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A review of thermal and thermocatalytic valorization of food waste

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Abstract

Food waste (FW) remains a global challenge due to the increasing demand for food production to support a growing global population and the lack of effective waste management technologies for recycling and upcycling. Unique compounds in FW - such as carbohydrates, proteins, lignin, fats, and extractives - can be repurposed to produce important biobased fuels, bulk chemicals, dietary supplements, adsorbents, and antibacterial products, among many others. We review the thermal and thermocatalytic FW valorization strategies and the fundamental pathways. We discuss the potential integration of various valorization processes, their economic viability, the technical and marketing challenges, and the need for further developments. By overcoming several technical hurdles, repurposing FW into modular plants can create exciting economic and environmental prospects.

Keywords: Food Waste, Sustainability, Kinetics, Valorization, Circular Economy, Biorefinery, Catalysis

Broader context

The amount of food waste and the environmental footprint from discarding it in landfills are vast. Major societal and ecological drivers demand improved management strategies. Valorization of food waste by repurposing it into a biorefinery could enable a circular economy. Food waste contains unique compounds, is distributed, and exhibits large diversity and a short lifetime, making its valorization challenging but financially appealing. The majority of prior studies have focused on biological valorization targeting gaseous and liquid fuels. More recently, thermal and catalytic processes have gained traction for valorization into high-value biochemicals. This review summarizes advances on these valorization strategies and mechanistic insights and highlights key challenges and perspectives on future research directions.

1.0 Introduction

Food waste (FW) arises in all stages of the food supply chain, from production to transportation to distribution to processing to consumption. In high-income regions, aesthetic preferences and ambiguous data labels contribute to the generation of high FW volumes at the processing, distribution, and consumption stages. In contrast, in low-income countries, FW occurs in production and post-harvesting due to inadequate infrastructure, lack of knowledge on storage and handling, and unfavorable climatic conditions[1]. About half of the globally produced fruits, vegetables, roots, and tubers at the retail and consumer level end up as waste (Figure 1).

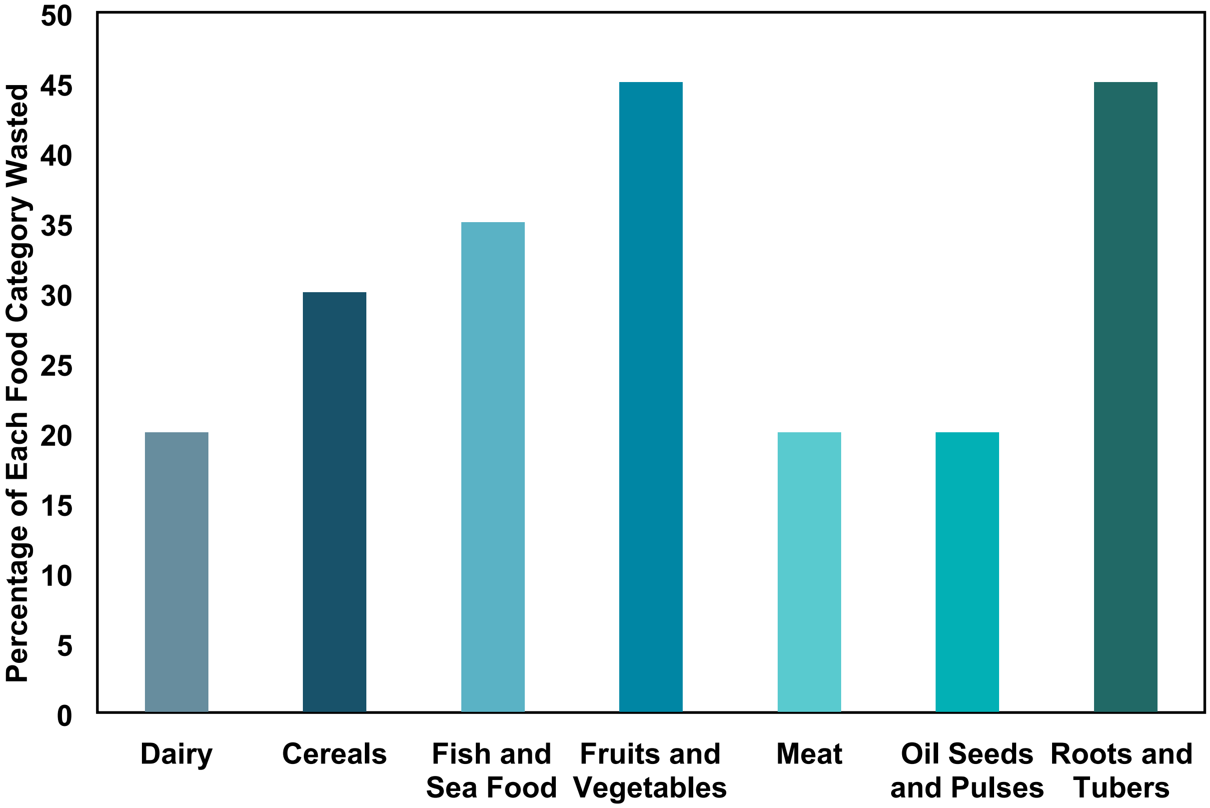


Figure 1. The fraction of key food commodities at retail and consumer level ending up as waste[2].

1.1 A global concern

Globally, about one-third of the food produced, equivalent to 1.3 billion tons per year, is wasted[2–4]. FW implies a loss of resources, reduced food security, and significant greenhouse gas (GHG) emissions. In the US, 82% of the emissions from the waste sector[5] comes directly from municipal landfills. This number increases to 90% when emissions from industrial landfills are accounted for. Thus, environmental, social, and economic factors motivate the development of efficient FW management strategies. The United Nations has set a goal to ensure sustainable food production and consumption by halving FW per capita[6] by 2030. While FW at home and restaurants could be minimized, it could hardly be avoided during production and processing. Instead, FW can be a renewable resource to manufacture bioproducts. It can drive circularity by providing an alternative to making, using, and disposing of paradigm and keeping resources in use for as long as possible, extracting maximum value. Figure 2 shows the magnitude and implications of FW. An astonishing 26 Exajoules is the estimated energy embedded in food waste, equivalent to one-quarter of the US energy consumption. GHG emissions from food waste in landfills and the associated disposal methods amount to 3.3 billion CO_2 equivalents, placing FW (if it were a country) as the third-largest contributor to global GHG emissions, behind China and the US. Finally, the monetary worth of wasted food is equivalent to the gross domestic product of Mexico ($1 trillion). Its magnitude, sustainability, energy content, and financial impact underscore the remarkable size of the FW valorization opportunity[4,7,8].

Figure 2. The magnitude of food waste. Opportunity for transforming linear FW economies into circular economies. Reproduced from ref[9] with permission from the American Chemical Society.

1.2 Food-waste (FW) composition

Across different food categories (Figure 1), between 20 - 45% of food ends up as waste. Table 1 shows the composition of various FW streams obtained using the National Renewable Energy Laboratory (NREL) characterization protocol[10], the Association of Official Agricultural Chemists (AOAC) characterization protocol[11], or modifications of both. These methods are used to characterize biomass. Biomass can be defined[12] as the biodegradable fraction of products, waste, and residues of biological origin from agriculture (including vegetable and animal substances), forestry, and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. However, most publications in the biorefinery space describe biomass solely as “lignocellulosic biomass”, which often excludes food waste. FW contains five major components, i.e., carbohydrates, proteins, extractives, lignin, and lipids. The presence of unique components in FW, such as starch, essential oils, extractives, lipids, and proteins, distinguishes it from lignocellulose (consisting of cellulose, hemicellulose, and lignin) warrant a detailed summary of research progress of thermal and thermocatalytic valorization of FW towards a holistic valorization of all forms of biomass. The relative composition of each component can vary significantly among feedstocks. For example, potato and banana peels are predominantly composed of carbohydrates, milk and meat are rich in proteins, and oil consists only of lipids. Extractives constitute a significant fraction of FW (Table 1) and contain various components. For example, apples contain pectin, oranges - limonene, potatoes - chlorogenic acid, and tomatoes - lycopene. This diverse composition of FW offers opportunities to valorize individual components towards different products and maximum profit.

Table 1. Composition of select food-waste feedstocks.

Feedstock	Carbohydrates (%)	Proteins (%)	Extractives (%)	Lignin (%)	Lipids (%)
Potato peels[9]	55.3	-#	22.9	11.4	-
Banana peels[13]	68.5*	5.1	14.5	2.9	-
Tomato pomace[14]	25.7	19.3	-	33.3	5.9
Kiwifruit[15]	61.2	6.6	9.3	14.0	3.3
Watermelon rinds[15]	48.7	13.5	13.3	16.7	4.5
Olive pomace[16]	49.0	6.7	2.4	19.8	10.9
Grape pomace[17]	26.2	-	-	56.7	-
Apple pomace[17,18]	75.3	2.6	-	24.7	2.5
Acid whey[19]	67.5	2.9	-	-	2.1
Legume waste[20]	38.0	16.7	-	28.6	-
Orange peels[21]	80.7*	9.1	4.5##	7.5	4.0
Ground nut shell[22,23]	50.4	5.4	-	36.1	0.1
Shrimp waste[24]	48.2**	19.8	-	-	1.00
Rice husk[25]	71.6	5.5	-	6.5	0.9
Wheat straw[26]	57.5	4.3	7.5	16.3	-
Spent coffee grounds[27]	51.5	17.4	-	23.9	2.3
Cocoa pod husk[28]	74.0	7.7	-	14.7	4.4
Waste cooking oil[29]	-	-	-	-	100

#Other PPW characterization studies report protein content between 2 – 10 wt%[30–32]. *Contains pectin. ##limonene accounts for 3.8 % of orange peel dry weight. **Contains chitin. Mineral ash makes up the rest. Percentages are weight percents. Compositions are reported on a dry-weight basis.

1.3 Overall management strategies

FW management strategies, arranged from the most to the least desirable, are depicted in Figure 3. 83% of FW still ends up in landfills[33], with landfilling and composting facilities accounting for 88.9% of the total GHG emissions from FW management in the US[34].

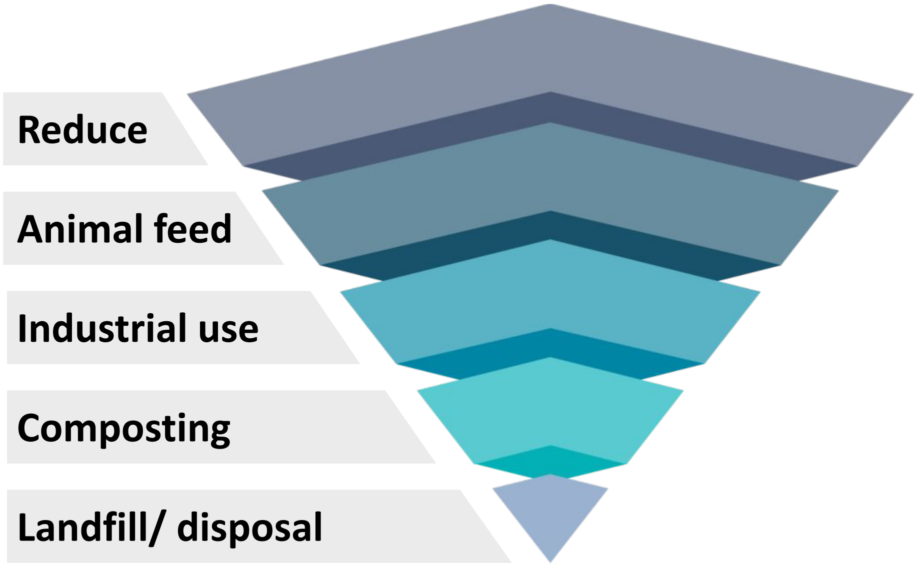


Figure 3. Food recovery hierarchy[35]**.**

The most prevalent FW management includes animal feed[33,36], composting[37,38], anaerobic digestion[39,40], and fermentation[30,41], as reviewed in various articles[8,13,16,21,38,42–45]. Current legislation emphasizes FW repurposing into biorefineries[44,46,47], with the biological and thermocatalytic valorization of FW and its components falling under the industrial food recovery hierarchy. Biological valorization producing low-value products, such as compost, biogas, and ethanol, has limited economic viability. Besides, biogas leak from digesters contributes to GHG emissions[48].

1.4 Biological vs. thermocatalytic conversion

Biological conversion has been applied to bread waste[49], banana peels[50], citrus waste[50], tomato waste[50], potato peel waste[50–53], meat[49,54–57], rice[49,54–58], wheat straw[59], sugar beet[53,60], swine slaughterhouse waste[61], waste cooking oil[62], and fruit and vegetable waste[49,50,54–57,63]. Despite its wide applicability, it also exposes several challenges. First, the number of products made is currently limited. Producing a diverse slate of molecules requires the production of platform molecules that can be converted *via* downstream thermocatalytic, electrochemical, or biological processes. Second, biological transformations are inherently slow (processing takes weeks to months) and need large volumes, preventing distributed, small scale processing required due to the large FW-water content and putrescible nature. Third, the products are of low molecular weight and low chemical complexity, demanding a rebuild to higher carbon number molecules. This reduction in and the remake of the number of carbon atoms is energy inefficient. Fourth, some FW components, like proteins and furfurals, inhibit microbial growth[64], and halt the process. Fifth, microorganisms are susceptible to process conditions changes (temperature, pH) requiring a great deal of process control and instrumentation, significantly impacting product yields, energy inputs, and overall process economics[40,44,65,66]. Sixth, unlike the biological conversion of sugarcane and corn into ethanol, FW's diversity and complexity (Table 1) make biological valorization difficult. A set of nearly feedstock-agnostic technologies is needed.

The challenges above have driven research on thermal and thermocatalytic valorization technologies[67–71] due to their higher economic potential[45,72], less environmental impact[21,73], and ability to produce various platform molecules beyond fuels[30,37–39,41]. For example, carbohydrates can be converted thermochemically to glucose[19,74,75], 5-hydroxymethyl furfural (HMF)[9,15,76–78], galactose[19,75,79], and glucosamine[80–82], products extensively used in the food and pharmaceutical industry. In particular, pentose-rich sugar oat hulls waste from Quaker Oats[83] are used to synthesize furfurals. Proteins can be converted to aminoacids[82,84,85] used as flavor enhancers, nutritional supplements, and sour agents frequently added to organic acids. Lignin can be upgraded to alkyl phenols[86,87] and vanillin[88]. The latter is extensively used in the food industry, with an anticipated global market size by 2025 of $724.5 million[89]. Additionally, lipids from waste cooking oil can be converted to lubricants[90–92] and biodiesel[93–99], currently in operation by Big Wheel Burger. Furthermore, FW's extractives can have diverse applications[100,101]. Examples include phenolic acids[9,102–106] for antioxidants, terephthalic acid for PET resin and polyester films, and p-cymene[107–109] and limonene[21,110,111] for the food and pharmaceutical industry. Limonene is a vital intermediate for producing value-added chemicals such as turpentine, terpineol, and pine oil. Preparing tea blends from coffee plants prunings by Wize Monkey and converting the potato waste to produce bioplastics and health supplements[112] by Fright Food Waste CRC are example toward a circular economy[113]. Thermal and thermocatalytic conversion of FW to biochemicals can be more profitable than its biological counterpart for electricity generation, animal feed, and transportation fuel by nearly 10, 7.5, and 3.5 times, respectively[45,72,44].

1.5 Scope of this review

Currently, reviews on the thermal and thermocatalytic valorization of FW and recommendations for future research are lacking. Here, we comprehensively review FW valorization to bioproducts using this general conversion platform. Section 1 above describes the motivation. Section 2 focuses on processes, conditions, and potential bioproducts. Section 3 focuses on kinetic studies, reaction models, and pathways. Section 4 covers the integration of valorization processes, energy, and economic implications, and Sections 5 and 6 discuss challenges and an outlook, respectively.

2.0 Food-waste (FW) valorization

This section provides an overview of FW valorization, covering technologies, reaction conditions, and valorization products. We organize the discussion on the valorization of carbohydrates, proteins, lignin, extractives, fats, and the entire feedstock.

2.1 High-temperature upgrade technologies of the entire FW feedstock

Thermochemical technologies, including gasification, pyrolysis, and hydrothermal processes, have been widely applied for whole FW conversion and are discussed next.

2.1.1 Gasification. Gasification employs high temperatures (700–900 °C) and a gaseous stream, such as steam, carbon dioxide, nitrogen, or a combination of these[114,115] to produce syngas. The syngas is composed mainly of hydrogen, carbon monoxide, carbon dioxide, and possibly nitrogen, a platform feedstock used to produce hydrogen, ammonia, and methanol. The residue consists of chars, ash, oils, and tars[116]. The waste-to-energy is significantly affected by the elemental composition, heating value, ash content (and composition), moisture content, volatile matter content, inorganics (N, S, Cl, alkalis, heavy metals, etc.), bulk density, and particle size of the FW[117]. Recently, supercritical water-based technologies were developed to gasify FW streams, including tofu[118], zoomass[119], and dried mixed FW[120]. Overall, gasification is a very energy-intensive technology that forms tiny molecules. On the positive side, syngas is one of the most crucial industrial platforms of commercial value.

2.1.2 Pyrolysis. Pyrolysis involves FW's breakdown, in an oxygen-free environment at temperatures above 400 °C, primarily to bio-oil and some syngas and biochar[121]. A significant drawback is the high energy requirement for complete drying of the feedstock. The FW composition and process conditions impact the product composition[122]. Elkhalifa *et al.*[123] summarized recent developments and potential opportunities for FW pyrolysis reactors and process conditions to biochar and gaseous products (Table 2).

Table 2. Pyrolysis reactors, process conditions, and biochar characteristics from different FW streams

Food waste	Reactor type	Process conditions		Product yield (%)		
		Temperature (°C)	Time (h)	Oil	Char	Gas
Soybean protein[124]	Fixed bed reactor	400-600	-	6 – 9	22.2 - 26.6	-
Peanut shell[125]	Tube furnace	350-900	1	-	43.2 - 30.1	-
Mixed food waste and digestate[126]	Fixed bed and tubular reactor	300-700	4	60 & 52	32.3 - 42.3	5.3 - 7.4

Waste cereals & peanut crisps[122]	Tube furnace	800	-	46 – 62	˜25	15 – 25
Coconut pith[127]	Stainless steel device in a tube furnace	300 – 900	1		27.8 - 61.2	-
Potato peel[31]	Auger reactor	450	8 s	~22.7	30.50	-
Orange peel	Muffle furnace[128]	400-800	2 & 6		23 - 33 (2 h) 20- 30 (6 h)	
	Ceramic pot[129]	150–700	6	-	22.2 – 82	-
Waste animal fats[130]	Fixed bed reactor	400-500			32 – 42	53 – 75
Almond, walnut shell and olive stone[131]	Fixed bed reactor	600	60		23.9 - 26.8	45 – 55
Soybean stover and peanut shells[132]	-	300 & 700	-		22 – 37	-

In an interesting study, Tang *et al.*[124] co-pyrolyzed waste protein with polyvinyl chloride (PVC) plastic waste in a fixed bed reactor. The results indicated that the char yield decreases with increasing temperature and PVC content due to the secondary reaction of tar promoted by HCl evolved from PVC. Co-pyrolysis produces less nitrogen-containing compounds and more biochar. FW's oxygen and water can provide exciting opportunities for FW co-processing with plastics by improving catalyst stability from coke produced in the thermocatalytic processing of plastics.

Biochar has been exploited for adsorption and purification. For example, Johari *et al.*[127] pyrolyzed coconut pith at 300 - 900 °C into biochar for mercury adsorption. The 900 ^{o}C biochar had a higher adsorption capacity than commercial activated carbon (Darco KB-B). Liang *et al.*[31] pyrolyzed potato peel waste (PPW) and PPW fermentation residue (PPW-FR) into bio-oil and biochar at 450 °C. The bio-oil derived from the lipid and suberin contained a significant fraction of alkanes and alkenes (C_{16}–C_{26}). In this carbon number range, alkanes are valuable as fuels and light lubricants. Olefins can easily be functionalized to produce useful molecules. Tran *et al.*[128] compared the Cd adsorption capacity of biochar from different FW and biomasses and found the orange peel one had the highest absorption capacity. These studies indicate that pyrolysis-produced biochar has excellent adsorption properties.

2.1.3 Hydrothermal processing. Hydrothermal processing involves simultaneous heating and pressurization of FW in H_2O. A primary benefit compared to pyrolysis is that the FW feedstock does not need drying before use, minimizing the required energy. Hydrothermal processing can be broken down into hydrothermal liquefaction (HTL) and hydrothermal carbonization (HTC).

2.1.3.1 Hydrothermal liquefaction (HTL). HTL applies high pressure and supercritical water (250−400 °C)[133,134] to produce fuels. It is rapid and importantly compatible with many feedstocks, including woody biomass, algae, and moisture-rich FW[135]. It has been studied with homogeneous[136] and heterogeneous catalysts[137]. Minowa *et al.*[138] converted FW with 90 wt% moisture into bio-oil at 300 – 340 °C under nitrogen pressure (12-18 MPa) with and without sodium carbonate as a catalyst. The oil yield strongly depended on the catalyst and reaction temperature. Oil with a calorific value of 36 MJ/kg and a viscosity of 53,000 mPas was obtained at a maximum yield of 27.6%. Homogeneous catalysts improve bio-oil yield/quality while retarding char[139,140]. However, homogeneous catalysts cannot easily be recovered and require neutralization, increasing cost and generating waste.

Recent interest has shifted to heterogeneous catalysts, owing to greater recovery efficiency, thermal stability, and lower corrosion[141,142]. A stable acid−base catalyst, CeZrOx, improves bio-oil yield by catalyzing aldol reactions converting small water-soluble molecules into oil-soluble ones[143]. CeZrOx afforded a bio-oil with a high carbon content, low oxygen content, and high heating value compared to using Na_2CO_3. Maxime Deniel *et al.*[144] reported experimental and modeling studies of model mixtures and food processing residues (blackcurrant pomace, raspberry achenes, brewer's spent grains, grape marc) at a dry-matter concentration of 15 wt% and 300 °C. The maximum bio-oil yield was 30% in 60 min. Microwave hydrothermal liquefaction (MHTL) of watermelon peel by Shao *et al.*[145] afforded a small HMF yield of 3.8% at 135 °C, 6 min, at a liquid-to-solid ratio of 12:1. Cheng *et al.*[146] evaluated red mud as an inexpensive mixed metal oxide heterogeneous catalyst for catalytic hydrothermal liquefaction (CHTL) of a surrogate mixture, representing institutional FW, namely American cheese, canned chicken, instant potatoes, green beans, white rice, apple sauce, and butter. At 300 °C, 7.6 MPa nitrogen pressure for 1 h, the bio-oil yield was 39.5 – 47.0%. The heating value of 37.7 - 40.2 MJ kg^{-1} was greater than that of oils obtained without a catalyst (HHV of 36.1 MJ kg^{-1}). While the number of studies is rather small, it appears that CHTL gives a higher oil yield with excellent heating value and does not require drying. However, further studies in improving the catalyst activity and selectivity to promote aldol condensation and deoxygenation and the catalyst separation and regeneration from biochar are still needed. Microwaves can be efficient in reducing processing time due to the polar nature of many FW constituents. Yet, comprehensive studies are missing.

2.1.3.2 Hydrothermal carbonization (HTC). HTC is the most recent and cheapest hydrothermal technique[77,78]. It operates at lower temperatures of 180–350 °C[147], 2–6 MPa, and 5 – 240 min[148] and can handle wet feedstocks. Carbonization generates solid, liquid, and gaseous products through hydrolysis, dehydration, decarboxylation, aromatization, and recondensation[148–150] and results in an energy-dense char, referred to as hydrochar, with composition and energy content similar to lignite coal.[151] These chars can serve as energy storage. Because of the high moisture of FW, HTC could be more attractive than other thermal conversion techniques. Li *et al.*[152] carbonized FW collected from restaurants and associated packing materials at 225 - 275 °C and concentrations of 5 – 32 wt%, dry. At 250 ^{o}C and 96 h, >70% of the initial carbon remained in the solid phase. Changes in the reaction temperature only slightly influenced carbonization[152].

2.1.4 Thermo-catalytic reforming (TCR). TCR is a modern pyrolysis technique that utilizes a wide variety of feedstocks such as sewage sludge, grass, and algae, and FW to produce 50% liquids, 25% char, and 25% gas[153]. The temperature range (350 - 450°C), heating rate (a few minutes), and residence time (multiple seconds) are usually lower than traditional pyrolysis methods[154]. Catalytic steam reforming of the pyrolysis vapor further enhances the H_2 content and lowers the liquid viscosity. Efforts have focused on improving the bio-oil physical and chemical properties, such as corrosiveness, viscosity, and thermal stability, using steam reforming. TCR of sugarcane bagasse and sugarcane have been studied to produce bio-oil, biochar, and syngas[155]. The bio-oils obtained have a higher calorific value than conventional pyrolysis. Ouadi et al.[156] converted food waste from restaurants, markets, canteens, and hotels for TCR to 7 wt% organic bio-oil, 53 wt% permanent gas, and 22 wt% char. Brewers' spent grains have also been used as a potential feedstock for TCR to produce high-quality biofuels[157]. Sattar et al.[158] investigated subsequent gasification of rapeseed and miscanthus biochar after intermediate pyrolysis to increase the volume fraction of hydrogen to 58.7%.

2.1.5 Summary of conversion technologies and products. The aforementioned thermal and catalytic technologies, valorizing the entire FW, form a small slate of low-value products. Gasification is ideal when syngas is of interest. Given the abundance and low cost of shale gas, we do not foresee it as a future competitive technology. Hydrothermal valorization is ideal for processing high moisture FW, yielding mainly bio-oil and gaseous products (CO_2 and water vapor). It bypasses the need for drying and a liquefaction solvent, reducing energy and materials cost. Bio-oil and biochar can be produced via dry pyrolysis. Similar to lignocellulose, the bio-oil from starchy FW needs significant hydrodeoxygenation to remove the excess oxygen. Co-pyrolysis of multiple feedstocks of widely varied composition (high protein content waste – legumes, high carbohydrate content waste – fruits, high ash content waste – vegetables) is an opportunity to be further exploited. Hydrothermal treatment and pyrolysis are typically performed at moderate temperatures (200 - 500 ^{o}C), whereas gasification at very high temperatures (>700 °C) with a corresponding higher energy demand. All these methods are, to an extent, agnostic to the feedstock and thus reasonably versatile. However, the main products, bio-oils and biochars, are of low value, retain very little of the original FW's functionalities, and are unfit for high-value chemicals[121]. Pyrolysis and hydrothermal carbonization give biochar and hydrochar, respectively, with numerous applications, as discussed in review articles[159–161]. Examples include membrane separation[162], carbon capture[163], catalyst synthesis[68,164–166], organic dye adsorbents[167], water treatment[9,13,168], and electrodes for high-energy supercapacitors and fuel cells[164,169–180]. Nitrogen-doped carbon materials have also been synthesized from waste chitin and chitosan[133–137,181,182] and can be useful as catalysts.

2.2. Valorization of carbohydrates

This subsection covers catalytic valorization to convert carbohydrates to simple sugars, HMF, and other valuable intermediates.

2.2.1 Valorization of carbohydrates in fruits, vegetables, and starchy food waste (FW)

Valorization of starch-rich carbohydrates obtained from vegetables, fruits, and tuber residues can give products typical of sugars dehydration, as shown in Table 3 and Table 4. First, sugars are obtained via acid hydrolysis of the carbohydrate feedstock and then upgraded to chemicals.

Table 3. Catalytic conversion of food waste (FW) into HMF.

Feedstock	Catalyst	Solvent	Temperature (^{o}C)	Time (h)	HMF yield (wt.%)
Melon rind[76]	100 mg montmorillonite clay, 350 mg NaCl	Water/THF (1:3 v/v)	180	0.5	6.0
Catering waste[78]	2 wt.% $Zr(HPO_4)_2$ calcined at 400 ^{o}C	Water	160	6.0	4.3
Unskinned kiwifruit[15]	55.5mM $SnCl_4$	DMSO/water (1:1 v/v)	140	0.33	13.7
Watermelon flesh[15]	55.5mM $SnCl_4$	DMSO/water (1:1 v/v)	140	0.33	13.2
Vegetable waste[15]	55.5mM $SnCl_4$	DMSO/water (1:1 v/v)	140	0.33	4.9
Vegetable waste[183]	Amberlyst 15/Amberlyst 36	DMSO/water	135-150	0-2*	12
Bread waste[67]	55.5mM $SnCl_4$	DMSO/water (1:1 v/v)	140	1.0	26
Bread waste[77]	Sulfonated bio-char	DMSO/water	180	0.33	22
Bread waste[184]	55.5mM $SnCl_4$	γ-valerolactone /water (1:1 v/v)	120	0.33	14
Bread waste[184]	55.5mM $SnCl_4$	Propylene carbonate/water (1:1 v/v)	120	0.125	14
Bread waste[185]	H_3PO_4-activated biochar	DMSO/water	180	0.33	22
Rice waste[186]	55.5 mM $AlCl_3$,13.9 mM maleic acid	Acetone/water (1:1 v/v)	140	0.33	25.2
Soybean peel[187]	4 wt.% H_2SO_4	[BMIM][Br]	120	3.0	3.4
Potato peel waste[9]	0.05 M H_2SO_4 + 25 wt.% LiBr	Water	160	3.0	39.4

*Microwave heating

Table 4. Catalytic conversion of food waste (FW) to various platform chemicals.

Feedstock	Catalyst	Solvent	T (^{o}C)	Products	Yield (wt%)
Rice[185]	H_3PO_4-activated bio-char	Water	150	Glucose	86.5
Empty fruit bunch[188]	H_2SO_4	Water	198	Furfural	19
Rice husk[189]	HCl	Water	170	Levulinic acid	59
Rice husk[190]	SBA-15	Toluene	177	Furfural	6
Rice husk[191]	Cr(II)/Ni(II)/Zn(II)	Water	300	Lactic acid	6.7
Sorghum straw[192]	H_3PO_4	Water	134	Furfural	57

Rice straw[193]	Pt/Al_2O_3	Ethanol + MIPK	150	Furfural	22
Tomato plant waste[194]	HCl	Water	225	Levulinic acid	45
Potato peel[195]	H_2SO_4	Water	170	Levulinic acid	15
Corn stover[196]	H_2SO_4	Water: GVL=2:8	-	Levulinic acid	47
Wheat bran[191]	Cr(II)/Ni(II)/Zn(II)	Water	300	Lactic acid	7.4
Vegetable waste[183]	Amberlyst 36	DMSO-water	135-150*	Levulinic acid	10.9
Melon rind[76]	H_2SO_4 and Montmorillonite KSF	Water/THF=1:3	180	Levulinic acid	2

*Microwave heating

The reaction conditions (temperature, time), the solvent, and the catalyst determine the products. The intermediates from carbohydrate hydrolysis are xylose and glucose. As shown in Tables 3 and 4, these monomeric sugars can be converted to HMF, furfural, lactic acid, and levulinic acid, among the US Department of Energy Top 10 value-added chemicals from biomass[197]. With a few exceptions, the product yields are medium to low, and the catalysts have mainly been homogeneous. Given experience from sugar dehydration of lignocellulosic biomass, suitable biphasic systems, low pH, high temperatures, and short residence times are expected to improve yields significantly.

2.2.2 Valorization of carbohydrates in dairy waste streams

Since lactose accounts for about three-fourths of the total solids in acid whey waste, whey waste is valuable for producing glucose/galactose syrups. Its acid-catalyzed hydrolysis[198] is preferable over enzymes due to the high costs of the latter[199]. Ramsdell *et al.*[79] investigated the factors affecting the acid hydrolysis of pure lactose aqueous solutions and whey. Hexose sugars up to 93% of the theoretical yield were obtained by hydrolyzing a 30% lactose solution using 0.007 M HCl at 147 °C. At high temperatures and long reaction times, lactose and whey protein result in charring and caramelization. Other researchers have also studied the production of such syrups from aqueous lactose solutions[200–203]. Ion exchange resins were used as catalysts at pH 1.2 and 90 – 98 °C[198,204]. One challenge is that the proteins condense with the sugar monomers. de Boer *et al.*[198] achieved 80% lactose acid-hydrolysis in 3 min using whey ultrafiltrate at 150 °C. They further demonstrated that lower nitrogen content in the whey resulted in a less intense brown hydrolysate using demineralizing ion exchange resins and reverse osmosis as pre-hydrolysis filtration. Selectivities and yields of the monosaccharides produced were not reported. Recently Huber *et al.*[75] applied non-ion exchange resin solid catalysts and homogeneous acids at 120 -160 °C to pure lactose and acid whey. Hydrolysis of untreated acid whey gave a monosaccharide selectivity of 90% at pH 2.3 after 1 h at 150 °C. Ultrafiltration removal of the protein and fat followed by non-protein nitrogen species removal by activated charcoal improved the monosaccharide selectivity above 94% over the solid acid catalyst (Amberlyst 70) and the homogeneous catalyst (sulfuric acid) with a maximum ~80% sugar yield. Huber and coworkers further developed an integrated process for converting acid whey waste streams into whey protein concentrate and glucose/galactose syrups[19]. It is clear that unlike pure lactose hydrolysis, acid-catalyzed condensation of proteins and sugars in the actual acid whey waste creates challenges. Separation of the N-containing compounds and fat before hydrolysis can circumvent this issue and result in a high yield of monosaccharides. One could then leverage carbohydrate conversion technologies discussed above.

2.2.3 Chitin and chitosan hydrolysis to glucosamine monomers

Chitin is the second most abundant natural polysaccharide after cellulose. As shown in Figure 4, chitin is comprised of repeating units of β-(1–4)-2-acetamido-2-deoxy-β-D-glucose and β-(1–4)-2-deoxy-β-D-glucopyranose structures, and chitosan is the N-deacetylated derivative of chitin producing poly(β-(1–4)-N-acetyl-D-glucosamine). Chitin and chitosan can be hydrolyzed into monomers, N-acetylglucosamine (GlcNAc) and glucosamine (GlcN), respectively (Figure 4) that are used in health applications[205], cosmetics[206], and food additives[207,208]. Recently, GlcNAc was considered for bioethanol production through fermentation[209]. These monomers also can be upgraded into platform chemicals such as acetic acid, HMF, and amine-containing monomers for biobased polymers, polyamides, pharmaceutical, and biomedical applications[210,211].

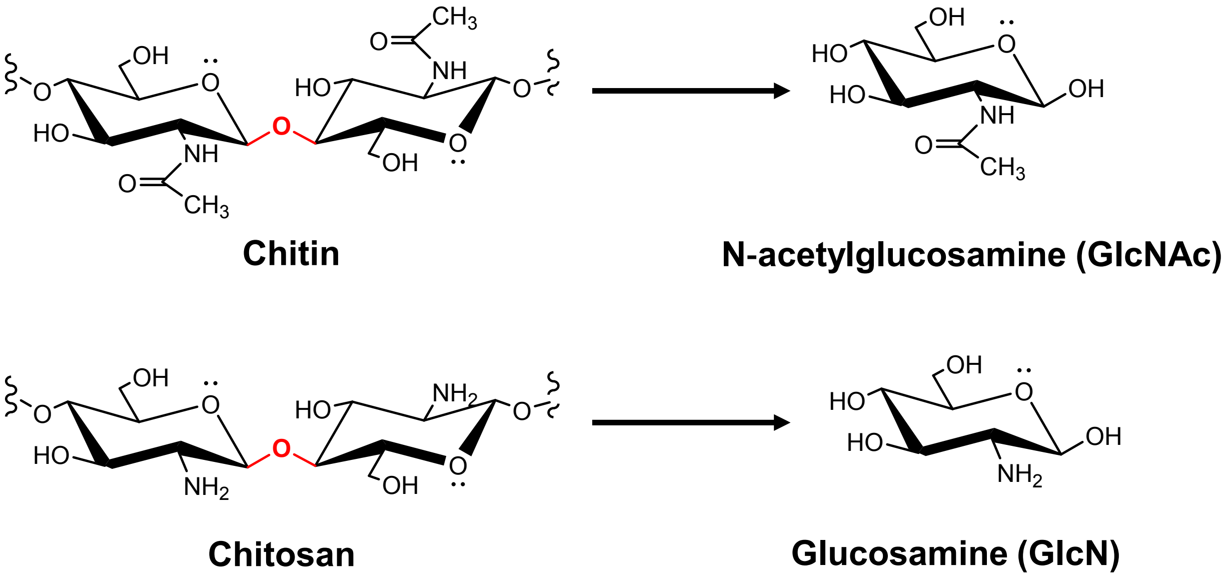


Figure 4. Chemical structures of chitin and chitosan and their respective monomers.

Hydrolysis of chitin and chitosan is traditionally performed using a strong acid catalyst, e.g., HCl[212]. Depending on process conditions, either GlcN or GlcNAc is produced. GlcN is usually obtained from chitin with concentrated HCl (20–37%) at 100 °C[81]. GlcNAc is obtained at lower temperatures (40–80°C)[213] or by re-acetylation of GlcN with acetic anhydride[214]. Ferrer *et al.* hydrolyzed shrimp-shell waste using HCl, giving a glucosamine yield of 80%[82]. The glucosamine hydrolysate was further fermented to a single cell protein. Yan *et al.* transformed raw shrimp shells into 47.9% acetic acid yield in 2 M NaOH at 300 ^{o}C over CuO with O_2 in 35 min[215]. A comparable yield was obtained in 90 min at 235 ^{o}C. Sutheerawattananonda *et al.* observed that hydrolysis of waste mushroom chitin proceeded faster in H_2SO_4 than HCl due to the quicker dissolution rate and higher solubility[80]. At optimum reaction conditions (mushroom to acid volume of 1:10; 6 M

H_2SO_4, 100 °C; and 6 h), the glucosamine yield from waste enoki, wood ear, shitake, oyster, and straw mushroom was >95%. Given the limited N content in typical lignocellulosic biomass, exploring the N-containing compounds for value-added chemicals is a worth pursuing direction.

2.3 Waste protein valorization to amino acids

Distiller's spent grain, castor bean meal, soybean meal, poultry feather meal, dairy waste, shrimp waste, crab processing waste, lobster shells, prawn shells, and krill shells[216–218] are examples of protein-rich FW. Whey is rich in proteins, lactose, and salts. Hence, recovery of protein and valorization of the lactose-rich residue, discussed in Section 2.2, has been of interest. Jaswal[84] investigated the acid hydrolysis of crab processing waste using 5 N HCl and achieved 28-31% amino acid yield in 12 h. Dalev *et al.*[85] reported a combined enzyme-alkaline technology for processing poultry waste feathers into a protein concentrate. Feathers were pretreated with 0.3 M NaOH solution at 80 °C to be fully solubilized and then hydrolyzed via enzymes at 55-60 °C. The product was spray-dried to a powder with a protein content of 795 g/kg. Ferrer[82] *et al.* extracted protein from shrimp shell waste at pH 12 for 2 h at 30 °C with constant stirring and a solid/solvent ratio of 1:20. 90% of the extracted protein was recovered from the extract at a pH of 7-8. Compared to the valorization of carbohydrates, oils, and the whole FW, waste protein valorization has been less studied. Yet, there is an opportunity to produce unique nitrogen-containing chemicals for existing or new applications.

2.4 Conversion of waste oils and fats to biodiesel and other value-added products

Waste cooking oils (WCOs) are valuable for applications ranging from fuels to lubricants to soaps. Production of biodiesel by transesterification of WCOs and fats is an established technology [96–99] and is not reviewed here. Luque and Clark[93] produced biodiesel with quantitative yield from waste rapeseed, sunflower, and olive oil using acidic mesoporous carbonaceous materials (Starbon acids) with conventional and microwave heating in 18 h and 40 min, respectively. Sanjel *et al.*[94] investigated the transesterification of waste vegetable oil at three molar ratios of oil:methanol (1:6, 1:12, and 1:18) in supercritical ethanol and methanol between 210 °C and 350 °C. A maximum conversion of 99% was reached at 290 °C in ethanol and 330 °C in methanol. Gan *et al.*[95] applied three ion-exchange resins (Amberlyst-15, Amberlyst-16, and Dowex HCR-W2), investigating the effects of catalyst concentration, temperature, and methanol to oil molar ratio on the esterification of free fatty acids (FFA) from WCO (Table 5). A maximum FFA conversion of 60.2% was obtained using 4 wt.% Amberlyst-15, 65 °C, and methanol to oil molar ratio of 15:1. Janajreh *et al.*[219] performed transesterification of WCO in a tubular semi-continuous reactor at 50 and 60 °C and different waste oil to methanol ratios (1:0 to 1:24) in NaOH. They achieved higher conversion and product yield at relatively higher temperatures, larger methanol to triglyceride molar ratios, and longer residence times.

Table 5. Esterification/transesterification of waste cooking oil.

Catalyst	Conditions	Conversion
Starbon-400	1:3 oil/methanol ratio (v/v), 0.1 g of catalyst at 80 °C. 18h for conventional heating and 30-40 min for microwave heating	100%[93]

-	Molar ratios of oil: methanol (1:6, 1:12 and 1:18), 210 °C - 350 °C, supercritical ethanol and supercritical methanol	99% at 290 °C for methanol and at 330 °C for methanol[94]
Amberlyst-15, Amberlyst-16 and Dowex HCR-W2[95]	4 wt% catalyst, 65 °C and a methanol to oil molar ratio of 15:1	60.2% over Amberlyst-15
Porous carbonaceous materials prepared from corncobs[166]	32:1 methanol/oil ratio, 3 wt% catalyst, 6 h, 80 °C	(>95%)

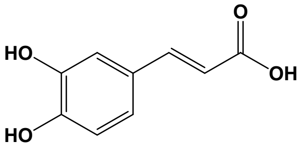
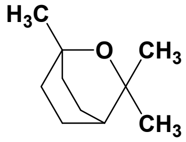
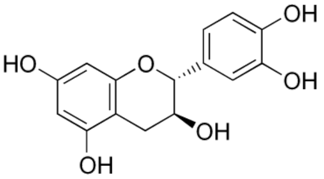
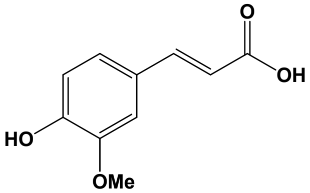
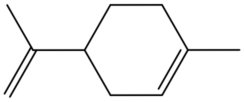
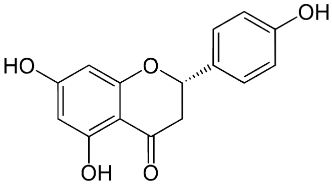
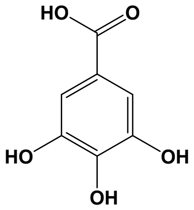
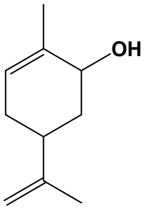
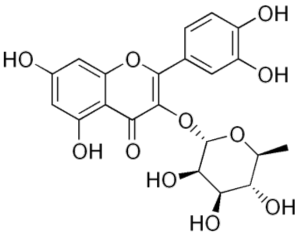
Aside from biodiesel, recent studies have investigated other products. Hydrodeoxygenation (HDO) of WCO to gasoline and jet fuels is an attractive catalytic strategy[220–223]. Liu *et al.*[220] prepared diesel-range alkanes in 79–85 wt% yield by HDO of vegetable oils and WCO over ReOx modified Ir/SiO_2 catalysts at 180 °C and 2 MPa H_2. Vu *et al.*[221] and Ahmad *et al.*[222] performed catalytic hydrotreating of WCO over zeolites to produce gasoline-range hydrocarbons. Guo *et al.* reported good activities of Ru/La$(OH)_3$[224] and Ru-hydroxyapatite (HAP)[225] catalysts for the HDO of different vegetable oils and WCO at 180 °C, achieving approximately 80% yield of diesel-range alkanes.

Another valorization strategy of fatty acids entails hydrogenation to alcohols and aldehydes. These products then undergo condensation with furan based compounds to renewable lubricant base oils[90–92]. Other applications of WCO include plasticizers, polymers, and surfactants[226,227]. Specifically, Pleissner *et al.*[226] investigated the formation of plasticizers and surfactants from lipids. Lipids were extracted using supercritical carbon dioxide and then transesterified with methanol. For producing plasticizers, the double bonds in the unsaturated fatty acid methyl esters (FAMEs) were epoxidized using peroxoformic acid, formed in situ from H_2O_2 and formic acid. Saturated and epoxidized FAMEs were transesterified with polyglycerol, forming fatty acid polyglycerol esters for producing surfactants. Plaza *et al.*[227] reported epoxidation and further synthesis of polyurethanes from waste cocoa butter in batch and continuous flow reactors. While most work has focused on valorizing WCO to fuels (high volume, low-value products), we expect that upgrading WCO to lubricants, surfactants, and other high-value products is more commercially attractive.

2.5 Extractives and essential oil extraction

Extractives, such as polyphenols, anthocyanins, tannins, terpenes, flavonoids, and essential oils (Table 6), possess antioxidative, antibacterial, antiaging, and anti-mutagenic properties, making them valuable in food preservatives[228], perfume[88,229], cosmetic[230,231], and pharmaceutical formulations[8,232,233].

Table 6. Typical phenolics abundant in food-waste extractives and essential oils.

Polyphenols	Essential oils	Flavonoids
 Caffeic acid	 Cineole	 Catechin
 Ferulic acid	 Limonene	 Naringenin
 Gallic acid	 Carveol	 Quercitrin

These components are abundant in FW materials, with the type and quantity varying with the feedstock's nature, extraction method and solvent, duration of extraction, sample particle size, feedstock storage conditions, and solvent/sample ratio[234] (Table 7).

Table 7. Common extractives and their yields obtained from different feedstocks.

Extract	Feedstock	Solvent	Yield
Artemisin[102]	*Artemisia annua L.*	Polyethylene glycol	14 mg/g
		Ethanol	10 mg/g
		Ethyl acetate	9 mg/g
		n-Hexane	7 mg/g
Astaxanthin[103]	Shrimp shell waste	Acetone/ethanol	20 ml/g
Polyphenols	Pomegranate peel[104]	Ethanol	308 mg/g
	Potato peels	Methanol[105]	80 mg/g
		Methanol + Water[9]	220 mg/g
	Blueberry pomace[106]	Ethanol	23 mg/g

	Grape pomace[235]	Water + Ethanol	1.57 mg/g
	Olive mill residue[236]	Ethanol	24 mg/g
	Appletree wood residue[237]	Water + Ethanol	40 mg/g
Flavonoids	*Cassia angustifolia*[238]	70% ethanol	28 mg/g
	Orange peels[21,101]	Hexane	15.2 mg/g
Anthocyanins[106]	Blueberry pomace	Ethanol	2.1 mg/g

Extractives and essential oils are isolated from plant materials using the Soxhlet extraction[239,240]. The extraction is slow, and the yield is often not as high. Recently, more efficient and "greener" extraction processes, such as ultrasound-assisted extraction[43,241–243] (UAE), microwave-assisted extraction[237,244–248] (MAE), pressurized fluid extraction[104,106] (PFE), supercritical CO_2 extraction[233,249] (SC-CO_2), and enzyme-assisted extraction[233] (EAE) were introduced. As shown in Table 7, fruit and vegetable wastes possess many extractives that can be isolated and used as-is[228] or further upgraded. Unlike lignocellulosic biomass, the extractives-rich FW can give value-added products and increase the viability of biorefineries[9]. Consequently, more studies optimizing their extraction and isolation would be welcome. Attention should be on assessing and improving the entire extraction and purification flowsheet's economic viability, as the energy demand and cost for separations of the low concentration level of extractives in solvents can be high.

2.6 Waste lignin depolymerization to phenolics

Recently, an unusual catechyl lignin (C-lignin) was discovered in the coats of waste vanilla, castor seeds, and various Cactaceae members of the genus Melocactus[250]. The absence of O-methyltransferase (OMT) activity for converting catechyl to guaiacyl (G) and, subsequently, to syringyl (S) monomers, results in 100% catechyl (C) units in the cell wall. This C-lignin is a homopolymer synthesized almost purely by β–O–4 coupling of caffeyl alcohol, producing benzodioxanes as the dominant unit (Figure 5). Hydrogenolysis of C-lignin[86,87] resulted in high yield catechyl-type monomers (>90%), rendering C-lignin an attractive feedstock. Furthermore, its benzodioxane homopolymer network lacks condensed units; its one monomer type (compared to woody biomass containing syringol, guaiacol, and hydroxyphenol monomers) circumvents product separation issues.

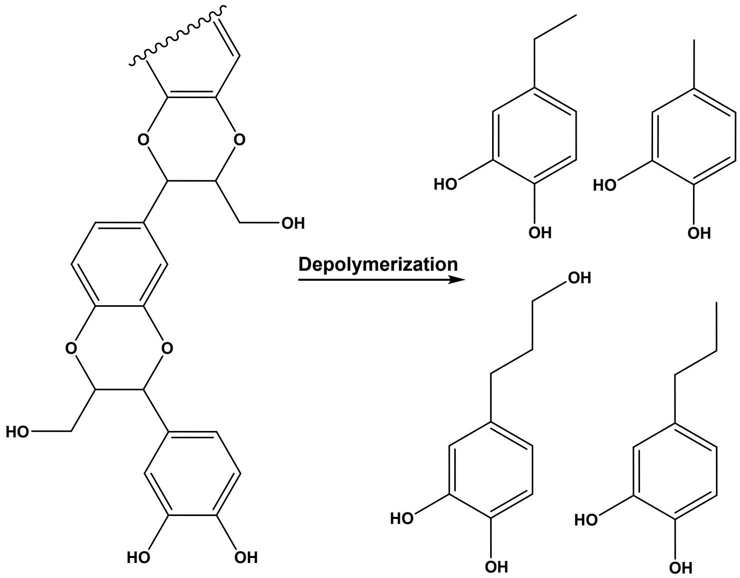


Figure 5. Structure of catechyl (C) lignin and obtained monomers following depolymerization.

Asides from a few studies on C-lignin depolymerization, there is limited research on the upgrade of FW-containing lignin. Table 8 summarizes related literature findings. Cravotto *et al.*[88] performed oxidative depolymerization of tomato waste lignin to obtain vanillin, syringaldehyde and other bio-aromatics (acetovanillone, *p*-hydroxybenzaldehyde, and carboxylic acids). With global challenges sourcing natural vanilla essence[229], vanilla sourced from FW-vanillin is attractive. Cashew nut[251,252], vanilla seed waste[86,87], and castor seed coat[253] have been upgraded into alkyl catechol lignin monomers. Lignin valorization of feedstocks containing S, G, and H (hydroxyphenyl) units has mainly focused on wood (pine, poplar, birch) and herbaceous biomass (miscanthus, corn stover, switchgrass), and less on FW. Nutshells and brewer spent grains have high lignin (Table 1) of aromatic chemicals. These aromatics have wide applications[232,254] as dietary supplements, food[229,255], and cosmetics additives[230]. Further developing FW-lignin depolymerization methods is worth pursuing.

Table 8. Monomer yields obtained from food waste lignin depolymerization.

Feedstock	Catalyst	Solvent	Environment	T (°C)	P (bar) at RT	Time (h)	Monomer yield (wt.%)
Tomato waste[88]	-	pH 14 NaOH	Oxidative (O_2)	170	15	0.25	19
Vanilla seed waste[86],[87]	Pt/C	Methanol	Reductive (H_2)	200	40	15	84.2*
	Ru/C	Methanol	Reductive (H_2)	200	40	15	88.86*
	Pd/C	Methanol	Reductive (H_2)	200	40	15	88.55*
	Ni/C	Methanol	Reductive (H_2)	200	30	16	14

Cashew nut shell liquid[251]	Ni/NiO	Octane	Reductive (H_2)	300	70	6	95
Castor seed coat[253]	Pd/C	Methanol	Reductive (H_2)	200	30	4	29.6

* Yield reported based on C-lignin content.

3.0 Kinetics and modeling of FW valorization

This section focuses on the mechanistic insights, kinetics, and reaction profiles of different FW components.

3.1 Kinetics of the entire FW depolymerization

The kinetics of real feedstocks is hard to interpret, and that of model compounds is idealistic. This situation is reflected in the following discussion. Thermal decomposition results mainly in methane, other gaseous products (carbon dioxide and water), and biochar. Pyrolysis has been investigated[122,256–259] using thermogravimetry. Yoo *et al.*[256] studied cereals, meats, vegetables, and mixed foods and found that the onset and terminal temperatures vary among food types (250 °C and 400 °C for cereal; 200 °C and 500 °C for meat; 160 °C and 450 °C for vegetables; and 150 °C and 450 °C for mixed foods). As expected, the feedstock composition affects the pyrolysis product yield, product distribution, and energy input. Based on the FW type (Figure 6a), the activation energy ranges from 10 to 50 kJ/mol and is generally low. The low values may indicate transport limitations (see next).

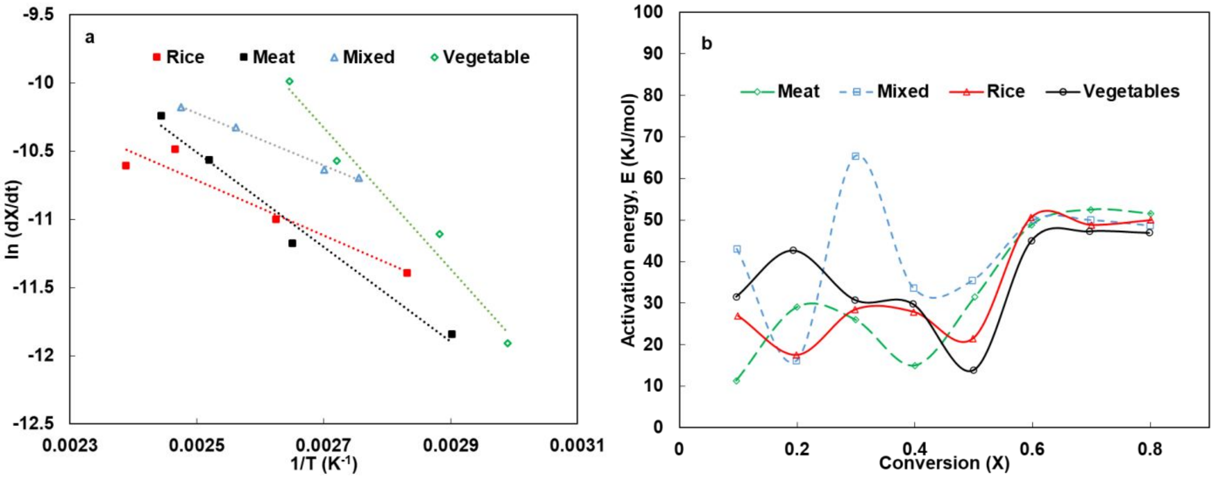


Figure 6. a) Variation in activation energy (slopes of lines) for various FW feedstocks. b) Estimated activation energies in pyrolysis of different FW vs. conversion. Redrawn from ref.[256]

The activation energy varies with the extent of the reaction in a nonlinear manner and increases at higher conversions (Figure 6b). We hypothesize that this nonlinear behavior occurs in part due to the varying bond strength of various compounds (weaker bonds get pyrolyzed earlier than stronger bonds) and in part due to temperature gradients and diffusion limitations. Since pyrolysis is often heat transfer controlled, a temperature front evolves with time inwards. The varying bond strength and temperature gradients result in a complex pyrolysis profile, with multiple reactions co-occurring and being affected by diffusion and heat transfer limitations. Typical reactions reported during pyrolysis include dehydration, decarboxylation, and decarbonylation[7,122–124,126,260]. The average activation energy also depends on the composition of FW material. Tran *et al.*[261] estimated the activation energy to be 20–57 kJ/mol for lignin, 40–100 kJ/mol for hemicellulose, and 100–104 kJ/mol for cellulose. This variation in activation energy arises from different bond types and strengths, attractive forces holding the polymer network, and the degree of biopolymer crystallinity. Depending on the kinetic model applied, the activation energies vary widely, probably due to the compensation effect (in simple terms, the same rate constant can result from various combinations of activation energies and pre-exponentials, compensating for each other).

For example, Yoo *et al*. estimated apparent activation energies for pyrolysis of cereals, vegetables, and meat to be 10 – 70 kJ/mol using the Friedman model. Sayan *et al.*[259] obtained 90 – 110 kJ/mol for spent coffee grounds using the Coats–Redfern, the Flynn–Wall–Ozawa (FWO), the Kissinger–Akahira–Sunose (KAS), and the Starink models. Tian *et al.*[257] obtained values 130 – 250 kJ/mol for kitchen and municipal solid waste using the distributed activation energy model (DAEM). The use of different models makes direct comparison across studies not as insightful.

The reaction temperature affects the selectivity of aromatic hydrocarbons (for fuels) over oxygenated species[260,262] owing to the prevalence of deoxygenation, decarboxylation, and decarbonylation in converting long-chain carboxylic acids in biocrude at high temperatures into long-chain alkanes. Similarly, Chen *et al.*[120] identified that increasing temperature increases the H_2 yield in FW gasification at the expense of CO with an increase in biochar. Corresponding kinetic studies on gasification have also been published[263,264]. The strong effect of temperature on selectivity is expected.

Prior models that describe the FW thermal transformation are mainly empirical and not universal, and there is a gap in fundamental and mechanistic understanding. Predictive process modeling would require (1) Generalized kinetic models capable of predicting the rate of pyrolysis and the product distribution from the FW composition. The adoption of a general kinetic model will facilitate comparison among research groups but is currently lacking. (2) Heat and mass transfer models for estimating the solid temperature profiles and diffusion of products out. (3) Coupling of kinetics and transport models in a grain. And finally, (4) hydrodynamic and heat transfer models for entire reactors. Addressing these modeling needs is difficult given the complexity of the feedstock, its unknown composition, and its multiscale and multiphase nature. Machine learning (ML)-based models, using massive datasets of feedstock characterization along with correlations to pyrolysis rates and product attributes (descriptors) may provide a means toward achieving this goal. Initial examples of linking complex feedstocks, process, and performance via ML-based models in other contexts close this gap are emergings[252,253].

3.2 Kinetics of FW-carbohydrates valorization

The carbohydrate composition of FW varies widely depending on the polysaccharide framework. Starch- and cellulose-containing FW, like potato peels and spent coffee grounds, comprises glucose monomers, whereas dairy waste, like acid whey, comprises glucose and galactose monomers; and orange, apple, and grape pomace contain simple reducing sugars like fructose. Shell-fish waste contains chitin and chitosan, composed of glucosamine monomers. Mechanistic understanding of carbohydrate hydrolysis to simple sugars (glucose, galactose, xylose, glucosamine) is vital toward producing platform chemicals.

3.2.1 Hydrolysis of bond scission in polysaccharides

Various hypotheses for the hydrolysis of inter-unit C-O linkages in linear polysaccharides have been reported[267–274]. These include: (1) Bonds at the reducing and non-reducing terminal ends are hydrolyzed faster than all other bonds. (2) All bonds are hydrolyzed at the same rate, irrespective of their position and the degree of polymerization (DP). (3) The bond at the non-reducing end is hydrolyzed faster and all other bonds are hydrolyzed at the same rate. (4) The hydrolysis rate constants progressively decrease from the terminal bond towards the interior bonds. Figure 7 illustrates non-reducing terminal bonds with a hydrolysis rate constant of k_1 and other interior or reducing terminal bonds with a hydrolysis rate constant of k_2 for linear saccharides. Prior research by Freundeberg *et al.*[275] and Nguyen *et al.*[276] support hypotheses 1 and 4; the most widely accepted hypothesis, consistent with experiments[74,268–274,276,277], is 3. An overview of kinetic studies for cello-, malto- or xylo-saccharides and the ratio of hydrolysis rates of the non-reducing terminal bond to all other bonds is given in Table 9. Joksimovic *et al.*[278] identified, using PM3 molecular-orbital calculations, that the glycosidic bond acid hydrolysis follows a random protonation and scission along the carbohydrate chain. Analysis of time-dependent reaction profiles indicates that k_1 is 1.3 - 1.8 times larger than k_2 (Table 9)[268–270,272,274].

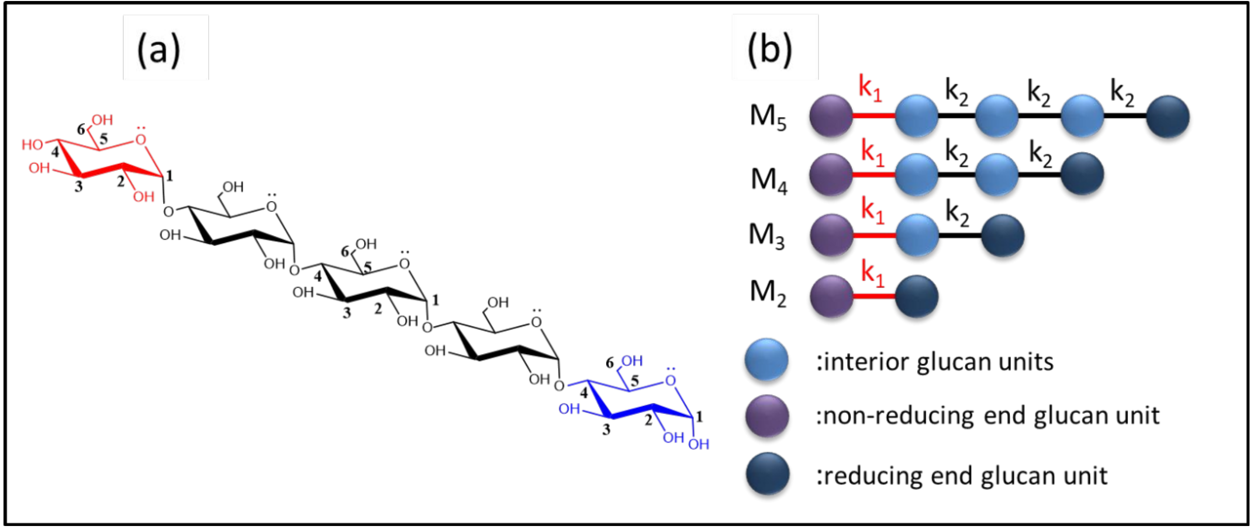


Figure 7. Glucan unit and bond nomenclature. (a) The reducing end (colored blue) has an anomeric carbon, C1, with the hemiacetal unit not involved in a C-O linkage. The non-reducing end (colored red) has C4 not involved in the C-O linkage. The interior units have both C1 and C4 involved in a C-O linkage. (b) Schematic showing non-reducing end bond (with a rate constant k_1) and other bonds (with a rate constant k_2) in select oligosaccharides. Reproduced from ref.[74] with permission from the American Chemical Society.

Table 9. Ratio of bond scission rate constants for the acid-catalyzed hydrolysis of various saccharides[74].

Substrate	k_1/k_2	Reaction conditions
Cello-oligosaccharide[268]	1.7	T: 90 - 135 °C $C_{substrate}$: 0.5 - 1 wt.% C_{H2SO4} : 0.05 - 0.1 N
Cello-oligosaccharide[274]	1.5	T: 30 - 120 °C $C_{substrate}$: 10 wt.% C_{H2SO4} : 0.5 - 14.2 N
Malto-oligosaccharide[272]	1.8	T: 95 °C $C_{substrate}$: 0.1 - 0.4 wt.% C_{H2SO4} : 0.01 N
Malto-oligosaccharide[269]	1.8	T: 75 - 95 °C $C_{substrate}$: 0.625 wt.% C_{H2SO4} : 0.01 N

Malto-oligosaccharide[270]	1.7	T: 70 - 135 °C $C_{substrate}$: 1 wt.% C_{H2SO4} : 0.2 N
Malto-oligosaccharide[74]	1.4	T: 40 - 60 °C $C_{substrate}$: 3 wt.% C_{H2SO4} : 0.1 N + 59 wt.% LiBr
Xylo-oligosaccharide[271]	1.7	T: 80 - 100 °C $C_{substrate}$: 1 wt.% C_{H2SO4} : 0.05 - 0.5 N
Chitin-polysaccharide[279]	2.0	T: 40 °C C_{HCl} : 12 N

3.2.2 Glucose-containing polysaccharides

Starch and cellulose consist of glucose monomers. Vlachos and co-workers[74] proposed a kinetic model describing the hydrolysis of malto-saccharides to glucose in acidified LiBr molten salt hydrate. They used a mass action kinetics model to describe the entire population of intermediates from FW-derived potato starch to glucose. As shown in Figure 7 and Table 9, two fundamental rate constants with similar apparent activation energies (~111 ± 7 KJ mol^{-1}) are adequate to model the hydrolysis, consistent with hypothesis 3 stated above. The hydrolysis rates difference is attributed to entropic differences of the transition states when these bonds are protonated[74,269,272]. The chain length (degree of polymerization) affects the hydrolysis rate and is inversely proportional to the glucose-formation rate constant (Figure 8).

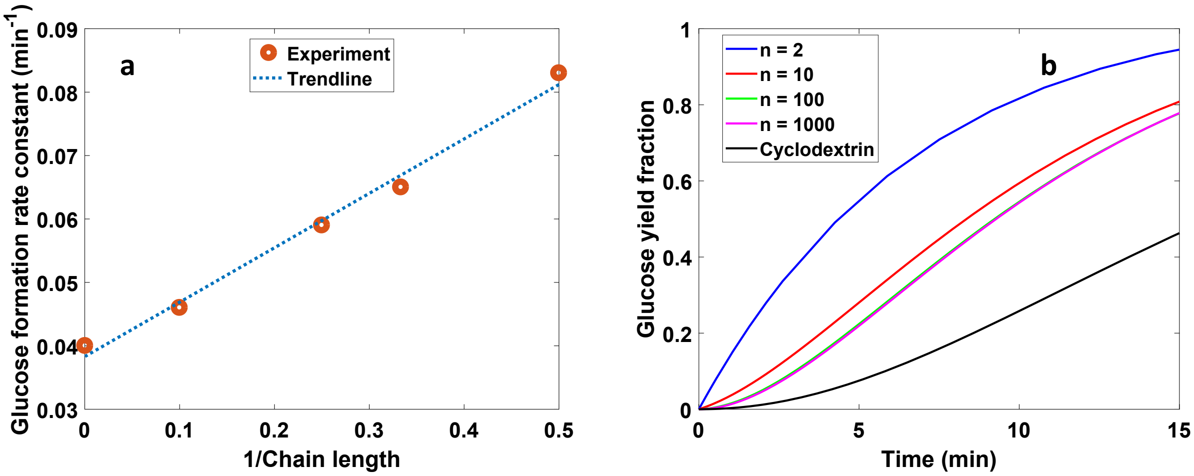


Figure 8. (a) Effect of chain length on glucose formation rate constant. Points are experimentally determined rate constants. Reaction conditions: 0.1 g of oligosaccharide in 3.64 ml LiBr AMSH, T = 60 °C. (b) Simulated glucose formation profile in the hydrolysis of saccharides of different chain lengths. Reaction conditions: 0.1 g of oligosaccharide in 3.64 ml of LiBr AMSH, T = 60 °C. Reproduced from ref.[74] with permission from the American Chemical Society.

Tandem hydrolysis and dehydration of bread waste was performed by Poon *et al.*[67], using metal salts. $SnCl_4$ converted glucose into 5-hydroxymethylfurfural (HMF) with higher yields and faster compared to $AlCl_3$. The isomerization of glucose to fructose followed by fructose dehydration is more effective than the direct Bronsted-acid dehydration to HMF. Earlier work[280–282] by Davis and co-workers showed that Lewis acid catalysts drive the isomerization of glucose to fructose by an intramolecular hydride shift. In contrast, Brønsted acids are responsible for the dehydration of fructose to HMF. Vlachos and co-workers[283,284] showed that asides from metal salts serving as Lewis acids in these transformations, the hydrolysis of metal aquo ion complexes release H^+ and decreases the solution pH. This Lewis acid-derived (intrinsic) Brønsted acidity also drives fructose dehydration to HMF without any *ex-situ* acid. $SnCl_4$ is a weaker Lewis acid catalyst than $AlCl_3$ (the rate constant of the isomerization in an aqueous medium at 120 ^{o}C is 2.5 x 10^{-5} s^{-1} in $SnCl_4$ vs. 4.5 x 10^{-5} s^{-1} in $AlCl_3$).

The product distribution profile over $AlCl_3$ differs from that over $SnCl_4$ (Figure 9). In the former, disaccharides form at short times, most probably because hydrolysis at low pH is rapid (1.2–1.5 in $SnCl_4$ vs. 2.3–3 in $AlCl_3$). $SnCl_4$ also gave a slightly higher HMF yield than $AlCl_3$ (29.5 ± 1 mol % vs. 25.6 ± 1 mol % at 160 ^{o}C). These differences can be rationalized by the stronger Brønsted acidity of $SnCl_4$ that accelerates hydrolysis to glucose[74] and the dehydration of fructose to HMF[285]. Under highly acidic conditions, and especially at high temperatures, glucose can undergo direct dehydration to HMF. The co-existence of direct and indirect pathways to HMF from glucose accounts for the better performance of $SnCl_4$.

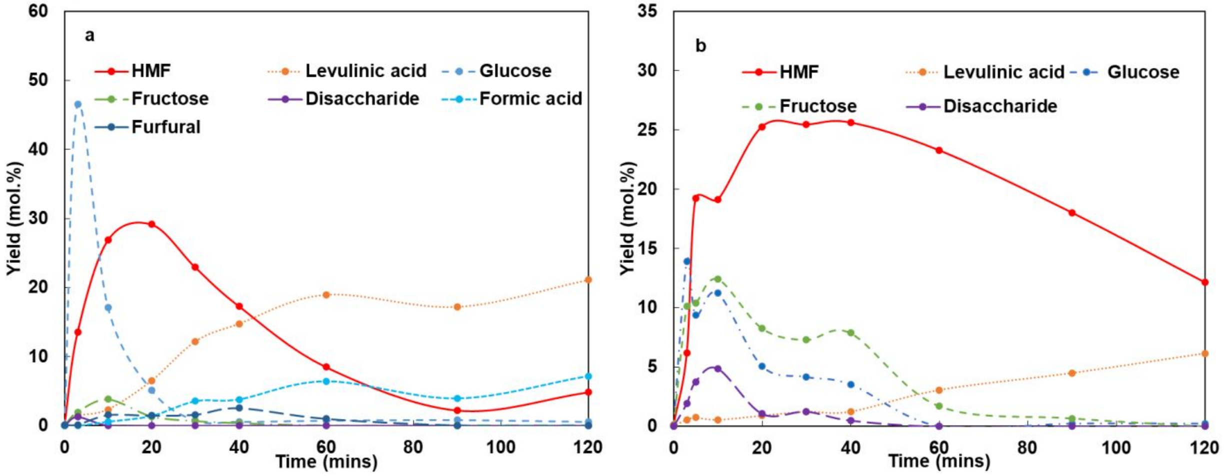


Figure 9. Time-dependent product profiles from bread waste conversion at 160 ^{o}C over a) $SnCl_4$ and b) $AlCl_3$. Redrawn from Ref[67].

These results highlight the importance of tuning the ratio of Brønsted acidity to Lewis acidity to increase selectivity toward desirable products. Dual catalysts have successfully been combined for hydrolysis and dehydration of pure carbohydrate model compounds[283,285]. There is ample experience on how how to tune catalysts amounts and reaction times. The efficacy of tandem catalysts needs to be evaluated for complex FW – derived carbohydrates.

3.2.3 Mixed sugar-based polysaccharides

Huber *et al.*[19,75] investigated the hydrolysis of dairy waste into simple sugars. They studied the kinetics of Brønsted acid-catalyzed lactose hydrolysis in acid whey solutions over sulfuric acid and solid acid catalysts between 120 to 160 ºC. Lactose undergoes both acid-catalyzed hydrolysis (activation energy of 135 kJ/mol) and thermal (non-catalytic) hydrolysis (activation energy of 156 kJ/mol) to produce glucose and galactose (Table 10). Using kinetic parameters for lactose hydrolysis and thermal degradation reactions of lactose, glucose, and galactose, a model, using Eqs. 1-4, was built.

Table 10. Kinetic rate parameters for hydrolysis and thermal degradation reactions of lactose, glucose, and galactose[75].

Rate constant	$\log_{10}$ (A/s^{-1})	E_a (kJ/mol)
k_1	16.39 ± 0.02	135.5 ± 3.9
k_8	15.27 ± 0.75	156.3 ± 20.1
k_9	8.40 ± 0.76	106.3 ± 20.7
k_{10}	9.73 ± 0.44	116.6 ± 9.8

Here the rates (r_i) 1, 8, 9, and 10 represent the acid-catalyzed lactose hydrolysis and the thermal (non-acid-catalyzed) degradation of lactose, glucose, and galactose, respectively. R is the ideal gas constant, T is the temperature, C_i is the molar concentration of the i^{th} species, A_i, and E_i, are the pre-exponential factor and apparent activation energy of the i^{th} reaction, respectively.

$$r_1 = A_1 \exp\left(-\frac{E_{a1}}{RT}\right) C_{lactose} C_{H^+} \qquad (1)$$

$$r_8 = A_8 \exp\left(-\frac{E_{a8}}{RT}\right) C_{lactose} \qquad (2)$$

$$r_9 = A_9 \exp\left(-\frac{E_{a9}}{RT}\right) C_{glucose} \qquad (3)$$

$$r_{10} = A_{10} \exp\left(-\frac{E_{a10}}{RT}\right) C_{galactose} \qquad (4)$$

The results (Table 10) indicate that the thermal degradation of glucose and galactose is favored over hydrolysis, requiring a balance of reaction temperature and time to achieve high yields (Figure 10).

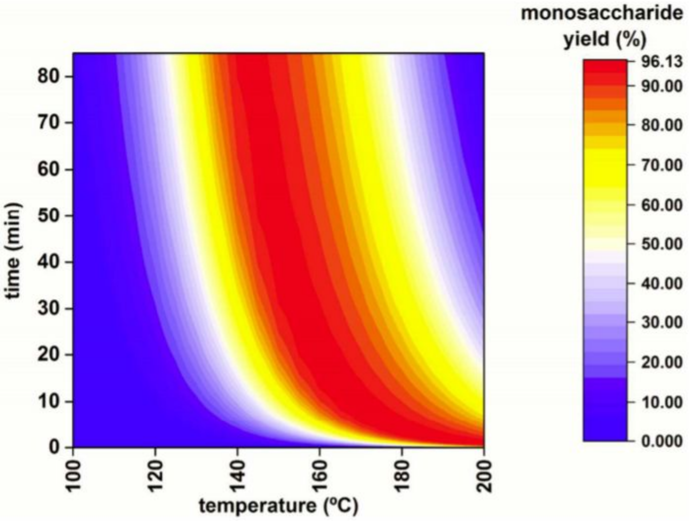


Figure 10. Model-predicted monosaccharide yields from acid-catalyzed lactose hydrolysis vs. temperature and reaction time. Reaction conditions: 0.11 M lactose in water; 0.005 M H_2SO_4. Reproduced from ref[75] with permission from the Royal Society of Chemistry.

In actual acid whey solutions, undesired reactions promoted by proteins and other nitrogen-containing species result in further degradation of the reactants and products[286] as discussed above. The acid whey hydrolysis rate (0.13 $s^{-1}M^{-1}$) is lower than that of pure lactose (0.32 $s^{-1}M^{-1}$) due to the fat and proteins. Ultrafiltration, activated carbon treatment, and nanofiltration can remove proteins, fat, and other nonprotein nitrogen species, improving monomer selectivity[286]. However, mechanistic insights into these multicomponent interactions on acid hydrolysis of carbohydrates are lacking.

3.2.4 Chitin and chitosan polysaccharides

Chitin in shrimp-shell wastes[82] can be hydrolyzed by hydrochloric acid to glucosamine. In the process[287], hydrolysis of the glycosidic linkages (main chain scission) and N-acetyl linkages (side chain scission) occurs at a higher rate at high temperature and high concentration

Table 11). Like hydrolysis of starch[74], lactose[75], and cellulose[288], chitin breakdown starts with protonation of the carbonyl oxygen[289] to form a carbocation, which subsequently undergoes a nucleophilic attack by a water molecule. The oxonium ion undergoes a series of transformations to the final products. The hydrolysis rate of the acetamide bond in the chitin monomer depends on the concentration (activity) of hydrogen ions and the extent of chain acetylation[290]. Similar to malto, xylo and cello-oligosaccharides and polysaccharides, the terminal bonds of the chitin chain are more reactive than the interior bonds[279,291] (Table 9). Varum *et al.*[279] used two rate constants for the glycosidic bond hydrolysis in chitin oligomers, assuming that the nonreducing end is hydrolyzed 2.0 - 2.5 times faster than the rest.

Table 11. Rate constants for the acid-catalyzed hydrolysis of chitin and chitosan saccharides.

Feedstock	Hydrolysis rate constant (k)	Reaction conditions
Chitin[289]	8.2 x 10^{-4} s^{-1}	6M HCl (80 °C)
	7.4 x 10^{-4} s^{-1}	6M $HClO_4$ (80 °C)
	3.0 x 10^{-4} s^{-1}	6M H_3PO_4 (80 °C)
Chitin[290]	7.8 x 10^{-5} s^{-1}	12 M HCl (50 °C)
Chitosan[290]	8.0 x 10^{-5} s^{-1}	12 M HCl (70 °C)
Chitin[292]	9.5 x 10^{-6} s^{-1}	11 M HCl (50 °C)
	1.9 x 10^{-4} s^{-1}	11 M HCl (80 °C)
Chitin tetramer[279]	2.4 x 10^{-5} s^{-1}	12 M HCl (40 °C)
Chitosan tetramer[279]	2.5 x 10^{-5} s^{-1}	13 M HCl (40 °C)
Mushroom chitin[80]	0.72 - 2.0 x 10^{-3} s^{-1}	6 M H_2SO_4 (90 °C)
	0.95 - 2.5 x 10^{-3} s^{-1}	6 M H_2SO_4 (100 °C)
	0.98 - 2.7 x 10^{-3} s^{-1}	6 M H_2SO_4 (110 °C)

Rupley *et al.*[292] obtained an activation energy for chitin hydrolysis of 5.3 kJ/mol, similar to the 7.2 kJ/mol reported by Meyer *et al.*[293], and the 2.2 - 19 kJ/mol of Osorio-Madrazo *et al.*[294]. The activation energies for mushroom chitin hydrolysis vary widely (6.6 –131 kJ/mol), depending on mushroom type[80], and slightly (152.2 - 158.1 kJ/mol) for de-N-acetylated chitosans[291]. The very low activation energies indicate that these may not be intrinsic kinetic parameters but rather affected by transport.

Irrespective of the carbohydrate type (cellulose, starch, chitin, chitosan), glycosidic bond cleavage occurs using acid hydrolysis. Temperature, acid concentration and strength, and reaction time should be controlled to minimize unwanted side reactions, like dehydration, deacetylation, oligomerization, and polymerization, leading to monomers' loss. Conversion of monomer sugars into stable derivatives, *e.g.,* through acetal and ketal functionalization[295,296], is a strategy to mitigate side reactions. Sugars converted into acetal or ketal forms are robust against dehydration/degradation and can be converted back to simple sugars or serve for further reactions. As FW contains carbohydrates with other components, like proteins, fat, and ash, more investigations into the stability and reusability of catalytic systems will be needed. Catalyst deactivation kinetics would yield insightful data on strategies toward robust and feedstock agnostic catalytic systems irrespective of feedstock heterogeneity.

3.3 Kinetics of waste-protein conversion to amino acids

Distiller's spent grains[297], crab processing waste[84], shrimp waste[298], poultry feather[85], and dairy whey waste[19,75] are all protein- and thus nitrogen-rich FW feedstocks. After the recovery of protein waste, hydrolysis proceeds using prolonged treatment with acids or alkalis. This treatment is harsh on some amino acids. As a result, milder enzymatic hydrolysis with proteases to make commodity chemicals has been used widely [299,300] for nutritional supplements, food additives, and fertilizers. Enzymes have higher specificity, lower energy requirements, and improved sustainability.

Yan *et al.*[301] demonstrated two routes for amino acid (alanine) formation from waste-derived sugars comprising indirect (I) and direct (II) pathways (Figure 11). Pathway I entails dehydrogenation to a ketone and reaction with ammonia to an imine, followed by hydrogenation. Pathway II involves a S_N2 substitution of the -OH group with an $-NH_2$ group. When the absence of an α-H in the substrate does not hinder the formation of the amino acid, the reaction proceeds *via* direct amination; otherwise, the indirect route is dominant.

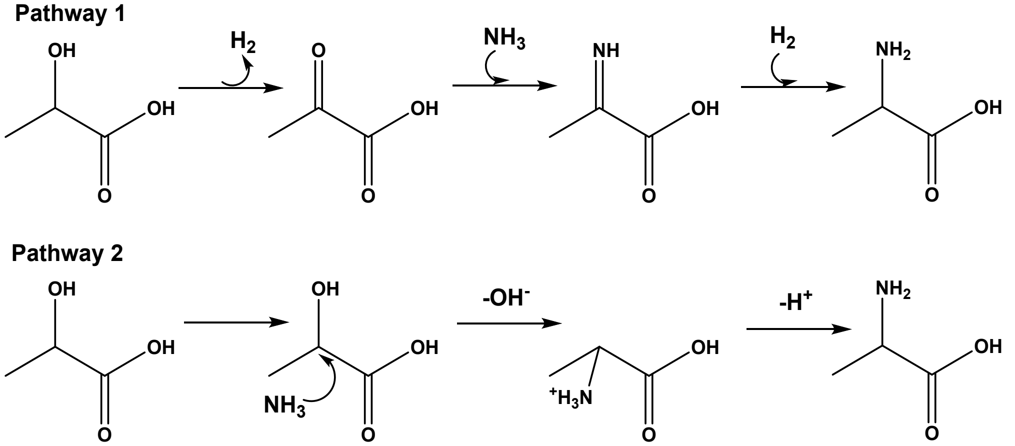


Figure 11. Reaction pathways for amination of lactic acid to alanine. Redrawn from ref[301].

Current thermocatalytic methods for protein-containing systems are too harsh. Discovering milder conversions could enable a "one-step" breaking down proteins and carbohydrates (using acid catalysis). Further work on separating protein and carbohydrate monomers after hydrolysis and improving the thermal and thermocatalytic transformations to enhanced yield and selectivities to specific amino acids is needed. Mechanistic studies on product distributions and kinetics, e.g., rate constants and activation energies, can provide necessary information on the hydrolysis of protein polymers to valuable amino acids.

3.4 Kinetics of waste oils and fats valorization

Waste cooking oil (WCO) is a cheap[94,95,166,219,302–305], environmentally friendly feedstock for biodiesel produced *via* transesterification between alcohol (usually methanol) and vegetable oils or animal fats has been studied by Noureddinni *et al.*, Leong *et al.*, Diouri *et al.*, amongst other researchers. The oil and alcohol initially form a two-phase liquid system which becomes miscible at reaction temperature[304], with reaction products (methyl esters) acting as mutual solvents. The general reaction is

$$Triglyceride + Alchohol \overset{catalyst}{\longleftrightarrow} Methyl\ Ester + Glycerol \qquad (5)$$

Kinetic models for the transesterification reaction typically assume reversible reaction kinetics, negligible non-catalyzed reaction, the reaction occurring in the oil phase, and a constant methanol concentration (due to its excess). Both acid and base catalysts are employed, with the latter being the most widely used. Base-catalyzed transesterification has been modeled[95,219,304] with three overall reversible reactions in addition to the overall reaction (Eqs. 6-9).

$$Triglyceride + Alchohol \overset{k_1,k_2}{\longleftrightarrow} Methyl\ Ester + Diglyceride \qquad (6)$$

$$Diglyceride + Alchohol \overset{k_3,k_4}{\longleftrightarrow} Methyl\ Ester + Monoglyceride \qquad (7)$$

$$Monoglyceride + Alchohol \overset{k_5,k_6}{\longleftrightarrow} Methyl\ Ester + Glycerol \qquad (8)$$

$$Triglyceride + 3\ Alchohol \overset{k_7,k_8}{\longleftrightarrow} 3\ Methyl\ Ester + Glycerol \qquad (9)$$

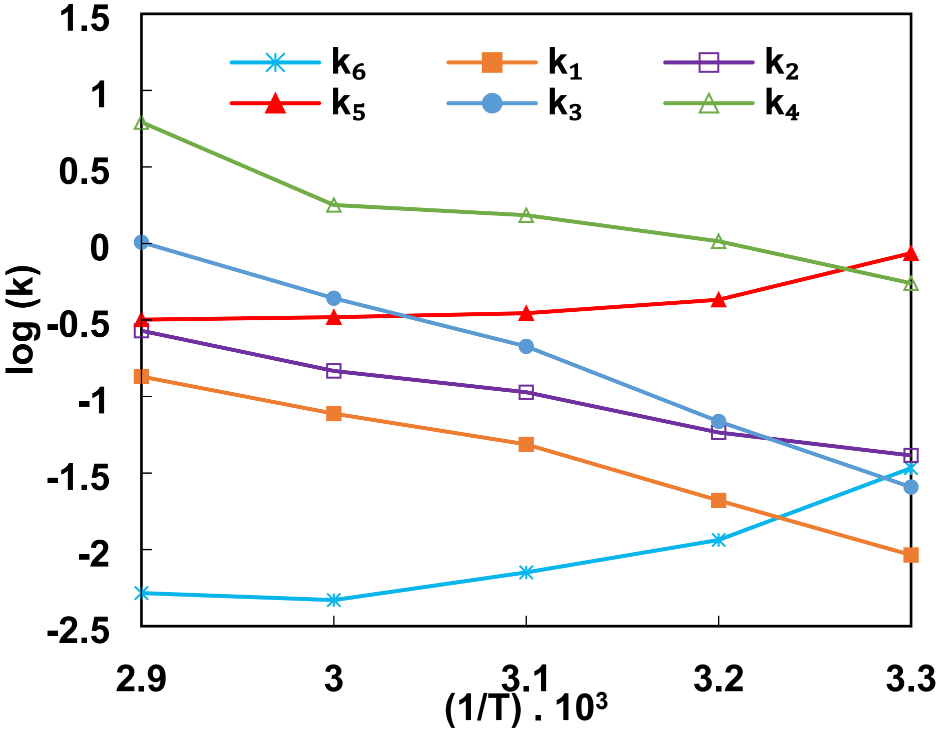
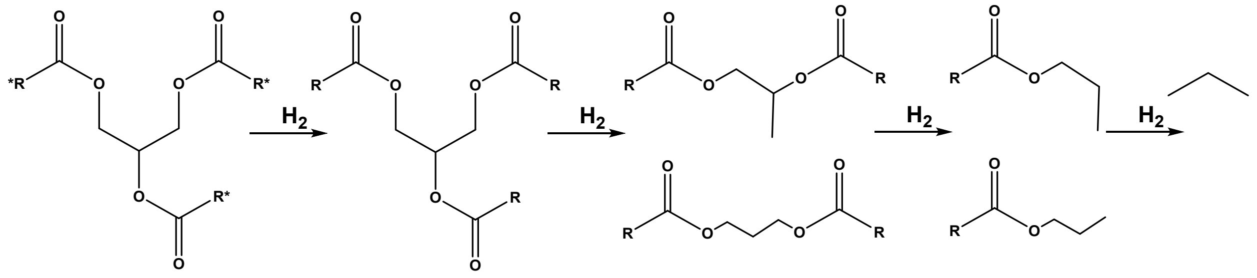


Figure 12. Temperature dependence of the reaction rate constants at N_{Re} = 12,400. Redrawn from ref[304].

The conversion of diglyceride to monoglyceride is the most kinetically limited step in the transesterification process, with forward reactions favored at higher temperatures (Figure 12). For the acid-catalyzed transesterification reaction, Leong *et al.*[95] *o*btained activation energies values of 77.2 and 21.8 kJ/mol for the forward and backward reactions of the rate-controlling steps, respectively. An activation energy of ~50 kJ/mol was estimated by Berrios *et al.*[306] They observed that the activation energy[306] for the forward reaction decreased with increasing catalyst concentration: from 51 kJ/mol with 5% sulphuric acid to 45 kJ/mol with a 10% concentration of the acid. For the base-catalyzed reaction, activation energies[94,219,304] ranged from about 2 to 5 kJ/mol. The results suggest that the reaction pathway over acid and base catalysts is different, with the base-catalyzed pathway possessing a lower activation barrier. Further mechanistic studies elucidating the energy landscape profile of both base and acid-catalyzed transesterification will be insightful towards revealing the mechanism for these reactions. As of now, transesterification reactions use homogeneous catalysts; however, heterogeneous catalysts such as zeolites have become popular in biomass conversion processes[307]. The application of heterogeneous catalysts might offer processing advantages (separation and recyclability), different reaction pathways, and lower energetic barriers for waste cooking oil transesterification.

Hydrodeoxygenation (HDO) of waste cooking oils is another catalytic valorization route[91,220,308,309] that yields long-chain alkanes[91,251] for jet fuels, diesel fuels, or lubricant base oils. Based on control experiments, Vlachos and co-workers.[220] elucidated a reaction pathway for HDO of vegetable oils and WCO (Figure 13) over ReOx-modified Ir/SiO_2. The sequence is initiated by the hydrogenation of C=C bonds of unsaturated triglycerides and free fatty acids to their corresponding saturated analogs. Saturated triglycerides are further converted to alkanes by direct hydrogenolysis of acyl C-O bonds of three ester groups, followed by sequential hydrogenation of the resulting aldehyde to alcohols and hydrogenolysis of the alcohol.



R*: unsaturated alkyl chain (mainly C_{15} and C_{17})

Figure 13. Proposed reaction route for the HDO of vegetable oils and WCO. Redrawn from ref[220].

Concurrently, 1,2-propane diester and 1,3-propane diester and their monoester intermediates (e.g., n-propyl stearate, iso-propyl stearate, n-propyl palmitate, and iso-propyl palmitate) form which can be converted to long-chain alkanes and propane in the same manner as triglyceride conversion to alkanes. In the case of fatty acids, hydrogenation results in the formation of the corresponding fatty alcohols via aldehyde intermediates that can be converted to alkanes. Considering the abundance of lauric acid[95,219] in WCO, its ketone derivative could also be upgraded to lubricants[90–92] *via* aldol condensation.

3.5 Kinetics of extractives and essential oil valorization

Orange peel waste-derived[21,73,110,310] limonene is an industrial byproduct that can be upgraded. Limonene can be oxidized to carvone, carveol, and carvacrol or dehydrogenated to p-cymene (Figure 14). Direct oxidation of limonene has been performed by Oliveira *et al.*[311]. While limonene epoxides form at low conversions[311] via an electrophilic attack, the selectivity to carvone and carveol (from allylic oxidation with hydrogen abstraction and/or from limonene oxides) increases time. In acidic media, the limonene oxide may be hydrolyzed into limonene glycol. Asides from molecular oxygen, tert-butyl hydroperoxide (t-BHP) and other peroxides are also used as oxidants.

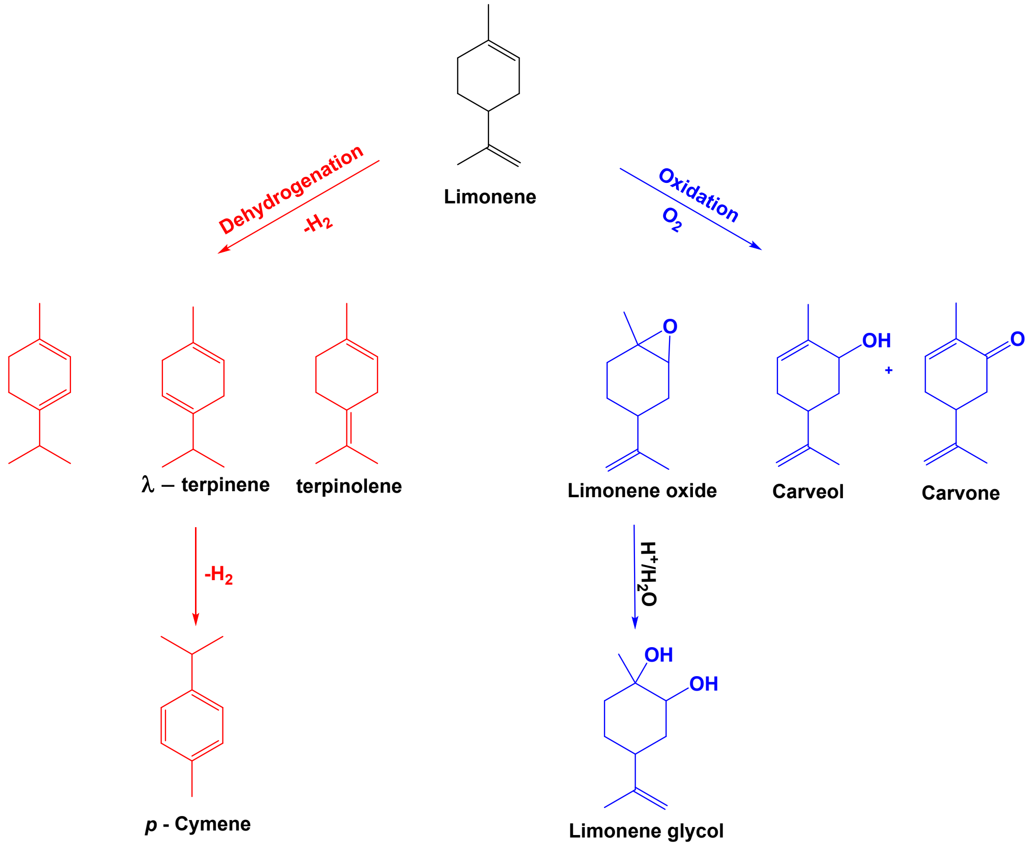


Figure 14. Reaction pathways[310,311] for the catalytic upgrade of limonene.

Carveol and carvone may form directly from limonene *via* allylic oxidation and from limonene glycol undergoing acid-catalyzed epoxide hydration. Furthermore, carveol may be oxidized to carvone. Details of the reaction network are not fully known.

Dehydrogenation of limonene[310,312] to p-cymene is usually performed over Brønsted sites, which protonate the unsaturated molecule and initiate dehydrogenation and polymerization. This reaction is typically governed by the dispersion and accessibility of the acid sites and the specific surface area, pore volume, and average pore size of the catalyst supports[109,313]. The reaction of limonene and other terpenes over solid acids has been related to an initial isomerization on acid sites, followed by dehydrogenation of these intermediates to p-cymene. In some cases, polymerization to side products occurs. The key reaction intermediates (Figure 14) are α-terpinene, terpinolene, λ-terpinene (from isomerization), and p-cymene (from dehydrogenation).

P-cymene[73] can further be oxidized to terephthalic acid[107] over iron, manganese, titania, and sepiolite heterogeneous catalysts, with up to 51% yield in O_2. The mechanism occurs through parallel and consecutive reactions (Figure 15). Both the methyl and isopropyl groups are oxidized, generating several products. The oxidation of the isopropyl group leads to tertiary cymene hydroperoxide (TCHP), p-cymenol (COL), p,α-dimethyl styrene (DMS), p-methyl acetophenone (MAP), p-tolualdehyde (TALD), and p-toluic acid (TOA). Oxidation of the methyl group leads to cuminaldehyde (CA) and p-isopropyl benzoic acid (IBA). Terephthalic acid is the product of these consecutive oxidations. Given the use of terephthalic acid (TA) in plastic bottle production and the projected growth in the global biobased PET market by up to 68% from 2015 to 2019[107], this is an appealing production process to manufacture biobased TA.

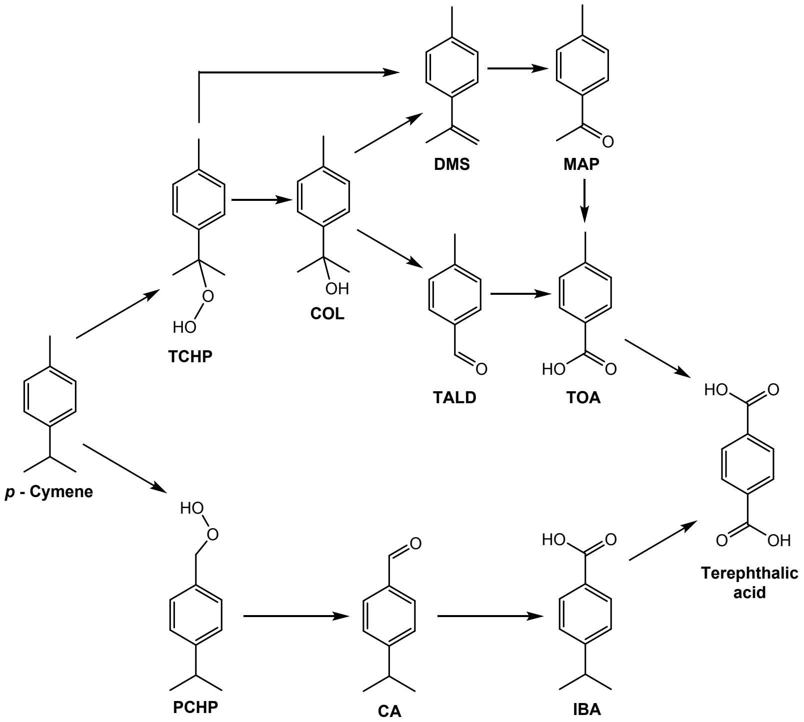


Figure 15. Reaction scheme of the oxidation of *p*-cymene to terephthalic acid. Redrawn from ref[73].

1,8-cineole, sourced from the steam distillation of eucalyptus waste[108,313], was converted to p-cymene. Alumina and palladium on alumina are active catalysts for this transformation, the latter producing p-cymene in near quantitative conversion. The reaction mechanism involves C–O bond fission in cineole, followed by dehydrogenation/isomerization to p-cymene.

Unlike other FW components, extractives and essential oils are not polymers and can be isolated pure. They possess multiple functionalities to provide platforms for new bio privileged chemicals – a direction that requires further studies.

3.6 Mechanisms and kinetics of waste-lignin depolymerization

The lignin polymer consists of aromatics that are valuable chemicals. Table 1 shows that ground nutshell, grape pomace, spent coffee grounds, and legume waste contain high lignin content. Catalytic lignin transformation involves cleavage of ether linkages, naturally present in the lignin polymer via reductive or oxidative pathways. Lignin in tomato waste,[88] cashew nut[251,252], vanilla seed waste[86,87], and castor seed coat[253] has been upgraded into multiple products. First, lignin is solubilized into a reaction solvent and separated from holocellulose. Next, the solubilized lignin is converted to vanillin and aldehydes (oxidative pathway – colored blue in Figure 16) or alkyl-substituted guaiacols, syringol, and catechol (reductive pathway – colored red in Figure 16). Metal catalysts, such as Ru, Pd, and Ni on C, alumina, or silica stabilize reactive intermediates and prevent them from condensing to oligomers giving higher yield to monomers.

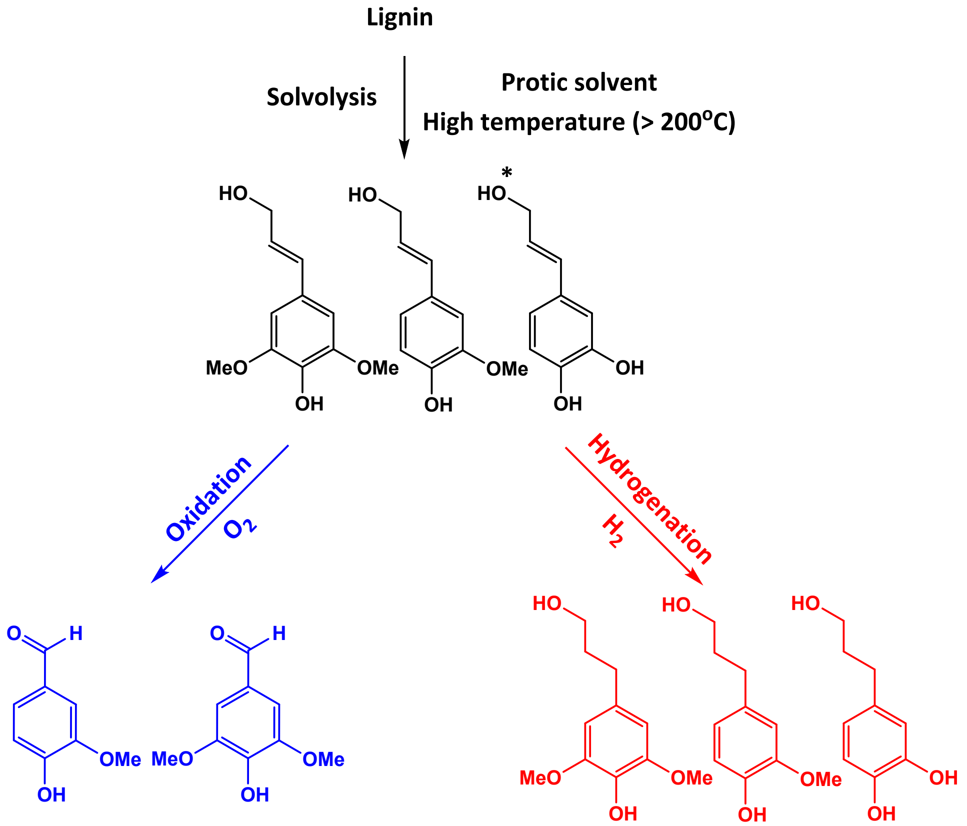


Figure 16. Reaction scheme for herbaceous lignin depolymerization into monomers.

*This monomer is obtained from the unique oxoaromatic polymer structure in vanilla seed coat lignin and is distinct from hydroxyphenol, syringol, and guaiacol monomers in woody and herbaceous biomass.

The hydrogenation pathway, known as the reductive catalytic fraction (RCF)[314–317], is the most popular, as the reactive intermediates are quickly stabilized to yield close to theoretical lignin monomer yields. Currently, there are few lignin depolymerization studies on FW feedstocks. Softwood, hardwood, and grassy biomass possess different monolignols and afford several monomeric products. However, there are no commensurate characterization studies to detail the composition and structure of various lignin-rich FW to know the potential products. Reactivity studies of lignin, mechanistic model compound studies, mechanistic modeling of reaction mechanisms on multiple catalysts, and catalyst development will be required.

4.0 Process integration, energy, and economics of FW-based biorefineries

This section covers integrating different valorization technologies and considering multiple FW components and the implications on the energy requirements and economics of future FW-based biorefineries.

4.1 Concepts for process and energy integration of FW-based biorefineries

An integrated biorefinery converts FW into multiple biobased products, maximizing carbon recovery and feedstock utility. Integrating different thermal and catalytic processes improves valorization, generating a diverse range of bioproducts, driving circularity, and generating additional revenue. Based on FW's composition, volume, and heterogeneity, an integrated approach should be adopted with a focus on commercial and industrial FW reduction and separation, followed by repurposing. One of the technical bottlenecks in valorizing FW *via* thermal and catalytic processes is the presence of non-digestible contaminants, such as plastics and wood. Zhang *et al.*[318] proposed a novel combination of gasification for producing hydrogen-rich syngas, and anaerobic digestion, for methane-rich biogas. The integration improved the total electricity and heat output and the biochar produced. We believe this is a fertile area for research, also given the recent emphasis on plastics recycling and upcycling. Clearly, the development of identification/diagnostic tools and separation methods of various non-FW streams and/or of technologies that can convert simultaneously mixed and contaminated feedstocks is one of the outstanding opportunities.

Pham *et al.*[319] compared the environmental, energy-economic, and health aspects of pyrolysis, gasification, and hydrothermal treatment. Hydrothermal treatment was found to need less energy than other thermal conversion technologies. Further comparison of various technologies for the same feedstock is strongly encouraged to create a roadmap for practical implementation.

Technologies already implemented in the food industry, such as microwave heating (used for commercial pasteurization and sterilization of prepared food[38]) and supercritical CO_2 (used for the decaffeination of coffee[320]), are ideal for process integration and intensification. However, only a few studies have reported catalytic pyrolysis[321–323], hydrothermal liquefaction[145], carbonization[324], and extraction of essential oils and bioactive compounds from FW[325–328] using microwaves. There is room to exploit process intensification, especially given that the electricity cost is rapidly reduced, and the energy can be green. Furthermore, microwaves are by nature intensified and modular, and thus, suitable for distributed processing.

Specific FW types should be treated either on-site by the same producing industry or at a local/regional industrial site minimizing transportation costs and spoilage. This is particularly relevant for FW processing due to (1) the large amount of water it contains, which makes transportation uneconomical, and (2) its short lifetime, compared to that of woody and other agricultural waste. This distributed processing is against the economy of scales of large chemical plants and challenges commercialization. Yet, it is amenable to modular manufacturing of having many small units, agile, and lower business risk.

Novel processes could combine the extraction of high-value products with subsequent thermochemical conversion to biobased chemicals, materials, and fuels. For instance, the utilization of olive pulp waste and orange processing waste could be economical only when other added-value products (e.g., extraction of limonene and pectin from orange processing waste) are co-produced in the current food chain[329,330]. Fractionation of dairy waste whey stream into a lactose-rich and a protein-rich fraction could produce high-value whey protein hydrolysates for protein nutritional/dietary applications and lactose for sugars[75]. The process-sequence should be closely considered. For example, hydrolysis of carbohydrates first renders the lignin less valuable due to irreversible lignin condensation[86,331,332]. Upgrading lignin first (lignin-first approach) leaves behind a carbohydrate pulp for hydrolysis to simple sugars. The process sequence becomes more complicated since the FW feedstock contains many valuable fractions. Extraction of valuable ingredients should be the first process as high temperature thermal and thermocatalytic technologies are harsher to the feedstock.

4.2 Economic potential of FW-based biorefineries

Many studies have analyzed the economics of different FW valorization processes. Preliminary analysis of bread waste[67] valorization showed a net gain of \$43/kg of bread waste, with HMF as the essential profit-making product and \$236/kg, if high purity chemicals were co-produced. Techno-economic analysis[19,75] of an acid whey-based biorefinery showed that the glucose/galactose syrup sweetener product could be sold for \$301- 631/ton. It could be used for sweet dairy products, a replacement for high fructose corn syrup, or sold as-is. Among other products, the whey protein concentrate could be either added to dairy products to increase the protein content or sold at \$1,760/ton as a dietary supplement or a food additive. p-cymene[109] extraction from orange peel coupled with pectin production has a high-profit margin: \$11/kg p-cymene and \$138/kg when pectin is a co-product. Clark *et al.*[21] obtained limonene and pectin, valued at \$0.5/kg and \$9/kg respectively from orange peel waste, in comparison to a total pectin and limonene production cost of \$3.1/kg, demonstrating the economic feasibility of the orange peel waste.

Cravotto *et al.*[88] suggested that their tomato waste oxidation process could be profitable considering an estimated market for lignin-based vanillin of \$100 billion in 2020. Ebikade *et al*. recently showed that zero-value potato peel waste (PPW) could be converted to antioxidants, HMF, and biochar, generating ~\$ 6,000/ton of PPW[9].

These initial studies support the idea that FW valorization technologies from zero-value feedstock could be economically profitable. Such biorefineries could serve as novel waste management, effectively diverting FW from landfills and reducing the environmental impact while creating commodity products for existing and new markets. However, further studies, including the effect of flooding the market with large quantities of known products and the risk of creating new markets with new products, need to be conducted to infer the potential of this feedstock.

5.0 Challenges and Opportunities

Current greenhouse gas emissions and groundwater contamination from FW decomposition at landfills are too large to be ignored and can be avoided. Policies should drive a reduction of FW whenever feasible, and technologies should be developed to treat the inevitable portion. FW has the potential to be effectively upcycled to produce valuable products instead of being disposed of in an environmentally unsustainable way, supporting circularity. The volume of FW is sufficient to make many valuable chemicals but much lower than needed for the production of fuels.

This review highlighted recent technological advances in the thermocatalytic and thermal valorization of FW, including reaction kinetics and pathways towards obtaining biobased products. Technoeconomic analysis demonstrates that FW-based biorefineries have higher economic viability compared to lignocellulosic and ethanol biorefineries due to the high-value products obtained from compounds uniquely found in FW, like extractives and proteins. The presence of high-value components in FW, like extractives and essential oils, increases the biorefinery's economic viability due to the high-value (cosmetics, antioxidants, food, and drug) markets.[100,101] In general, the economic viability of biorefineries will be enhanced by focusing on high-value biobased products than low-value ones, such as fuels or heating sources, and utilizing all components of these feedstocks. Such functionality is absent in lignocellulosic biomass, rendering FW an advantaged feedstock. With the current biorefinery heavily focusing on ethanol and lignocellulose, feedstock diversification by valorizing FW creates opportunities for novel chemistries and products beyond the conventional ones. Leveraging FW components (Table 1), a possible array of products can be obtained, creating a food waste biobased product map (Figure 17). Given the abundance and low cost of shale gas and the low value and large volume of fuels, biobased chemical production is the recommended viable FW valorization strategy (Figure 17). For example, the high energy input of pyrolysis and thermal gasification processes pose a challenge to the overall economics and sustainability. These methods could occasionally be useful given they are agnostic to the feedstock. Recovery of valuable ingredients should be a high priority due to their financial impact and natural rather than the synthetic form. Yet, extraction of small quantities of compounds of low solubilities by large amounts of non-green solvents and their eventual recovery from dilute solutions are obvious energy and cost challenges. Methods are clearly needed for their efficient and economic recovery. Market needs and trends should also be considered. While this review focused on FW's thermocatalytic valorization, we believe that the future biorefinery could leverage both thermochemical and biological transformations.

A key challenge with FW is its diverse and sparse distribution and geographical diversity. The main components and physicochemical composition of FW vary significantly with the source, posing challenges for FW biorefineries. Its large water content and short lifetime add to the challenges and call for distributed, intensified, small footprint processing rather than centralized conversion plants. One way to circumvent this set of challenges is to integrate FW-based biorefineries with facilities and locations where the waste is generated, e.g., production sites in Florida and California, distribution sites, and the food industry. While this may be feasible, unlike electronics, car engines, etc., the manufacturing of modular chemical processing units is not widespread, and economies of numbering rather than scaling up are not proven for the chemical manufacturing space. This distributed and modular processing imposes a high business risk that needs to be debottlenecked. More robust feedstock processing or ancillary technologies need to be investigated toward integrating FW biorefineries into the generation locations and facilities. Feedstock supply chain, purity, variability, composition, cost, storage, and transportation and distribution logistics also need to be considered.

Protein and fat-containing waste streams (*e.g.,* acid whey, soybean waste) cause unwanted side reactions and decrease the selectivity to desired products. Catalyst deactivation is proportional to the amount of mineral and nitrogen-based cations in the feed. This necessitates more research into FW pretreatment processes and separations and the development of more robust catalyst systems and milder chemical catalytic methods that provide high product specificity, less undesirable side reactions towards harnessing the rich pool of components of nitrogenous waste protein. Similar food waste feedstocks, such as tubers, e.g., potato, cassava, and yam, could be co-processed to minimize process and equipment specificity. Stepwise fractionation of mixed FW feedstocks into individual fractions would be necessary to reduce unwanted side reactions while yielding high purity streams for further processing. The processing of mixed feedstreams is an area that needs significant development. We propose that farm and industrial food waste should be the short-term targets due to providing a small number of waste components. In general, process conditions (temperature, time, catalyst type, and concentration) influence the FW valorization process; therefore, a thorough understanding of the interplay of these factors for tuning product yields is critical.

Aside from extraction compounds, more research into technologies to manufacture other novel performance-advantaged products is needed. These biobased chemicals offer the opportunity to enter new markets, deliver advantaged properties compared to petrochemical alternatives, and offer a new revenue source for biorefineries. This task necessitates rigorous technoeconomic analysis and life cycle assessment and a systems approach to the FW challenge. Principles of green chemistry need to be considered in developing these chemical and thermal transformations.

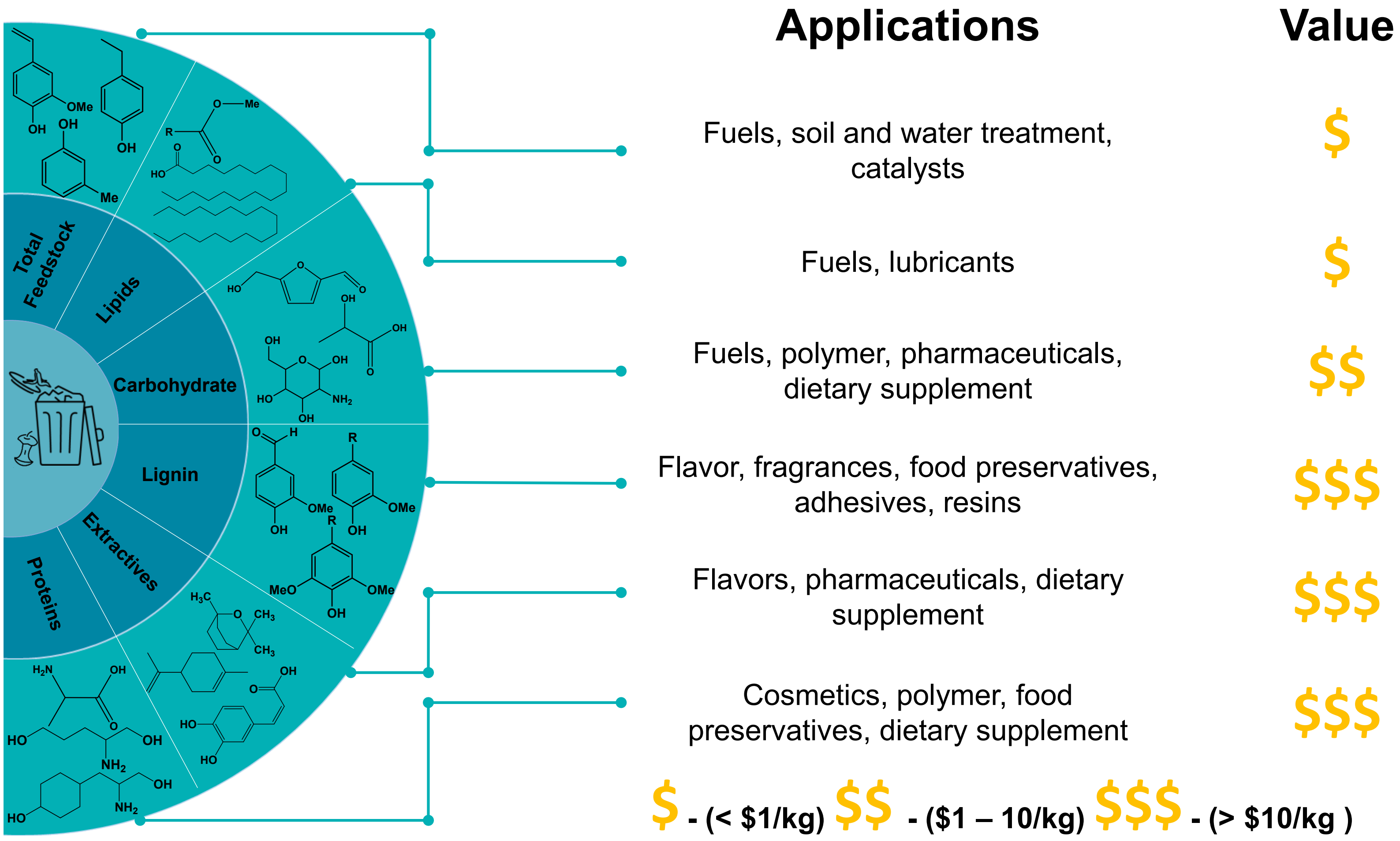


Figure 17. Food waste biobased product map, harnessing its compositional complexity.

Given the complexity of the feedstock, we propose to employ data science-based methods for creating data-driven surrogate models to enable optimization and systems analysis. Growing attention to FW valorization research unlocks a broad array of potential biobased chemicals. In order to efficiently map FW feedstock composition, target product functionalities, and potential industrial applications, data mining techniques might provide more in-depth insights towards navigating this multivariate landscape. Combined computational and experimental research for identifying structure/function relationships for targeted bioproducts, structure matching of existing chemicals with FW derivatives, and performance advantaged chemicals as renewable building blocks are possible areas that can be unlocked using data mining.

Proteins' upgrade and specifically the hydrolysis of non-essential amino acids have been addressed less than carbohydrates and lignin. Traditionally, this process involved prolonged treatment with concentrated mineral acids at elevated temperatures, forming large amounts of inorganic salts as waste. This led to the alternative use of protease enzymes. Given the high cost of the enzymes, there are opportunities for developing more cost-effective, greener technologies.

There is a little fundamental and mechanistic understanding of most of these systems in part due to their inherent complex composition and structure. Understanding the interactions between different compounds in FW, catalyst surfaces, and solvents will provide fundamental insights into the key factors that govern the chemical transformation of FW feedstocks and can improve the design and optimization of catalytic processes.

With the circular economy and convergent research gaining traction at society-government-academia cycles, new technologies will be required. For the most part, carbohydrate derivatives, such as ethanol and HMF, have been the "poster children" of the biomass/waste valorization community. However, new opportunities from FW's unique compounds, such as proteins and extractives, are yet to be harnessed. Developing valorization pathways for upgrading waste oils into plastics and surfactants is currently unexplored. The separation and transformation of less popular FW fractions, like proteins and extractives, need to be developed. There are also opportunities to foster a circular economy in the chemical industry by integrating bio-waste into the existing chemical supply chain. While lignocellulosic biomass refers to chemical composition and food waste biomass to origin, both feedstocks contain valuable ingredients that require existing or new thermo-catalytic, chemical, biochemical processes, or their combinations to create valuable biobased products for a viable biorefinery. These valorization studies need to be followed by rigorous life cycle assessment and techno-economic analysis. In particular, the high moisture content of FW feedstocks needs to be accounted for when energy and economic assessments of associated biorefineries are performed.

Closer collaboration between academia and food processing companies, producers, and distributors is pivotal in creating practical and implementable solutions. Alignment with companies interested in making biobased industrial and consumer products and entering new markets is equally fundamental in making meaningful FW valorization advancements. Finally, favorable policies are essential to make this happen.

Conflicts of interest

There are no conflicts to declare.

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