). Highly specialized techniques, such as 2D GC or advanced NMR spectroscopy (e.g., HSQC or ^{31}P NMR spectroscopy), may not be suitable for biorefinery labs because they are expensive and require significant expertise for operation and data analysis. Several of the previously discussed approaches are good candidates for HT characterization strategies (e.g., py-MBMS, FTIR/NIR spectroscopy, NMR spectroscopy) because they are fast, use small sample volumes, and generate minimal waste (98, 121). For example, an estimated 250 and 350 samples/day could be run in triplicate with py-MBMS and NIR spectroscopy, respectively (98). Alternatively, increased automation of wet-lab steps can increase reproducibility and reduce labor intensity. For instance, automation of the NREL LAP has been investigated with a claimed throughput of up to 100 samples/day; however, this automated system measured only the carbohydrate content, not lignin content, and still generated relatively large amounts of chemical waste versus other characterization strategies (122). Recent developments in HT methods have been reviewed for biomass characterization (98), but further efforts are required to ensure that accuracy and consistency are maintained as these approaches are scaled up to characterize a diverse range of possible biorefinery feedstocks.

TRL: technology readiness level

Inline characterization methods are also valuable for LCB biorefineries because they offer real-time measurements that can be leveraged for proactive process control and optimization. Spectroscopic techniques, such as FTIR spectroscopy, are commonly used in petrochemical manufacturing to control and/or optimize blending, monitor chemical reactions, and ensure product quality (123). Similarly, NIR spectroscopy has been deployed to automate plastics sorting at recycling centers (124). Analogous approaches could be implemented in biorefineries to improve safety, economics, and energy efficiency (125, 126). For example, IR spectroscopy could screen feedstock compositions for LCB entering the biorefinery (116), and inline IR spectroscopy or other real-time analytical techniques could be leveraged to monitor deconstruction progress and implement robust process control systems (98, 117). In conjunction with HT characterization strategies, inline monitoring enables the closing of mass/mole balances, prediction of polymer properties, and management of biorefinery outputs (127).

6. PRODUCT PURIFICATION

Product purification is an essential, but often energy-intensive, step in many industrial operations (128). Chemical separations accounted for up to 22% of all industrial energy use in the United States in 2005, primarily from distillation, evaporation, and drying steps (129). Major separations technologies for LCB biorefineries are shown in **Figure 4**, along with key considerations for the overall economic and environmental impacts of each. Technology readiness levels (TRL) ranging from 1 (i.e., scientific research is started) to 9 (i.e., application of the technology) demonstrate the industrial maturities of the techniques as applied specifically to LCB biorefineries (88). In addition to the technological readiness of the unit operation, the fractionation/deconstruction methods chosen significantly impact the composition of the output streams to be purified. Lignin-first deconstruction approaches produce a bio-oil with high lignin phenolic content, an aqueous phase rich in sugars, and a solid polysaccharide pulp. Traditional carbohydrate-first extractions prioritize the generation of the solid cellulose pulp, resulting in a liquid phase with solubilized technical lignin and some hydrolyzed sugars. The solid pulps and liquid phases can be separated through a simple filtration step, but further purification to isolate components of interest [e.g., aromatics from lignin-first bio-oils, technical lignins from cellulose-first liquor streams (130, 131)] is required for many high-value applications, especially in the polymer space. Given the complex and variable nature of LCB product mixtures, the isolation of specific targets or groups of compounds can prove challenging and require multiple unit operations (24). Thus, separations techniques with low costs, low energy inputs, and high yields of valuable or upgradable compounds are essential to improve biorefinery viability.

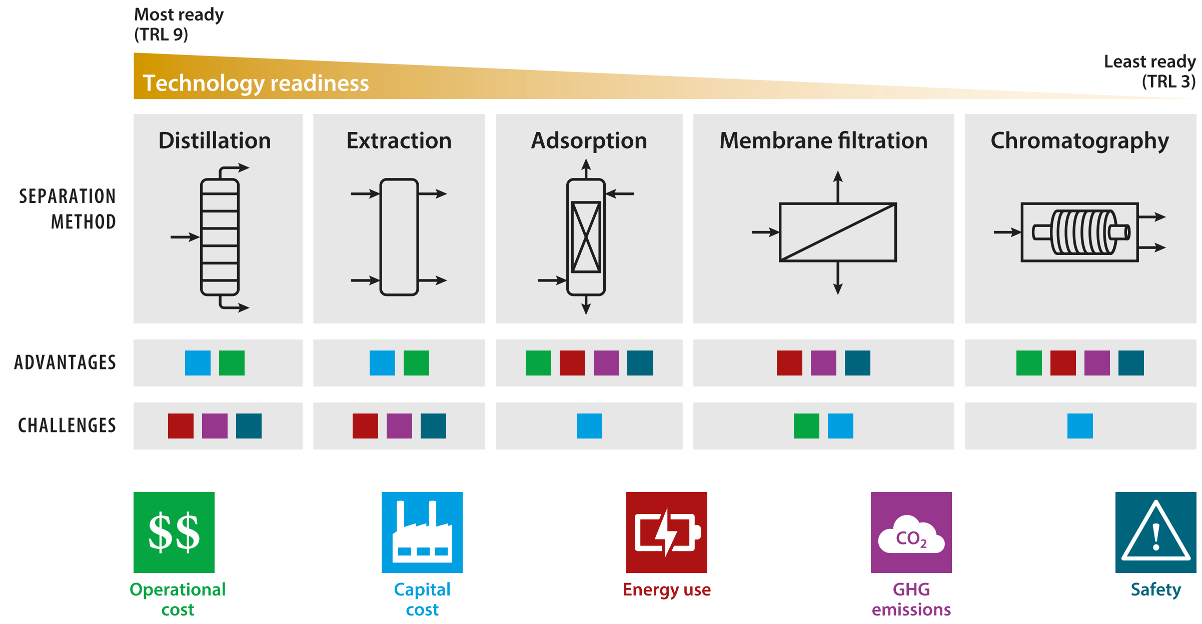

Figure 4

Major separations methods—arranged from most to least industrially ready for specific application in lignocellulosic biomass biorefineries, based on the technological readiness scale. The major advantages and challenges of each method are indicated by colored squares. These are generic assessments, and individual readiness and pros/cons can vary within a given setup or process portfolio. Abbreviations: GHG, greenhouse gas; TRL, technology readiness level.

6.1. Separation by Volatility

Distillation is a common industrial unit operation that is employed to separate compounds based on differences in volatility. For example, distillation of crude oil is an initial step in oil refining, and this operation is used extensively in upstream and downstream petrochemical processing. Distillation also has been implemented in cellulosic ethanol biorefineries to recover ethanol from fermentation broth (132). Yet, despite its widespread use, distillation is particularly energy intensive—in a model RCF biorefinery, solvent recovery via distillation accounted for 83% of the facility's total heat demand and 35% of the total operating costs (24). Furthermore, effective separation of biobased mixtures often requires vacuum distillation because many bio-derived products have relatively low thermal stabilities and high normal boiling points, leading to increased capital and operating costs for biorefinery distillation systems (133). Together, the high energy demands and operating/capital cost of distillation necessitate the development and scale-up of more cost- and energy-efficient separation units for biorefinery operations.

6.2. Separation by Solubility

Liquid–liquid extraction (LLE) relies on miscibility and solubility differences between components of a mixture. LLE commonly uses organic and/or aqueous solvents to selectively extract target compound(s). For example, bio-oil can be first extracted with dichloromethane and water to separate sugars and sugar derivatives from lignin-derived components and then washed with hexanes to separate nonpolar monophenolics and oligomers from more polar components (134), with the following caveat. The choice of extraction solvent is important to the overall cost, sustainability, and safety of LLE-based systems. Aqueous extractions are safe and low-cost separations but

LLE: liquid–liquid extraction

CCC: countercurrent chromatography

MF: microfiltration

generally are not selective enough to isolate high-purity products from bio-derived mixtures (135). Conversely, organic solvents or solvent mixtures can be more selective, but toxicity, flammability, and recovery concerns can hinder the feasibility of large-scale LLE unit operations (136). Also, LLE often requires multiple stages and large volumes of solvent, necessitating energy-efficient solvent recovery in the scale-up of such separations. ILs have been studied to address the safety concerns associated with traditional extraction solvents, but similar to the case in other IL-based fractionation techniques, economic limitations remain due to the high costs of ILs and the difficulties associated with their recovery (137). Supercritical fluids (e.g., supercritical CO_2) also have been explored as extraction solvents that generally achieve high product yields (138), but these extractions require high temperatures and pressures that result in increased environmental and energy costs.

Production-scale LC is a relatively inexpensive approach that primarily separates compounds in a mixture according to affinity for a solid stationary phase, but it has low volume throughput and is susceptible to irreversible adsorption (i.e., fouling) and clogging (136). Clogging/fouling are especially problematic for bio-oil purification because the mixtures are complex and can contain numerous impurities, such as char, catalyst particles, and other insoluble components [e.g., silica in corn stover (139)]. Countercurrent chromatography (CCC) addresses these issues because both the stationary and mobile phases are immiscible liquids, with the stationary phase being held in place using centrifugal force. Similar to conventional chromatography with a solid stationary phase, separation occurs along the length of the column based on affinity. CCC differs from simple LLE in that it is a true chromatographic separation—holding the liquid stationary phase in place via centrifugation is essentially equivalent to using a solid phase in a conventional column. CCC is low-cost and scalable in comparison to traditional column chromatography, and it is suitable for bio-oil separations because it can operate continuously with large volumes of product and handle solids in the feed (140). Subcategories of CCC include hydrodynamic CCC (i.e., elution-extrusion and dual-mode chromatography) and hydrostatic CCC (i.e., centrifugal partition chromatography) (141), which differ in their stabilization geometries but operate on similar chromatographic principles. Although LC techniques are common in the pharmaceutical industry [e.g., to separate charged biological molecules such as proteins and nucleotides (142)], they generally are absent from biomass processing. However, a recent strategy implemented a two-stage centrifugal partition chromatography system to effectively isolate monophenolics from an alkaline oxidative lignin deconstruction product mixture (141). Vanillin, syringic acid, and acetovanillone were recovered from the mixture with yields of 82, 86, and 91 wt.%, respectively, in the first stage and 72, 81, and 87 wt.% in the second stage (141). In another study, a predictive model for hydrodynamic CCC was leveraged to optimize operating and intrinsic CCC parameters to predict elution times for bio-oil components, leading to increased selectivity, yield, and throughput (143). Similar models can be extended to other CCC modes and LCB deconstruction mixtures to further increase the yields, purity, and diversity of isolated products, and a complete TEA/LCA analysis of CCC could be used to identify key areas for further optimization.

6.3. Separation by Membrane Filtration/Solid Adsorption

Membrane-based separation units are known for their high separation efficiency, low energy usage, and mild operating conditions. As a nonthermal separations method, membrane purification typically results in significant energy savings relative to distillation approaches (e.g., an estimated 90% in a petroleum refinery) (128). Two important design parameters for membranes are their pore size [i.e., microfiltration (MF), nanofiltration, or ultrafiltration] and gross composition (i.e., ceramic or polymeric). Multistage filtrations have used membranes of different sizes and materials to maximize separation efficiency and facilitate scale-up. For example, a polymeric MF membrane in series with a ceramic MF membrane can effectively purify an aromatic-rich bio-oil from an alkaline pretreatment process (139). The polymeric MF removed solid particles from the inlet stream, and the ceramic MF achieved a sixfold enrichment of phenolic components and rejected 98.5% of high-molecular-weight species (>1,000 Da) (139). The above filtration systems are still susceptible to fouling issues that decrease throughput and device lifetimes, and membrane costs are significant, accounting for up to 60% of the total major operating expenses in the separation of compounds from lignin bio-oil (139). Fortunately, filtration system geometry can reduce foulant buildup to enable improved throughput, longer membrane lifetime, and continuous operation (139, 144, 145). For instance, high flow rates in cascading tangential-flow filtration arrangements can ameliorate fouling concerns by reducing cake formation on the membrane surface (144). Similarly, hydrodynamic filtrations, such as rotating-disk membranes, can be employed for streams with high solid loadings to mitigate fouling (139). In one salient example, replacing a cellulose triacetate fixed-disk membrane with a similar rotating-disk membrane to recover technical lignin from Kraft black liquor increased the steady-state flux by 60% and reduced the change in flux from startup to steady state significantly—18 to 13 L/(m^{2}h) for the fixed disk (~28% reduction) versus 24 to 23 L/(m^{2}h) for the rotating disk (~4% reduction) (145). The improved performance via reduced fouling was expected to increase membrane lifetimes and lower the costs associated with membrane-based unit operations (145).

Finally, solid adsorption can separate numerous compounds from biorefinery liquid product streams based on their affinity for a solid substrate. For instance, 5-hydroxymethyl furfural was adsorbed selectively from aqueous sugar streams using a fixed-bed column with polymer-based spherical activated carbon beads (146). The column was cycled through adsorption and desorption steps seven times without a loss of selectivity, highlighting the potential for long-term operation (146). In cellulosic ethanol biorefineries, vapor-phase, molecular-sieve adsorption facilitates the dehydration of the ethanol beyond what could be achieved by ambient pressure distillation alone (i.e., the azeotropic composition) (132). Solid adsorption is also a scalable separations approach—it is employed in large-scale coffee decaffeination through the Swiss water process (147). Adsorption-based methods show great potential as emerging cost- and energy-efficient biorefinery unit operations, but adsorption strategies have been applied mostly to polysaccharide derivatives (132, 146). Additional studies to apply selective adsorption to more complex LCB deconstruction streams (e.g., RCF or pyrolysis oils) or design selective, multistage adsorption operations to isolate the many compounds of interest from LCB deconstruction products could facilitate the development of adsorption-based approaches for biorefineries.

7. POLYMERIZATION

Carbohydrate and lignin deconstruction products or by-product residues (e.g., aromatic dimers, trimers, larger oligomers) can serve as monomers or monomer precursors to facilitate the conversion of LCB into valuable, high-performance polymers (**Figure 5**). These macromolecules can be either drop-in replacements for petroleum-derived polymers or structurally distinct materials with unique and advantageous characteristics. Drop-in replacements tend to be easier to translate to industry because they are compatible with existing infrastructure (148); however, renewably sourced monomers often are more expensive to produce than their petrochemical analogs due to the scale and optimization of petrochemical manufacturing (149, 150). Government policies (e.g., carbon taxes) or high oil prices could improve the economic outlook for drop-in replacements (151), but without these favorable conditions, sustainability is likely not enough to incentivize widespread commercial adoption. For example, (bio)polyethylene prepared from cellulosic ethanol is chemically identical to petroleum-derived polyethylene, but its significantly higher market price [~\$1,900–2,000/ton versus ~\$600–1,300/ton in the United

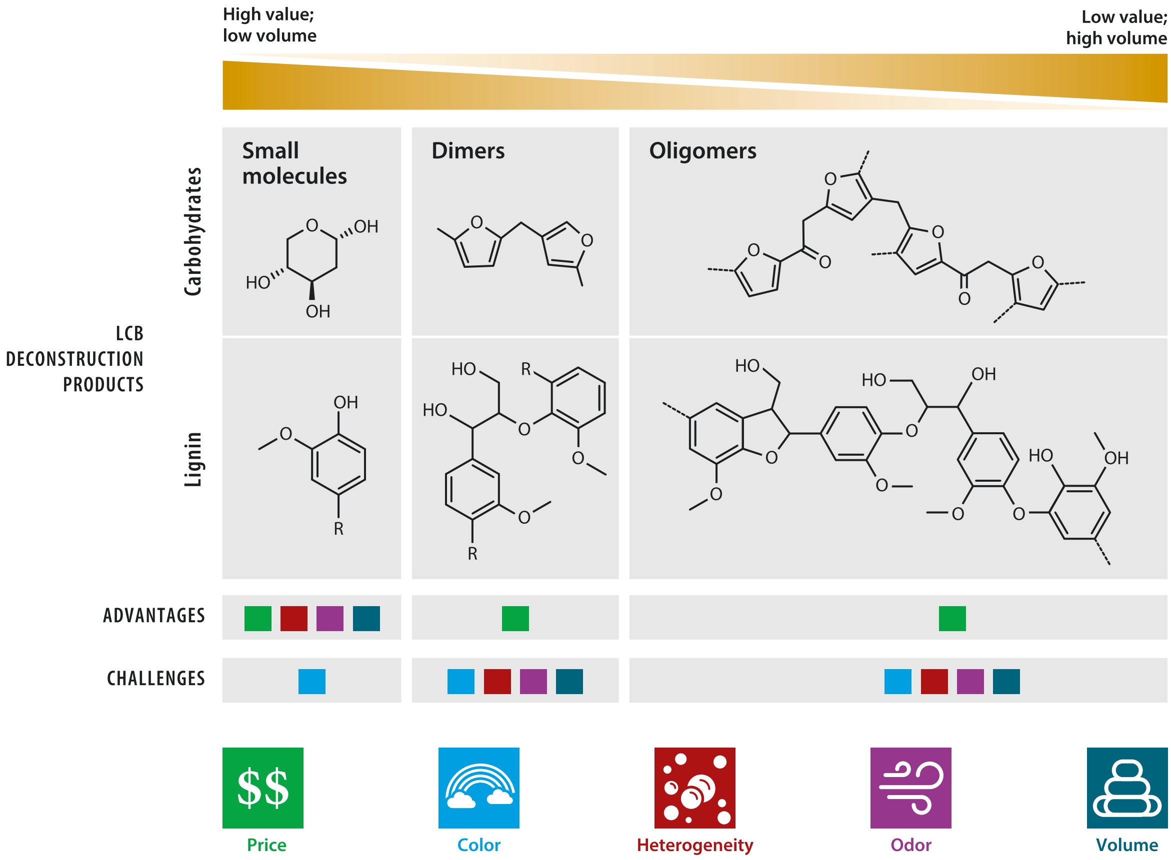

Figure 5

Lignocellulosic biomass (LCB) deconstruction products (e.g., small molecules, dimers, oligomers) and the advantages and limitations of their use in polymer synthesis. Note: The molecules shown are not representative of all possible deconstruction products, and specifically for lignin, examples are from a softwood (i.e., guaiacyl unit–rich) feedstock. Small molecules are inherently more valuable because they can be converted to higher-value materials, but oligomeric residues are available at lower costs in large quantities (25, 27, 94). The major advantages and challenges of using each deconstruction product to synthesize polymers are indicated by colored squares.

States (152)] limits its commercial potential. On the other hand, structurally unique bio-derived materials often are incompatible with existing manufacturing infrastructure and also tend to cost more than petrochemical-based materials, but application-specific performance advantages (e.g., improved thermal or mechanical properties, increased recyclability or degradability, enhanced safety profile) can help to overcome these barriers and facilitate large-scale market adoption (149, 150). For instance, poly(ethylene furanoate) (PEF) is a biobased polyester with improved barrier properties versus poly(ethylene terephthalate) (PET) [e.g., 10× and 20× higher barrier improvement factors for O_2 and CO_2, respectively (131, 153)], and the use of PEF in multilayer packaging applications is growing rapidly, though its cost likely will remain higher than the price of PET as PEF production ramps up [\$4.62–5.27/kg for PEF versus \$0.72–0.95/kg for PET projected from 2022–2027 (154, 155)]. Thus, biobased materials with clear performance and/or market advantages are critical for biorefinery profitability and may need to be prioritized, especially for refined small-molecule deconstruction products and their derivatives. Macromolecular deconstruction by-products (e.g., dimers, trimers, oligomers) also must bring supplementary

PEF: poly(ethylene furanoate)

PET: poly(ethylene terephthalate)

revenue streams to future biorefineries to ensure economic viability (22, 156). Similar to the small-molecule deconstruction products, performance-advantaged materials should be pursued whenever possible; however, additional, lower-value product streams are useful, as the use of all feedstock components can diversify revenues and ensure that minimal LCB goes to waste.

PSA: pressure-sensitive adhesive

Derivable: capable of being derived from a particular feedstock or class of feedstocks (e.g., bio- or lignin-derivable)

T_g: glass transition temperature

BPA: bisphenol A

7.1. Polymers from Small-Molecule Deconstruction Products

Functionalization of LCB deconstruction products enables the manufacturing of a wide range of high-performance polymers that can be attractive biorefinery targets. Deconstruction results in mixtures of compounds that tend to be rich in hydroxyl and carboxylic acid functional groups, and these chemical moieties can be leveraged to provide useful handles for various polymerization schemes, as highlighted in recent reviews (23, 157). One common route leads to lignin-derived (meth)acrylate monomers via the reaction of the phenolic hydroxyl group with (meth)acryloyl chloride or (meth)acrylic anhydride (7, 130, 158, 159). These acrylic monomers have been implemented in a triblock pressure-sensitive adhesive (PSA) that exhibited superior thermal stability (50°C-higher degradation temperature), comparable adhesive properties (3.1 and 2.2 N/cm 180° peel force and tack force, respectively), and a competitive minimum selling price ($6,000-$8,000/ton) versus a commercially available tape (7, 130). PSAs also have been synthesized from sugar derivatives, such as acrylated isosorbide, and similarly exhibited improved thermal performance (again a 50°C-higher degradation temperature) and similar mechanical performance (peel and tack forces of 2.9 and 3.2 N/cm at 180°, respectively) versus a commercial incumbent PSA (8, 130). Acrylated lignin-derived phenolics also have been used to synthesize mechanically robust, photocured polymers that were 3D printed. The prints had high storage moduli and tensile strengths relative to a commercial 3D-printing resin [3.4 GPa versus 2.2 GPa at 25°C and 62 MPa versus 33 MPa at the glass transition temperature (T_g) + 50°C, respectively], due to increased resistance to chain deformation and network breakage imparted by the aromatic moieties (9). Aside from acrylic monomers, LCB-derived small molecules have been converted to functionalized styrenic monomers via scalable synthetic routes [e.g., decarboxylation of lignin-derivable ferulic acid to 4-vinylguaiacol (11)]. These compounds produced polymers with comparable thermomechanical properties to petroleum-derived analogs (e.g., T_g of 110°C versus 100°C for styrene), with the additional advantages that the monomers are less volatile and anticipated to be less toxic than styrene (10, 11).

Individual deconstruction products also can be coupled to form larger monomers, such as alternatives to bisphenol A (BPA), synthesized through direct condensation of hydroxybenzyl alcohols with other phenolic compounds (160) or via the acetone- or formaldehyde-based coupling of monophenolic units (161). These alternatives potentially offer significant health advantages (e.g., 100× lower estrogenic activity than BPA), owing to bulkier substituents (methoxy or alkyl groups) on the aromatic rings that disrupt binding to estrogen receptors (162). Lignin-derivable alternatives can be used in many of the same applications as BPA [or other possibly toxic bisphenols (e.g., bisphenol F)] and can be cost competitive, especially in the context of consumer demands to replace petroleum-derived bisphenols with safer, more sustainable options (160). For example, 4-*n*-propylsyringol (i.e., one of the main products from RCF of hardwood lignin) has been coupled with formaldehyde to prepare a substituted bisphenolic alternative to BPA for use in aromatic polyesters with reasonable thermomechanical properties relative to BPA (160).

Another method to functionalize biorefinery products is catalytic and biological funneling, which facilitates the conversion of deconstruction mixtures to common product target(s) that are enriched in particular functional groups, such as acids, aldehydes, and ketones (85, 163). Funneling is an attractive strategy because it inherently lowers the complexity of product mixtures, and thus reduces the need for subsequent separations unit operations and their associated costs and energy requirements. For example, microbial funneling enabled the conversion of 59 mol% of the aromatic compounds from a catalytic oxidation lignin bio-oil to 2-pyrone-4,6-dicarboxylic acid, a potential polyester precursor (164). Both (bio)chemical funneling and synthetic routes to functionalize small-molecule deconstruction products can generate commercially viable bioproducts, and future efforts in application-specific performance testing, monomer hazard evaluation, and value-based pricing comparison could enable the translation of these bio-derivable polymers into industry.

7.2. Polymers from Biorefinery Residues

Valorization of polysaccharide and lignin residues (i.e., humins and lignin oligomers) is less researched in comparison to small-molecule products, and these by-products are inherently less valuable than more refined product streams owing to their dark colors, potentially unpleasant odors, and heterogeneous structures (13). However, upgrading these more recalcitrant fractions could provide additional revenue to biorefineries and thus enable other products to be more cost competitive with incumbent petrochemical derivatives (70). Among the most promising approaches to upgrade oligomeric lignin residues is to leverage the rich chemical functionality (i.e., high phenolic and aliphatic hydroxyl group content) for applications such as aromatic replacements for epoxies and polyols for polyurethanes (13, 70). The value of oligomeric lignin fractions could be improved by lightening their color, as was done in an aldehyde-assisted, active-stabilization fractionation process that resulted in a significantly lighter-colored lignin in comparison to technical lignins from common pulping processes (13). Polyurethanes synthesized from the lighter-colored lignin also had a higher tensile strength and elongation at break than analogous polymers prepared from Kraft lignin (13). In both cases, however, broad molecular weight distributions and uncertainties in functional group content resulted in high variability in the measured performance metrics. To overcome this variability, lignin residues could be selectively extracted to generate well-defined fractions with narrower dispersities and more consistent functional-group densities (165). For instance, uniform technical lignin fractions ($Đ = 1.16$) were extracted with acetonitrile and copolymerized with diglycidyl ether–terminated polyethylene glycol to synthesize elastomers (12). The additional carboxylic acid and alcohol functional groups in the fractionated lignin resulted in hydrogen-bonding sites that enabled self-healing at room temperature and improved tensile strength versus a control polymer without lignin (12). Unfortunately, these strategies to translate oligomeric residues to value-added products typically are not applicable to polysaccharide degradation by-products (i.e., humins). Humin residues have been incorporated primarily into lower-value products, such as composites for structural applications or supports for catalysts, owing to their recalcitrance and limited chemical functionality (166, 167). Although TEA and LCA are not commonly conducted to quantify the economic and environmental advantages of upgrading oligomeric by-products, any additional revenue from their valorization could improve plant economics and offset emissions and/or disposal issues associated with what would otherwise be treated as a waste stream.

7.3. Processing and End of Life

Once polymers are synthesized, they can be processed (e.g., extruded into pellets, molded into specific shapes, spun into fibers, pressed into films) to manufacture a variety of products (168). These materials are used for numerous applications, but all eventually reach the end of their usable life, with ~40 wt.% of plastics being discarded after just one use (169). Only 9 wt.% of plastics were recycled annually in the United States as of 2018, and the remainder was either incinerated, discarded to landfills, or released into the environment (1, 69). A major research thrust has focused on life-cycle management, with emphasis on sustainable sourcing, synthetic methods, processing techniques, and end-of-life properties (170–172). Among the most important life-cycle management considerations is the design of materials that are recycled or degraded easily. For instance, polymers that can be reprocessed through dynamic chemistries, degraded into benign substances, or depolymerized can mitigate plastics waste accumulation (173). Despite the efforts to develop polymers that are designed for circularity, translating these materials from university, government, or commercial laboratories to industrial production still requires significant investment (174). In the meantime, petroleum-derived polymers account for almost all manufactured plastics, and the chemical and biological deconstruction of existing plastics is a promising area of research that could enable the transformation of waste plastics or mixed LCB/plastics streams (e.g., MSW) into value-added products with more circular/closed-loop life cycles (2, 175, 176).

Depolymerization: breakdown of a material/polymer into its corresponding monomer(s)

Circular/closed-loop: capable of moving through repeated production and consumption cycles without significant loss in value or performance (i.e., fully recyclable or reusable)

RD-RCD: reactive distillation–reductive catalytic deconstruction

RCD: reductive catalytic deconstruction

8. OUTLOOK FOR THE GROWTH OF LIGNOCELLULOSIC BIOREFINERIES

LCB can decrease the global dependence on petroleum, and biorefineries that convert cellulose, hemicellulose, and lignin to valuable products, such as polymers, are crucial to facilitate this transition (5, 6, 25). Improved inventory management, long-term storage systems, and feedstock flexibility are also vital to avoid biorefinery downtime caused by feedstock supply variability. Additionally, as biorefineries leverage more underutilized feedstocks, nonstructural components (e.g., extractives, proteins, ash, starch) can comprise significant portions of the biomass (43, 96, 97). Further research is needed to understand how these nonstructural components impact the fractionation/deconstruction outputs, the accuracy and reliability of characterization methods, and the effectiveness of pretreatment or product purification processes. For MSW and other complex waste streams, strategies to concurrently deconstruct mixed LCB and plastics waste have been proposed to manufacture lower-value products such as lubricants and fuels (177); however, a significant opportunity remains for the development of catalytic or biological valorization strategies that can either serially or simultaneously upgrade LCB and plastics waste. Such approaches could improve biorefinery economics and reduce the environmental impacts of MSW by eliminating the need for expensive sorting mechanisms and minimizing the volume of waste that is landfilled or incinerated.

Thorough characterization of LCB feedstocks and their respective deconstruction products can be leveraged to inform the choice of deconstruction processes and reaction conditions, enable the prediction of fractionation/deconstruction yields and product distributions, and facilitate the design of effective product purification processes. For instance, a TGA-based method predicted lignin reactive distillation–reductive catalytic deconstruction (RD-RCD)/RCD yields from the thermal stabilities of a diverse set of technical lignins from different feedstocks and pulping processes (7). Lignin with higher thermal stabilities was more recalcitrant, whereas lignin with comparatively low thermal stabilities was easier to deconstruct (7, 94). This straightforward characterization approach could rapidly screen technical lignin, but it has not been applied to whole LCB because the presence of carbohydrate fractions tends to result in a more complicated thermal decomposition profile. Similarly, NIR spectroscopy was used to predict the yields of soluble carbohydrates from LCB feedstocks via a partial least squares analysis (116), but again, the method would need to be refined to also provide additional information, such as whole LCB composition or expected deconstruction yields. TGA or NIR spectroscopy also can be combined with complementary structural characterization techniques (e.g., HSQC NMR spectroscopy, py-MBMS) to estimate deconstruction product distributions for LCB feedstocks (106, 112). By anticipating product yields and distributions for diverse feedstocks and different deconstruction strategies, process conditions and purification methods could be tuned to favor the generation of target compounds for materials manufacturing.

Characterization data also can be used to predict polymer properties from feedstock and/or deconstruction product compositional information by leveraging macromolecular structure–property relationships (161). For instance, lignin-derivable, acrylic polymers exhibit a wide range of thermal and mechanical properties based on the phenolic precursor's structure (130, 158, 159, 178). Increasing the number of *o*-methoxy groups from 1 to 2 resulted in a significantly elevated T_g [205°C for poly(syringyl methacrylate) versus 120°C for poly(guaiacyl methacrylate) (158, 159)]. Altering the substituent at the 4-position also impacted the thermal and mechanical properties of this class of polymers, albeit to a lesser extent than *o*-methoxy content. For example, poly(guaiacyl methacrylates) with 4-position substitutions ranging from hydrogen to methyl, ethyl, and propyl chains exhibited tunable T_gs from 80°C to 130°C and viscosities from 730 kPa s to 34,000 kPa s at 150°C (158), with the T_gs of copolymers from these bio-derivable monomer mixtures predicted using only compositional information and the Fox equation (130, 158, 179). Similar structure–property relationships can be developed for other LCB-derivable materials, including polymers prepared from BPA alternatives, aromatic dimers/trimers/oligomers, styrenics, acrylamides, sugar dehydration products, and many others, to enable a wider range of materials outputs with broadly predictable thermal and mechanical properties (10–13, 150).

The predictive power of thorough feedstock characterization coupled with polymer structure–property relationships is an ideal approach for the management of biorefinery outputs, but unlocking the full potential of these large data sets and complex relationships will necessitate the use of computational tools. For instance, a lignin library was generated from stochastic structural modeling simulations for miscanthus, spruce, and birch to predict S/G/H ratios, linkage distributions, molecular weights, and branching coefficients that could be inputs to molecular simulations and kinetic models to estimate an array of properties (e.g., molecular weight, T_g, polymer solubility) (178, 180, 181). Similar libraries could be created for other biomass species and different structural components to predict the properties of biorefinery feedstocks, and these models could be extended to anticipate deconstruction yields and compositions (e.g., distributions of sugars from hemicellulose or phenolics from lignin) from different deconstruction process conditions (181). Importantly, feedstocks, deconstruction methods, operating conditions, etc., could be chosen to generate specified monomer mixtures and target polymer thermomechanical properties that are ideal for particular applications.

TEA and LCA are critical to quantify the profitability and sustainability of biorefineries, enable informed engineering decisions that balance economic and environmental considerations, and identify future research priorities (24, 43). These analyses inform choices about individual steps, such as the need to maximize local biomass use to decrease transportation costs or the importance of pre-drying and/or air-drying feedstocks to lower energy usage (40, 47, 64). Solvent recovery also has been identified as a major driver of both environmental impacts and operating costs, motivating process modifications to reduce solvent loadings [e.g., multi-pass FT systems (182)] or increase solvent recycling. Liquid-phase solvent recycling (e.g., nonthermal, membrane-based solvent recovery) is a promising strategy with the potential to significantly reduce energy demands versus solvent recovery via distillation (24). Factors that influence the techno-economic and environmental performance of biorefineries also are not always independent or obvious; thus, the development of integrated TEA/LCA to accurately capture and optimize complete biorefinery systems is necessary (183). For example, a combined TEA/LCA case study found that manufacturing lactic acid from corn stover had ~47% higher monetized environmental costs (i.e., human health, ecosystem quality, natural resource costs) than lactic acid generated from edible corn, although the lactic acid from corn stover had ~25% lower production costs (45). The environmental impact of corn stover–based lactic acid was driven by the high energy demands of steam explosion pretreatment/fractionation required for the fiber-rich corn stover, but lactic acid from corn stover was more profitable because of its low cost as a waste feedstock (45). Thus, the trade-offs between economic and environmental concerns are not necessarily apparent from any individual biorefinery stage or feedstock choice, and integrated TEA/LCA is a powerful strategy to estimate the true cost and environmental performance drivers across a biorefinery design and prioritize modifications that maximize profitability and sustainability.

In a related arena, process intensification (i.e., the elimination or combination of unit operations) enables biorefineries to run more quickly, inexpensively, and sustainably (32). Combined unit operations can facilitate solvent recycling, reduce water inputs, and lower capital costs (32). Other approaches to process intensification are more case specific, such as an intensified RD-RCD technique that combined lignin deconstruction and bio-oil distillation steps at ambient pressure to simultaneously generate and isolate valuable small molecules (7). This strategy reduced capital and operating costs, energy use, and safety hazards associated with conventional RCD and enabled a 62% lower minimum selling price for a PSA versus the same material prepared from RCD (7). TEA/LCA can ascertain both the areas that are most in need of innovative process intensification and the strategies that can have the greatest impact to lower net energy usage, mitigate the volume of wastes generated, and maximize production efficiency, thereby improving the economic and environmental viability of LCB biorefineries.

9. CONCLUSION

LCB has great potential as an alternative feedstock to petroleum for the manufacture of high-value products such as polymers. Underutilized waste LCB can provide an abundant, low-cost feedstock for biorefineries; however, handling the inherent variability of these waste streams requires further advances in preprocessing, feedstock characterization, and inventory management strategies, along with innovations in process design, separations methods, and product characterization. Coupling advanced characterization methods with computational tools and structure–property relationships can further improve biorefinery operations by enabling the prediction of polymer properties and active management of biorefinery outputs. Integrated TEA/LCA also can be leveraged to guide process decisions to balance economic and environmental concerns while maximizing the fraction of biomass translated into value-added products. Significant progress has been made toward commercially viable LCB valorization, and with additional innovations across all areas of biorefinery design and operation, next-generation biorefineries could become cost competitive with petrochemical-based materials and usher in a more sustainable, circular economy for performance-advantaged materials.

SUMMARY POINTS

1. Lignocellulosic biorefineries have great potential to transform cellulose, hemicellulose, and lignin into valuable products such as polymers.
2. Waste lignocellulosic biomass (LCB) feedstocks are ubiquitous and underutilized but highly variable, necessitating rapid and reliable biomass characterization to assist in feedstock selection and blending, preprocessing, and inventory management.
3. Computational tools can facilitate decision making in feedstock blending and deconstruction operations by leveraging large characterization data sets and macromolecular

structure–property relationships to aid in the prediction and control of downstream polymer properties.

4. Separations are a large driver of chemical plant costs and energy usage, and the development and implementation of selective, nonthermal purification methods may be critical for biorefinery economic and environmental feasibility.
5. High-value polymer production using both refined small molecules and oligomeric/macromolecular residues as monomers or monomer precursors increases the economic potential of LCB biorefineries.
6. Integrated technoeconomic analysis/life-cycle assessment is crucial to understand the operation of the biorefinery as a whole and to quantify the environmental and economic outlook for biorefinery systems.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

The authors thank the National Science Foundation (NSF) Growing Convergence Research program (NSF GCR CMMI 1934887) in Materials Life Cycle Management for supporting this work. A.J.S. acknowledges financial support from the NSF Research traineeship (NSF NRT-MIDAS 2125703) in Computing and Data Science Training for Materials Innovation, Discovery, and Analytics, and J.C.A. acknowledges financial support from the US Department of Energy, Office of Science, Basic Energy Sciences (DE-SC0021166) for the Center for Plastics Innovation, an Energy Frontier Research Center.

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