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Matching diverse feedstocks to conversion processes for the future bioeconomy

Corinne D Scown^{1,2,3,4}, Nawa R Baral^{1,2}, Deepti Tanjore^{2,5} and Vi Rapp⁶



A wide variety of wasted or underutilized organic feedstocks can be leveraged to build a sustainable bioeconomy, ranging from crop residues to food processor residues and municipal wastes. Leveraging these feedstocks is both high-risk and high-reward. Converting mixed, variable, and/or highly contaminated feedstocks can pose engineering and economic challenges. However, converting these materials to fuels and chemicals can divert waste from landfills, reduce fugitive methane emissions, and enable more responsible forest management to reduce the frequency and severity of wildfires. Historically, low-value components, including ash and lignin, are poised to become valuable coproducts capable of supplementing cement and valuable chemicals. Here, we evaluate the challenges and opportunities associated with converting a range of feedstocks to renewable fuels and chemicals.

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Introduction

The bioeconomy is poised to play a substantial role in deep decarbonization and the transition away from fossil-based fuels and products. Bio-based aviation fuels remain the most viable option for decarbonizing air travel and recent investments in alcohol-to-jet, hydroprocessing, and thermochemical processing routes suggest that rapid growth is possible, if not probable, in the next few decades [1]. Biomanufacturing promises to produce a wide array of drop-in replacements and bioadvantaged alternatives to conventional petrochemical products and fuels, which will be particularly essential to ensure an even drawdown of reliance on both fuels and products from the oil and gas industry. There has also been an increasing interest in the use of biomass for carbon removal and storage, typically relying on thermochemical pathways such as pyrolysis and gasification combined with capture and sequestration of CO₂ [2]. All of these industries will require substantial quantities of bio-based feedstocks. In a follow-up to the United States (U.S.) White House's Executive Order 14081, a set of goals for harnessing biotechnology and biomanufacturing were established, one of which is to collect and process 1.2 billion metric tons of feedstocks within 20 years [3]. This ambitious goal will necessitate the development of processes capable of converting a wide variety of organic materials, ideally prioritizing beneficial use of waste streams and other products with little or no land-use impacts.

Studies focused on large-scale decarbonization and carbon removal strategies typically treat all organic feedstocks as interchangeable and functionally equivalent on a mass basis. The proliferation of techno-economic analyses, some of which are based on idealized production systems that have been simulated in software but not yet demonstrated, can inadvertently give the impression that high yields and minimal costs are possible even with very-contaminated feedstocks. However, there is ongoing research specifically devoted to addressing feedstock-specific challenges in bioprocessing, such as the U.S. Department of Energy-sponsored Feedstock-Conversion Interface Consortium [4]. Here, we review recent work on the conversion of a wide variety of organic feedstocks to renewable fuels and products and highlight the challenges and opportunities

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CO, H ₂ , and CO ₂ needed hazardous contaminants impact on facility energy generation	Gaseous feedstocks	Syngas or waste gases	No further deconstruction of	Sulfur compounds and other corrosive or	Avoidance of flaring emissions, potential	[51] (clean
				hazardous contaminants	impact on facility energy generation	synthetic mixture only)

Type	Material	Products of deconstruction	deconstruction Processing challenges	Environmental cobenefits or risks of utilization Recent studies	Recent studies
	Biogas/landfill gas	No further deconstruction of CH ₄ and CO ₂ needed	No further deconstruction of Sulfur and siloxane contamination $\mathrm{CH_4}$ and $\mathrm{CO_2}$ needed	Avoidance of flaring or emitting methane	[52]
Bioprocessing by- products	Residual lignin from bioprocessing	Lignin-derived monomers and oligomers, including aromatics	Lignin composition heterogeneity across feedstocks and pretreatment methods	Reduced air pollutant emissions from solid fuel combustion at biorefineries	[34,53]
	Black liquor	Smaller lignin-derived monomers and oligomers	Large inorganic fraction and high Reduced air pollutant emissions frompositional variability, including large lignin liquor combustion at biorefineries molecules	Reduced air pollutant emissions from black liquor combustion at biorefineries	[54,55]
	Solid digestate/ sludge Variety of organic compounds, inert compounds, and macronutrients	Variety of organic compounds, inert compounds, and macronutrients	Depending on origin, may contain contamination including plastics, metals, pharmaceuticals, and other pollutants	Landfill methane avoidance, diversion of waste from landfills, and avoidance of water quality concerns from excessive land application	[56,57]

associated with different feedstock-conversion pairing strategies.

Biomass feedstocks for biochemical conversion to fuels and chemicals

There are a wide variety of potential feedstocks available for conversion to biofuels and bioproducts (see Table 1). The total availability, moisture content, composition, and physical properties all factor into determining the best use(s) for these materials. Some, such as crop residues and organic wastes, are already produced but have not yet been collected and converted at meaningful scales. Other feedstocks are purpose-grown and would require large-scale adoption by farmers to enable their use in commercial biorefineries. Diversifying feedstock supply for individual facilities is one way that companies can mitigate supply chain risks [5], but utilizing a mixture of multiple feedstocks, particularly if the relative quantities vary, presents practical challenges. There are two primary categories of feedstockspecific processing considerations that arise, although they can share some common root causes: 1) mechanical properties, which have been reviewed in a recent article by Yan et al. [6] and 2) composition (including moisture content and inorganic contamination), which will be the primary focus of this review.

As of 2023, all available data suggest that corn stover is the single most widely produced crop residue in the United States [7–9]. Corn stover is amenable to a range of deconstruction processes [10], although its true availability is impacted by hesitance on the part of some farmers to allow stover removal from their fields [11]. Sugarcane bagasse, unlike corn stover, is readily available because it is a by-product of the sugarcane juice extraction step and commercial-scale bagasse-to-ethanol conversion is now occurring in Brazil [12]. The primary challenge associated with converting these commonly used biomass feedstocks is largely centered around the severity of the pretreatment process, often gauged by temperature; harsh conditions that produce high-sugar yields can also generate furfural, hydroxymethylfurfural (HMF), acetic acid, and phenolic compounds [12]. Acidbased pretreatment processes, while relatively low-cost, are the most problematic in terms of forming inhibitors, whose effects on downstream conversion will vary by microbial host [13,14]. Teramoto et al. used biomass that had undergone dilute-acid pretreatment at 160°C [13]. Steam explosion can also form these compounds, but at lower concentrations; Caporusso et al. noted that 5-HMF, furfural, acetic acid, and lignin-derived compounds produced during steam explosion at 203°C of wheat straw all negatively impacted yeast growth for downstream lipid production [15]. One option for addressing inhibitors is to select pretreatment processes known to generate less of them, in large part because

Box 1

Impacts of composition on thermochemical conversion

Unlike biochemical conversion routes, thermochemical conversion routes can use more severe processing conditions (namely higher temperatures) to overcome feedstock heterogeneity at the expense of efficiency. Gasification and pyrolysis can both be leveraged to produce liquid fuels or the processes can be designed with the goal of maximizing carbon dioxide removal, in the form of injectable CO₂ (with H₂ as the main energy product), char, and/or pyrolysis oil for sequestration [69]. Such approaches can be particularly helpful in reducing the mass of residual-mixed organics, such as sludge, that cannot be beneficially converted nor land-applied [70]. For these thermochemical processes, minimizing moisture content of the incoming feedstock is crucial, given water's high latent heat of vaporization. Many of the other compositional issues discussed in this review may be addressed with engineered solutions, but processing feedstocks that are highly variable in composition and size adds further challenges. For example, a recent study by Lestander et al. explored the gasification of single components of spruce trees versus gasifying a mixture of stem wood, bark, branches, and needles. They found that even mixing parts of the same wood type could reduce the cold gas efficiency by more than 6% [71]. To avoid tars, fouling, and ash during the thermochemical conversion process, feedstocks should ideally have low mineral content and low-moisture content (less than 30%, see Figure 1) [72–74]. Additionally, feedstock shape, size, and density can impact char formation during the conversion process [74]. Organic wastes that contain a wider variety of plastic, paints, and other contamination present additional challenges. Processing chlorinated compounds, such as those originating from polyvinyl chloride (PVC) plastics and chloroprene (PCP), may be problematic depending on the reactor design, conditions, and level of preprocessing. Some chlorine-containing wastes can form HCl, posing corrosion concerns [75,76].

they can operate at lower temperatures: deacetylation and mechanical refining pretreatment (80–92°C) and ionic liquid pretreatment (up to 160°C) are two examples [16,17]. Alternatively, researchers have attempted to address the presence of inhibitors by either selecting HMF/furfural-tolerant microbial strains or adding detoxification strategies to the process [18,19]. Llano et al. used multicriteria analysis to explore different detoxification approaches, specifically targeting furan derivatives, phenolic compounds, and weak acids [20]. Unlike biochemical routes, thermochemical processes can increase operating temperatures to overcome some feedstock compositional variations (Box 1).

Even uncontaminated, single-source biomass feedstocks do pose challenges in bioprocessing based on their composition. Ash content can be inherent to the biomass and can also be introduced when harvesting practices disturb the soil and entrain it into baled biomass, thus introducing sand and other incombustible materials into the feedstock [21]. Although high-ash content is undesirable in bioprocessing — it translates to larger quantities of nonbioavailable material occupying space in pretreatment and bioconversion reactors and may cause corrosion issues - silica-rich feedstocks do offer the possibility of coproducing pozzolanic materials to decarbonize the cement industry by displacing the need for carbon-intensive portland cement. Rice straw ash, corn stalk ash, wheat straw ash, and forest residue ash are the four feedstocks with the largest global potential to yield secondary cementitious materials [22]. However, enabling coproduction of secondary cementitious materials would require combustion of residual solids at high temperatures following any biological conversion process because the silica is not reactive unless it is amorphous, or glassy.

Lignin as a feedstock

Much like high-ash feedstocks, high-lignin feedstocks have long been considered undesirable for biochemical processes because they are more recalcitrant to deconstruction. Because cost-effectively converting lignin to products or bioavailable intermediates is challenging [23], residual solids are typically combusted for heat and power [24]. Lignin content in woody and herbaceous feedstocks can vary considerably, from 10% or less in low-lignin forage sorghum to more than 30% in some woody feedstocks [25,26]. There is continued progress in the development of conversion routes for lignin-derived intermediate compounds, such as phenol, to adipic acid [27] and other salable products. Much of the published work focused on biological conversion still relies on proxy compounds because lignin depolymerization can result in complex mixtures that are difficult to characterize and contain compounds toxic to microbial hosts. Ultimately, research is progressing along several paths: a 'biological funneling' approach in which hosts are capable of utilizing a wide variety of ligninderived compounds to produce aromatic platform chemicals [28] and a 'lignin first' chemical conversion approach in which lignin is separated and valorized [29]. This is not yet evidence to suggest that either of these approaches has become sufficiently efficient to advantage high-lignin feedstocks over lower-lignin feedstocks, provided both are available at comparable delivered prices.

Organic wastes for bioprocessing

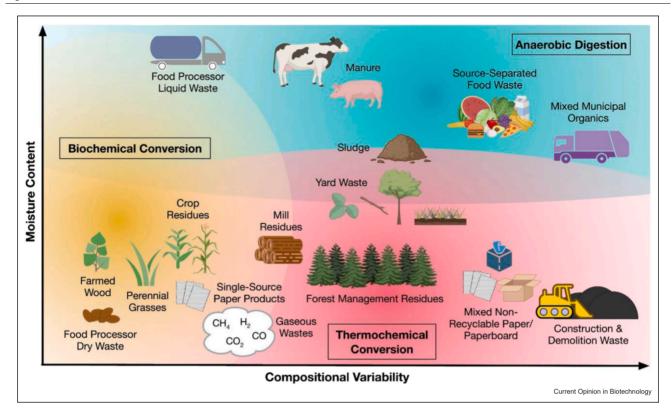
Compared to purpose-grown feedstocks and even many crop residues, the attractiveness of utilizing organic wastes is undeniable: they are currently available, may be acquired at low cost or negative cost if producers are willing to pay for its removal, and are not subject to the land-use concerns associated with dedicated crops. Additionally, some waste feedstocks have negative environmental impacts associated with their disposal, such as landfill methane emissions, so diverting them to biorefineries can vield considerable emission avoidance benefits (see Table 1). In other cases, the term 'waste' may be a misnomer. The uses of different organic wastes fall into a continuum between negative or very low-value fates to higher-value applications. Clean organic waste streams are often used in comparatively high-value applications. For example, almond hulls can be valuable animal feed, but if they absorb too much moisture during storage, both shells and hulls become a waste product in need of combustion or landfilling and would instead benefit from conversion to biofuels/bioproducts [58]. Some fats, oils, and greases (FOG) are used as animal feed supplements, while others serve as very attractive feedstocks for anaerobic digesters to boost biogas yield [59]. Brown grease (trap grease), conversely, can be contaminated with heavy metals and pathogens and does have a lower (or negative) value because it must be hauled away and treated as septage [60]. Thus, diverting brown grease for the production of biofuels and/or bioproducts (e.g. hydroprocessed esters and fatty acids) will have little-to-no opportunity cost [61].

Unlike separately collected wastes such as FOG, the composition of municipal wastes and the business-asusual management can vary depending on the level of source-separation implemented in each city. Even in municipalities that do not compost other materials, vard waste is typically collected separately and sent for composting. Yard waste is not generally used for highvalue applications but is an attractive input for composting facilities because of its low levels of inorganic contamination and minimal odor [62]. Mixed waste streams that include food and other municipal organics are more likely to be landfilled because they are unsuitable for animal feed and are similarly undesirable for composting facilities. This means facilities may receive mixed waste streams at little or no cost, or in some cases, they may even be paid to accept the material. For example, Smith et al. reported on the tipping fee structure for an anaerobic digestion facility in San Jose, California, where higher fractions of inorganic contamination corresponded to higher tipping fees paid to the facility to offset the cost of removing and landfilling the contaminants [63]. These materials can be deconstructed to yield sugars for bioconversion, as paper products (cellulose) make up a large fraction of the organic stream. Most research on conversion to biofuels has focused on blending municipal organics with cleaner feedstocks, such as crop residues [50], in part because the rheological properties of a 100% municipal organics stream make conversion challenging. These high-moisture wastes (see Figure 1) do come with a substantial downside. Unlike dry biomass, which can be stored for months, regulations often limit the time facilities can store new high-moisture waste shipments before processing. For example, waste at the anaerobic digestion facility analyzed in Smith et al. cannot be stored for more than 48 hours before being loaded into a digester [63]. Although these storage regulations minimize fugitive methane emissions, odor, and pests, they can increase costs if equipment must be sized to ensure adequate throughput of material.

Contamination in municipal waste streams (see Figure 1). which often comes in the form of plastic waste, adds cost at conversion facilities. Brown et al. developed cost estimates for different decontamination strategies, all of which were below the target cost of \$30/dry ton [48]. The impact on the cost per unit output from a conversion facility will be highly dependent on scale; many of the strategies for decontaminating feedstock involve equipment purchases that can increase the capital expenditures, particularly for smaller facilities. However, smaller decentralized facilities do have the advantage of tailoring preprocessing for a single locally sourced feedstock in some cases (Box 2). Decontamination processes also result in some losses. Press extrusion, for example, is a popular method for separating organic waste from plastic and metals, which involves forcing high-moisture waste at high pressure into a chamber with holes, leaving fibrous and other dry materials for separation and disposal [64].

Construction and demolition (C&D) wood waste, in contrast with mixed municipal organics, is relatively low-moisture and consequently is not subject to similar regulatory limits on storage duration. The fate of wood C&D waste is not well-documented at a U.S. national or global level, but estimates for California suggest that nearly 90% is landfilled and the remainder is combusted as fuel or reused [65]. As with other woody biomass, it can be deconstructed to sugars and lignin. The utilization of waste from C&D for production of fuels and/or chemicals appears to be mostly theoretical to-date, explored through modeling studies [66]. However, there is at least one recent study exploring gasification of construction wood waste in Brazil [67]. Inorganic contamination is likely to be a major challenge, particularly if nails and other items risk damage to equipment. Resins, paints, and other chemicals present may also impact conversion processes, particularly if they are toxic to host microbes. The degree to which C&D waste can be feasibly converted in commercial-scale biofuel or biochemical production facilities is still worthy of further exploration. There is intense interest in leveraging building materials as a mechanism for carbon sequestration [68] and the end-of-life fate of biogenic materials remains a limiting factor in the duration of carbon storage.

Figure 1



Compositional variability and moisture content of common organic feedstocks.

Box 2

Depot model for heterogeneous feedstocks

An alternative to designing flexible conversion processes that are tolerant to variable composition and potentially high levels of contamination is to build out a network of infrastructure capable of processing individual feedstocks in smaller local facilities and shipping standardized intermediates to centralized conversion and upgrading facilities. The smaller size allows depots to tailor their preprocessing and downstream processing to the contamination and compositional challenges specific to their locally sourced feedstock. Depots can produce anything, ranging from pellets to sugars, aromatics, carboxylic acids, platform chemicals, H₂, or their mixtures [77,78]. They can also enable blending of feedstocks to obtain a particular feedstock specification in composition and/or rheological properties that will enable higher conversion yields [79]. Even building facilities to densify biomass for shipping and storage can substantially reduce transportation costs [80]. This model is already taking hold in the biojet fuel industry, where preexisting corn-to-ethanol facilities are shipping ethanol to off-site alcohol-to-jet conversion facilities [78].

Conclusions

Building the future circular bioeconomy will necessitate utilization of a wide variety of feedstocks, each with their own unique set of challenges. However, the potential environmental benefits are considerable: diverting forest residues can reduce wildfire risk and harmful smoke emissions, while diverting high-moisture organic waste from landfills can avoid fugitive emissions of potent greenhouse gases. By shedding light on the compositional differences and practical considerations associated with converting each feedstock type, it is possible to identify and prioritize research and devel-

opment, demonstration, and deployment needs. Increasing demand for bio-based products and energy carriers presents a unique opportunity to address long-standing challenges in the management of waste from cities, agriculture, and food processing while reducing demand for fossil fuels and petrochemicals.

Data Availability

No data were used for the research described in the article.

Declaration of Competing Interest

N.R.B. has a financial interest in Erg Bio. All other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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