



Processes for the valorization of food and agricultural wastes to value-added products: recent practices and perspectives

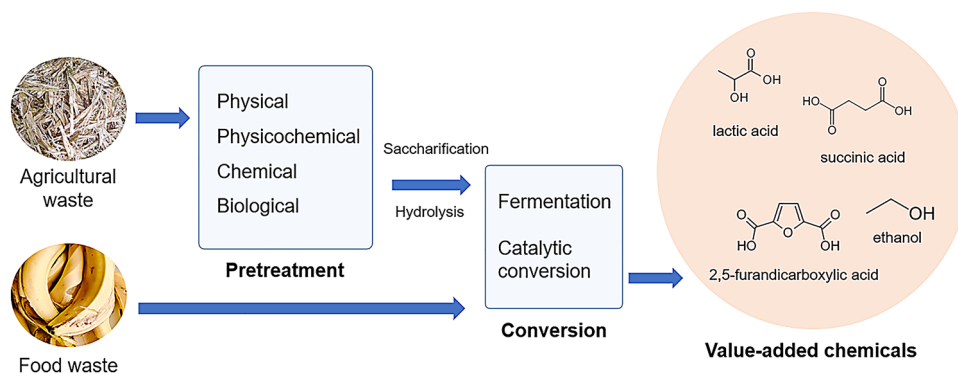
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Abstract

Biorefineries contribute to a circular bioeconomy using renewable feedstock to produce commodity and specialty chemicals as an alternative to petroleum chemicals. Using waste streams such as food waste and agricultural waste as a feedstock for biorefineries is a promising approach for obtaining value-added products in an economically feasible and sustainable way. The conversion of biomass to chemicals offers diverse opportunities but poses new technological challenges. This paper aims to review the current state of food and agricultural waste valorisation by giving a brief technical overview, summarizing the current state of the bio-based market, and identifying the current barriers to scaling-up biorefineries. Utilizing lignocellulosic biomass in biorefineries calls for pre-treatment due to its complex structure, in which biomass is broken into monosaccharides, building blocks of value-added products. Different state of the art technologies for lignocellulose pre-treatment is introduced in the review followed by a brief explanation of the role of the hydrolysis and fermentation. The economic aspect of chemical production from biomass waste at an industrial scale is also introduced by giving an overview of some recent techno-economic studies.

Graphic abstract



Keywords Biorefinery · Food waste · Biomass valorisation · Platform chemicals · Circular bioeconomy

Introduction

With the decreasing supply of fossil fuels, the demand for a renewable alternative to petroleum-based chemicals and fuels is rising. Bio-based chemicals and biofuels have drawn much interest in recent years as utilizing bioresources shifts the dependence of the chemical industry from fossil fuels to a more sustainable source. Furthermore, the use of low-cost and abundant waste biomass

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(agricultural residues, food processing waste, food residuals) provides a means to efficiently valorise the by-products of biomass production, thereby closing the loop and contributing to a global circular bioeconomy [1]. Although research interest has increased, the growth of the bio-based chemical economy is still slow, and the majority of bio-based chemicals are not yet market-competitive due to low oil prices, high feedstock costs, and a lack of consistent policies [2].

Integrated biorefineries offer an alternative to fossil-based refineries using different biomass feedstocks and a combination of technologies to generate biofuels and bio-based chemicals. Main platform chemicals, which can be the base for a range of different derivatives that are generated in integrated biorefineries, are alcohols, organic acids (e.g. formic acid, levulinic acid), and furanics (e.g. 5-hydroxymethylfurfural (5-HMF), furfurals) [3].

Food waste is a major organic waste stream, diverse in composition, and rich in functionalized molecules. Also, it is produced along all stages of the food supply chain -from agricultural production, storage and distribution to its consumption (Fig. 1). Disposal of food waste via landfilling, composting or incineration has adverse environmental impacts. According to a 2013 report from FAO [4], the carbon footprint of food losses is estimated at 3.3 billion tons of CO₂ equivalent of greenhouse gasses (GHG) and corresponds to a cost of US\$750 billion annually. The valorisation of food waste into value-added products is promising and has widely been studied [5].

Agricultural waste is another major stream of organic waste, originating from the non-edible part of plant material, produced during the harvesting and processing of agricultural crops (corn stover, rice husk, and sugarcane bagasse) [6]. It consists mostly of lignocellulosic biomass and is inevitably produced in large amounts for food production. Crop residues were estimated at 5 billion tons globally in 2013 [7]. Commonly, agricultural waste is composted or

simply disposed of, but it has been considered a feedstock for bioenergy as well as successfully utilized in biorefineries.

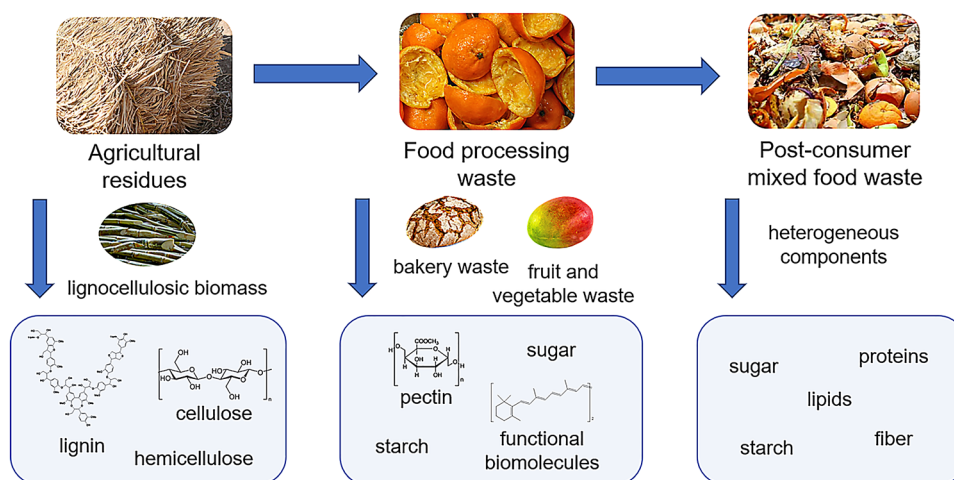
Unlike petroleum, organic matter is more variable in composition and generally contains more oxygen but less hydrogen and carbon than petroleum. This abundance in functionalized groups opens up new possibilities in terms of chemical products, but brings about some technological issues as the current industry is built around petroleum [8].

Lignocellulosic biomass consists of cellulose (35–54%), hemicellulose (19–34%), and lignin (11–30%) [9]. Cellulose has a complicated structure due to the repeating 1,4-beta glycosidic bonds between the glucose molecules and starch [10]. Lignin is a three-dimensional, cross-linked biopolymer with phenylpropane units, while hemicellulose consists of various pentoses with xylose being the most abundant component. Cellulose, hemicellulose and lignin do not have the same chemical reactivities [11] and are not efficiently converted into sugars by enzymes alone [12]. To make the biomass more available to enzymes and thereby improve conversion, physicochemical pre-treatments are used [12]. Efficient and affordable methods include depolymerization and partial deoxygenation [13], and hydrolyzation of lignocellulosic biomass [10].

Recalcitrance of lignocellulosic biomass, its ability to resist biological decomposition, is caused by the complex structures in the plant cell wall. Some factors that affect recalcitrance are the amount and structure of lignin and hemicellulose present, the degree of polymerization and crystallinity of cellulose, biomass porosity, and cellulose accessibility [14]. These various factors interact to create recalcitrance, and the degree of contribution of each factor is not well defined [15]. However, lignin content is considered as one of the most significant contributors to recalcitrance [16].

Thermochemical, biochemical, and chemical processes are three main pathways for the conversion of biomass. Thermal treatment of biomass results in solid, liquid or

Fig. 1 Stages of food waste production and their main components



gaseous products which are further upgraded to synthetic biofuels. In biochemical pathways, fungi generate enzymes that degrade lignin, hemicellulose, and polyphenols. This process has a slow production rate; therefore, the biological processes are often combined with appropriate pre-treatment methods [13]. Finally, the chemical pathway consists of the catalytic hydrolysis of cellulosic biomass with acids which are in an aqueous solution or in a heterogeneous phase [17].

Previous reviews have focused on either food waste or agricultural biomass as a stand-alone raw material/feedstock and the following aspects were considered: (i) the different pre-treatment techniques for food waste to enhance biofuel production and the recovery of value-added products, (ii) to assess the different food waste reutilization techniques such as composting, anaerobic digestion, fermentation, and thermochemical conversion based on their energy requirements, for the production of value-added products, (iii) the challenges and possibilities on the value addition of food and kitchen waste, (iv) the application of the yeast *Yarrowia lipolytica* for the conversion of agri-food wastes and related waste biomass into useful products, (v) the conversion of food waste to bioactive compounds, biofuels, and bioplastics, (vi) the framework for the design, analysis, and assessment of an agricultural and forestry waste based biorefinery, (vii) the production of nanocellulose-based value-added products from various biomass wastes, (viii) the recycling of food, agricultural, and industrial wastes as pore-forming agents for sustainable porous ceramic production, (ix) the application of agro-industrial biowastes as organic fertilizers and the production of biochar, and (x) the barriers in supply chain, technical knowledge and the need to efficiently implement policies and regulatory frameworks in "waste to wealth" projects.

This paper reviews the research advances and scientific knowledge on the utilization of food and agricultural waste for value-added chemicals. Both food waste and agricultural waste are presented due to the similarities of processing technologies and final products. Hence, the specific objectives of this review are to give an overview of: (i) the valorisation of food waste into chemicals, (ii) the valorisation

of agricultural waste into chemicals, and (iii) the economic feasibility of different valorisation technologies.

Chemicals

The global petrochemical production of chemicals and polymers is estimated to be 330 million tons, while the bio-based counterpart is estimated to be 90 million tons, mainly in the form of a handful of chemicals: methanol, ethylene, propylene, butadiene, benzene, toluene and xylene [2]. Bio-based chemicals play a major role in moving chemical production toward sustainability and challenging the linear nature of current petrochemical processes [18]. Currently, more than 80% of the global biochemical production capacity is for bioethanol production. Due to economic challenges, the co-production of various chemicals and materials in a biorefinery may be necessary to make the process feasible [2]. Many previous reviews have reported different methods of converting food waste or lignocellulosic biomass into chemicals, such as those listed in Table 1.

Platform chemicals

Platform chemicals are key building blocks that can be converted to a wide range of commodity and specialty chemicals. In 2004, the US Department of Energy screened 300 promising chemicals that can act as platform chemicals [19]. According to a 2010 analysis, the sugar-derived platform chemicals that continue to have high potential are lactic acid, succinic acid, glycerol, furanics, hydroxypropionic acid/aldehyde, ethanol, sorbitol, xylitol, and levulinic acid [2]. The platform chemicals that are currently being or have been produced from biomass on an industrial scale are ethanol, lactic acid, sorbitol, levulinic acid, succinic acid, and 2,5-furandicarboxylic acid. Additionally, various platform chemical-derived polymers have successfully been commercialized, including polylactic acid (PLA), polyethylene-furanate (PEF), poly- γ -glutamic acid (γ -PGA), and their products [20].

Table 1 Literature review on biorefinery approach for food and agricultural wastes

Feedstock	Process(es)	Product(s)	Review
Food waste	Bioconversion	VFAs, biofuels	[106]
Unavoidable food processing waste	Fermentation, extraction	Citric acid, levulinic acid, PHA	[107]
	Fermentation	Enzymes	[108]
	Bioconversion	PHA	[109]
Agricultural wastes	Fermentation, anaerobic digestion	VFAs, hydrogen, methane	[110]
Lignocellulosic biomass	Biosynthesis	2,5-FDCA	[111]
	Catalysis	Succinic acid, levulinic acid, furfural	[112]
Grape winery waste	Hydrolysis, fermentation	Lactic acid	[113]

The production of a target platform molecule can be selectively optimized for by the selection of the right strain of microorganism, or through bioengineering metabolic pathways, which also makes it possible to produce molecules that are non-natural metabolites such as 1,4-butanediol [21].

One example is the production of 2,5-furandicarboxylic acid (FDCA) by bioconversion. FDCA is a platform molecule synthesizable from C6 sugars via HMF that has promising applications in biopolymer production as a replacement for the oil-derived terephthalate. Conventional chemical routes of synthesis are harsh and require organic solvents or metal catalysts, so more environmentally friendly biological routes such as whole cell or enzymatic conversion processes have been proposed [22]. In a study by Yang et al. [23], 2000 mg/L of HMF could be converted to 1276 mg/L FDCA by *Burkholderia cepacia* H-2 at a pH of 7.0 and 28 °C.

Genetically engineering microorganisms by expressing the genes for enzymes that take part in the conversion process, such as HMF oxidase and HMF/furfural oxidoreductase has been used to increase the efficiency of conversion of HMF into FDCA [24] [25]. In a study by Yuan et al. [25], genetically engineered *Raoultella ornithinolytica* BF60 was used and compared to the wild type, the final FDCA concentration increased from 51 to 93 mM, and the ratio of conversion increased from 51.0% to 93.6%. Although the yield achieved by biocatalysis is comparable to metal catalysts, high concentrations of HMF are toxic to microorganisms and so only low HMF concentrations (under 2 g/L) can be used, reducing the overall productivity [26].

Sugars from food crops such as sugar beet and corn are commonly used as feedstock, but, to avoid competition with food sources and to minimize feedstock costs, food waste has been studied as an alternate feedstock [27]. The conversion of lignocellulose-containing food waste biomass is more difficult than that of starchy biomass since the cellulosic material has to be broken down by pre-treatment and chemical or enzymatic hydrolysis [28]. Cellulose can be broken apart by acid or enzymatic hydrolysis into monosaccharide glucose units, which can be further processed to a wide range of C1 to C6 molecules. Hemicellulose contains C5 sugars such as xylose, galactose, mannose, and arabinose which are precursors of xylitol or furfural. It is difficult to get high yields from lignocellulosic biomass due to the complexity of the biomass structure [3]. The pre-treatment of lignocellulose by thermochemical methods produces compounds that are inhibitory to microorganisms, such as aliphatic acids (acetic, formic, levulinic acid), furan derivatives (furfural, 5-hydroxymethylfurfural) and phenolic compounds (phenol, vanillin, p-hydroxybenzoic acid). Detoxification methods that are commonly used include evaporation, solvent extraction, overliming with calcium hydroxide, activated charcoal, ion exchange resins, and enzymatic detoxification [29].

Lactic acid (LA) is one of the top biomass derived chemicals, with a wide range of possible transformations to solvents, chemicals and fuel precursors [30]. LA is the basis of polylactic acid (PLA), which is a biodegradable polymer that can be used for packaging materials and currently makes up 35% of the bioplastic market. LA is produced primarily by fermentation as opposed to chemical synthesis, since lactic fermentation by the right microorganism can produce LA isomers with high optical activity [28], which is a crucial parameter in that it affects its intrinsic value and determines the structure of derived products [31]. It also has low costs as it can use cheap substrates, consumes little energy and produces high yields relatively quickly [32].

Lactic acid may be produced by naturally occurring or engineered bacteria such as lactic acid bacteria, *Bacillus* strains, *Escherichia coli*, and *Corynebacterium glutamicum* [28]. Particularly, high optical density lactic acid (99% enantiomeric excess) has been obtained in continuous batch fermentation by the strains *Sporolactobacillus laevolacticus* and *Sporolactobacillus inulinus* [33].

The main difficulties in producing LA- and LA-based chemicals are the separation and purification processes [3]. Additionally, the fermentation process is inhibited by low pH as the accumulation of lactic acid lowers the pH below the optimum value (pH 5–7). Therefore, alkali bases such as $\text{Ca}(\text{OH})_2$, CaCO_3 , NH_4OH or NaOH have to be added continuously to neutralize the fermentation broth. The addition of bases produces a stoichiometric amount of various lactate salts and low-value by-products like gypsum, which is formed when precipitating calcium carbonate with sulphuric acid [30].

Separation of LA from fermentation is conventionally done by precipitation, but other separation processes with less by-products have been developed, including dialysis, electro dialysis, membrane processes, and distillation [34]. Separation and purification stages take up half of the production cost, so optimizing these processes are crucial for the economic feasibility of lactic acid production [35]. Kwan et al. [36] investigated the production of lactic acid from various food waste types, mixed food waste, bakery waste, and food waste powder. Food waste powder is the product of a commercial food waste processor that reduces the size of food waste by 70%, reducing transport costs and improving the efficiency of collection and utilization. The food waste underwent fungal hydrolysis and then via fermentation by *Lactobacillus casei* Shirota, and produced lactic acid with conversion yields 0.27, 0.25, and 0.23 g/g for mixed food waste, mixed food waste powder, and bakery waste, respectively. The successful conversion suggests that mixed food waste in urban areas could be valorised by such a process [36].

Another one of the top bio-based chemicals is levulinic acid, a short chain fatty acid with a ketone and a carboxyl

group, which is a versatile platform molecule due to its functional groups [37]. It can be the precursor of various industrially significant chemicals like pharmaceuticals, solvents, polymers, and biofuels. Despite its various potential uses, commercial production is not yet fully developed, and technical advances need to be made before commercialization [38].

Levulinic acid can be synthesized from cellulose or hexoses like glucose and fructose with 5-HMF as an intermediate, and from hemicellulose or pentoses with furfural as an intermediate [39]. In the process of conversion, cellulose is hydrolyzed into hexoses which are dehydrated to 5-HMF by acid catalysis, then rehydrated to levulinic acid and formic acid [40]. This process can be effectively done in a one-pot approach with homogeneous acid catalysts [41]. Table 2 summarizes the important characteristics of some platform chemicals that can be derived from food and agricultural wastes.

Value added biomolecules

Bio-based molecules, biologically synthesized molecules such as phytochemicals and functional materials, natural biopolymers can be derived directly from biomass through extraction instead of being synthesized from petroleum-based chemicals [58]. Natural biopolymers such as cellulose, chitin, pectin, starch, and xylan can be extracted from food and agricultural waste, and have biocompatible and biodegradable qualities [59]. They have been used in pharmaceuticals, food and biomaterials but applications for biomedical purposes have also been explored [60]. Food waste streams like fruit wastes contain valuable compounds such as antioxidant phytochemicals (phenolic compounds, flavonoids, carotene) that can be recovered and reused. Phytochemicals are bioactive non-nutritive plant chemicals that may have health-related effects [61], and are in high demand for food, pharmaceutical, and cosmetic sectors [62]. These specialty chemicals are generally obtained from food waste by physical or thermal extraction [5].

Enzyme-assisted extraction (EAE) is an environmentally friendly approach to traditional extraction methods that increases extraction efficiency by increasing the permeability of the cell wall of plants. EAE uses lower temperature than conventional extraction methods, and combining it with solvent extraction has the benefit of requiring fewer organic solvents. Although EAE is a less harsh process and could potentially be useful in food applications, the current costs of enzymes still make it hard to implement [63].

Fruit waste is produced from fruit processing industries in a large amount. Industrial production of food waste allows the waste to be separated into homogeneous streams, making large scale extraction processes possible [64]. Mango peels contain 20–30% *w/w* pectin, and bioactive compounds such

as dietary fiber, polyphenols, and carotenoids. Processing mangoes leaves 35–60% of waste of which around a half is from peels [65]. Matharu et al. [58] studied the biorefinery of mango peels by microwave assisted extraction of pectin, reporting to have 11.6% *w/w* of pectin extracted. Banerjee et al. [66] studied the extraction of pectin from mango peels using lemon juice as an acidifying agent at 80 °C by boiling and by sonication reporting a yield of 0.27 g/g for both processes.

Citrus peel waste has been studied for several of its bioactive components, such as the pectin, dietary fiber, and essential oils like limonene [62]. Additionally, β -carotene has been extracted from orange processing waste by ultrasonic and enzymatic processes with pectinase and ethanol solvent, showing potential for commercial production [67]. The conversion of agricultural residues and biomass to value-added rare sugars and prebiotic oligosaccharides has been studied (Table 3), as they are a potential ingredient for functional foods with benefits to human health [114].

Integrated biorefineries

An integrated biorefinery is a facility that merges several conversion technologies to produce value-added products such as fuels, power, and chemicals from biomass [68]. Biochemical pathways are fundamental to establish integrated biorefineries. Agricultural waste (mainly lignocellulosic biomass) is widely known as a cleaner replacement for fossil fuels and is commonly used as a substrate in biorefineries. Agricultural residues such as wheat straw, sugarcane bagasse, corn stover, forest products (hardwood and softwood), and dedicated crops such as switchgrass and salix are all lignocellulosic materials [69]. Most plant materials mainly consist of cellulose, hemicellulose, lignin, and pectin [70]. These components are demanding in the sense of successful conversion of biomass to value-added products, and as such require sophisticated pre-treatment. The goal of pre-treatment is to disrupt the crystalline structure of cellulose by breaking down the lignin structure which surrounds it.

Further aims are the removal of lignin and hemicellulose, and the increase of the lignocellulosic biomass porosity. Under those circumstances acids or enzymes can easily access and hydrolyze the cellulose [69]. Nevertheless, pre-treatment processes are commonly the most expensive element of the whole biomass to fuel conversion process [71]. Pre-treatment must produce the following results: (i) excellent sugar formation or the ability to subsequently form sugars by hydrolysis, (ii) prevention of carbohydrate loss due to degradation, (iii) prevention of byproduct formation, (iv) profitability. Pre-treatment methods can be categorized into physical, physicochemical, chemical, biological, electrical, and hybrid technologies [69]. Choosing a pre-treatment

Table 2 Characteristics of some platform chemicals that can be derived from food and agricultural waste

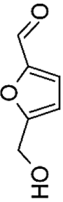
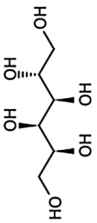
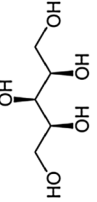
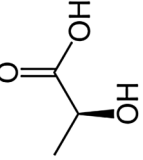
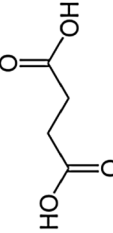
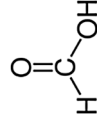
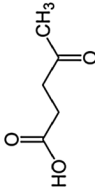
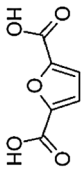
Chemical	Production technology	Molecular structure	Product value (USD/kg)	Microbes/catalyst	Application	References
Hydroxymethylfurfural (HMF)	Catalytic conversion		1.1	HCl, H ₂ SO ₄ , Metallic salts (AlCl ₃ , CrCl ₃ , SnCl ₄), sulfonated biochar	Precursor for pharmaceuticals, polymers, resins, solvents, fungicides, and biofuels	[42–44]
Sorbitol	Catalytic hydrogenation		0.5–1.5	Raney nickel	Food and pharmaceuticals industry, biofuel platform	[45, 46]
Xylitol	Catalytic hydrogenation, Fermentation		5–10	Ni-based catalysts, <i>Candida</i> sp.	Pharmaceuticals, nutraceuticals, food	[47, 48]
Lactic acid	Fermentation		1.3–2.3	Lactic acid bacteria (LAB), <i>Bacillus</i> strains, <i>Escherichia coli</i> , <i>Corynebacterium glutamicum</i>	Food, chemical, cosmetic, and pharmaceutical products, biodegradable polymers	[28, 34]
Succinic acid	Fermentation		5.9–9	<i>Actinobacillus succinogenes</i> , <i>Escherichia coli</i> , <i>Saccharomyces cerevisiae</i> , <i>Yarrowia lipolytica</i>	Surfactant, ion chelator, food, pharmaceuticals, precursor for biodegradable plastic	[49–51]
Formic acid	Chemical hydrolysis, oxidation		0.75–0.9	NaOH, H ₂ SO ₄	Chemical, agricultural, pharmaceutical industries, hydrogen storage	[52, 53]
Levulinic acid	Acid catalyzed dehydration and hydrolysis		0.3–3	Amberlyst 36, HCl	Pharmaceuticals, solvents, polymers, biofuels	[37, 54, 55]
2,5-Furandicarboxylic acid (FDCA)	Chemical oxidation, biocatalysis		2.5–3.2 (Minimum selling price)	Au, Pt, <i>Raoultella ornithinolytica</i> , <i>Cupriavidus basilensis</i>	Biopolymer production	[24, 56, 57]

Table 3 Production of value-added rare sugars and prebiotic oligosaccharide molecules from the agricultural residues/biomass

Source of agricultural waste	Name of the process	Products and/or by-products	References
Rice straw and corn cobs	Microbe mediated: <i>Penicillium citrinum</i> H9 and <i>Achromobacter</i> sp. BP(1)5	Crude biosurfactant	[115]
Onion waste	Microbe mediated: <i>Escherichia coli</i> TOP10F' and <i>E. coli</i> BL21 (DE3)	Purified Paenibacillus polymyxa L-arabinose isomerase (PPAI) for D-tagatose and L-ribulose production and bioethanol	[116]
Assam lemon waste (ALW)	Microbe mediated: <i>Trichoderma reesei</i> RUT C30, <i>Saccharomyces cerevisiae</i> , <i>Pichia kudriavzevii</i>	Cellulase, hexose, essential oils, ethanol and pectin	[117]
Corn stalk, peanut shells, and rice stalk	Pyrolysis coupled with hydrothermal conversion	Furfural, levoglucosan, nutrient solution and boiler fuels	[118]
Poplar	Hydrogen peroxide-acetic acid pre-treatment (HPAC)	Xylooligosaccharides (XOS) and monosaccharides: xylose, xylobiose, xylotriose, xylotetraose, glucose	[119]
Delignified sugarcane bagasse	Pre-treatment with hydrogen peroxide and acetic acid followed by the application of a recombinant xylanase from <i>Bacillus subtilis</i>	Various xylooligosaccharides	[114]
Sugarcane bagasse	12% sodium hydroxide treatment coupled with steam application	XOS namely xylose, xylobiose, xylotriose	[120]
Sweet corn	In vitro incubation using <i>Enterococcus faecalis</i> CCD10, <i>Enterococcus faecium</i> TCD3, <i>Lactobacillus maltromicus</i> MTCC108 and <i>Lactobacillus viridiscens</i> NCIM2167	Xylose, xylobiose, xylotriose, xylotetraose and total reducing sugars	[121]
Sugarcane straw	<i>Lactobacillus acidophilus</i> LAC 4, <i>Lactobacillus paracasei</i> LBC 81–82, <i>Bifidobacterium longum</i> BL04–300B, <i>Bifidobacterium lactis</i> B101	Monosaccharides: glucose and xylose, and XOS: xylose (X1), xylobiose (X2), xylotriose (X3), xylohexaose (X4), xylopentaose (X5), and xylohexaose (X6)	[122]
Whey	Probiotic cultures: <i>Lactobacillus reuteri</i> TP-1, <i>Lactobacillus plantarum</i> NCDC 627, <i>Lactobacillus rhamnosus</i> GG, <i>Bifidobacterium breve</i> NCTC11815, <i>Bifidobacterium longum</i> D2 and <i>Bifidobacterium animalis</i> BL3 Pathogenic strains: <i>Salmonella typhimurium</i> RSSK95091, <i>Escherichia coli</i> BC1402, <i>Bacillus cereus</i> BC6830, <i>Yersinia enterocolitica</i> ATCC27729 and <i>Staphylococcus aureus</i> ATCC25923 Yeast strains: <i>Saccharomyces cerevisiae</i> and <i>Kluyveromyces marxianus</i>	Lactose derivative hetero-oligosaccharides containing (1,2)Glc-(1,3) Glc-(1,4)Glc units up to DP 7	[123]
Deacetylated sugar cane straw	Thermostable recombinant endoxylanase of <i>Cryptococcus flavescens</i> in synergic association with α -L-arabinofuranosidase (GH 51) (Megazyme®)	XOS: xylose (X1), xylobiose (X2), xylotriose (X3), xylopentaose (X5), and xylohexaose (X6)	[124]

strategy that can efficiently hydrolyze the carbohydrates in the biomass into monosaccharides leads to a quicker process with a higher yield of sugar. Furthermore, the particle size of lignocellulosic biomass is minimized and the glucose yield is increased due to the quick enzymatic hydrolysis. Finally, there is a decrease in enzymatic action inhibition, as well as in energy needs [72].

While food waste composition differs source to source, its main constituents are organic fractions, carbohydrates, proteins, and lipids [62]. As these constituents are easily biodegradable, food waste can be directly fed to the bioreactor without pre-treatment [73].

Saccharification

Saccharification process breaks lignocellulosic biomass compounds into monosaccharides which act as platform chemicals for value-added products. The predominant monosaccharides obtained are glucose and xylose [74]. When talking in general terms, saccharification of lignocellulosic biomass which is not pretreated can yield less than 20% of aggregate sugars. On the other side, when lignocellulosic biomass is pretreated, the yield can reach up to 90% with diverse pre-treatment strategies [75]. The processes that

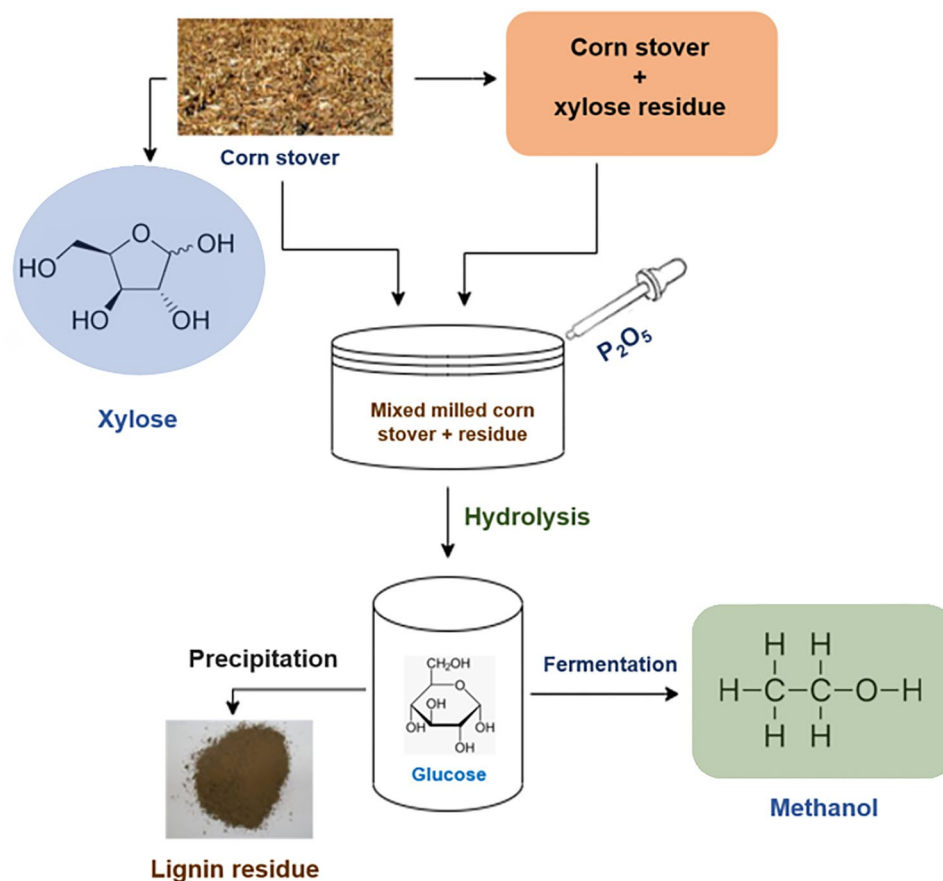
integrate different saccharification pre-treatment techniques are introduced below.

Mechanocatalytic process

Liu et al. [76] designed a particular mechanocatalytic process to produce high-quality glucose with high sugar titer and high yield from agricultural cellulosic biomass. The process unites mix-milling of solid P_2O_5 with corn stover or corn stover-xylose residues and successive saccharification ahead of which hemicellulose is recovered. They indicate that the precipitation of lignin allowed fermentative upgrading to ethanol without the need for detoxification treatment. Direct hydrolysis of the milled cellulose in water without adding mineral acids for the production of ethanol is the new approach. Typically, enzymatic saccharification is used. Figure 2 schematically shows the described mechanocatalytic process.

The mechanocatalytic process conducted by Liu et al. [76] resulted in a high yield of fermentable sugars (app. 75%) with high concentrations up to 31 g/L with no use of organic solvents. Furthermore, the hemicellulose was recovered in the form of xylose which led to a decrease of furfural and acetic acid concentrations in the hydrolysate from the remaining residue. The sulfur-free lignin

Fig. 2 The mechanocatalytic process for the production of high-quality glucose and ethanol introduced by Liu et al. [76]



was obtained from the hydrolysate with precipitation. Finally, with fed-batch fermentation of undetoxified concentrated hydrolysate, ethanol titer of over 42 g/L from corn stover-xylose residues was obtained. P_2O_5 , added in Liu et al. [76] during the mix-milling process, engenders decrystallization, and depolymerization of cellulose into oligosaccharides. H_3PO_4 is generated in the process, which hydrolyzes oligosaccharides into glucose.

Mechanoenzymatic process

Biocatalytic processes that depend on the action of cellulase or hemicellulase enzymes are characterized as promising milder alternatives to the chemical hydrolysis of cellulose and hemicellulose. Unfortunately, these enzymes are too slow in depolymerizing cellulosic biomass and as such require pre-treatment to make the biopolymers more available for the enzymes [74]. Mechanoenzymatic reactive aging (RAging) process is a novel approach for enzyme catalysis and cellulose saccharification without a need for pre-treatment, bulk solvent, acids, or transition metals [77].

According to Zhou et al. [17], catalytic conversion of lignocellulosic biomass faces a big challenge due to its complex chemical composition which makes production of target fuels and chemicals less convenient. A great part of lignocellulosic biomass is cellulose [9], which has the simplest structure of all components. Cellulose is made up of only anhydrous glucose units, making it significantly simpler than the structure of hemicelluloses, which consist of numerous diverse sugar monomers, or lignin, which consists of complex biopolymers. Nevertheless, the decomposition of hemicellulose and lignin can be executed more easily than that of cellulose, which is energy-intensive and demanding [17]. High solids concentrations reduce the conversion rate for enzymatic processes due to mass-transfer limitations and enzyme inhibition by hemicellulose, reaction products, or other compounds [78, 79]. This is known as the solid-state effect.

One of the promising technologies to overcome this effect is mechanoenzymology, which is a technology that combines mechanical and enzymatic treatments to enhance their joint impact on fiber reactivity [80]. Hammerer et al. [74] reported approximately 90% yields of glucose and xylose monosaccharides with mechanoenzymatic saccharification. Lignocellulosic biomass was pre-milled for 60–90 min into a fine powder to which enzymes were added. During the mechanoenzymology process, enzymes tolerate mechanical stress [77]. Furthermore, they stay active in most solid mixtures [81]. Most importantly, mechanoenzymology is not affected by solubility issues and the solid effect state which normally weakens enzymatic saccharification of lignocellulosic biomass at high solid loadings [74].

Hydrolysis

Hydrolysis is the degradation process of polysaccharides in an aqueous medium catalyzed by an enzyme or acid [82]. Correspondingly, food waste and agricultural waste undergo acid or enzymatic hydrolysis to generate glucose, peptides, and amino acids [83]. Hydrolysis of cellulose and hemicellulose yields hexoses and pentoses which can be further transformed to ethanol, lipids, bioproducts, and chemicals with fermentation [84]. When looking from the economic point of view, enzymatic hydrolysis has been recognized as most crucial to achieve efficient conversion of biomass to biofuel [85]. There are many other advantages of enzymatic hydrolysis over chemical hydrolysis including high efficiency, low energy requirements, low deterioration, low corrosion impact, and decreased generation of fermentation inhibitors [86]. The optimal conditions for enzymatic hydrolysis of cellulose are temperatures between 45 and 55°C, pH values 4.5–5, and mixing conditions that are necessary to allow adequate mass and heat transfer for enzyme–substrate interaction [87].

Fermentation

Fermentation is the biological conversion process of complex substrates into simple compounds by different microorganisms, for instance, bacteria and fungi [88]. The hydrolysate recovered after chemical and enzymatic hydrolysis is frequently used as feedstock material for the fermentation process, which results in value-added products [85]. Various studies using biological treatment of food waste types are outlined in Table 4. Solid-state fermentation uses low-cost agricultural residues as the substrate.

Bioprocesses are carried out in the absence or near-absence of free water. Nevertheless, moisture content of a substrate must be sufficient to support the growth and metabolic activity of microorganisms. The solid matrix can act as the source of carbon and other nutrients or it can be an inert material which serves as a platform for growth of the microorganisms. Solid-state fermentation gives higher yields compared to the liquid fermentation due to its design which resembles closely to the natural environment where used microorganisms thrive. Industrial products developed by solid-state fermentation are various enzymes, biopolymers, biosurfactants, organic acids, pigments, secondary metabolites, biofertilizers, and biopesticides, and flavoring agents [89]. Dark fermentation or acidogenesis is a bioprocess which converts food waste into carboxylic acids (lactic, propionic, butyric, acetic, valeric acid) and solvents in the liquid phase, and biohydrogen and CO_2 in the gas phase [90].

Table 4 Examples of integrated biorefinery concepts for the generation of platform chemicals from different food waste types

Food waste	Pre-treatment	Treatment	Product	Yield	Application	Refs
Waste activated sludge and food waste	–	Cathodic electro-fermentation using mixed microbial consortium	Lactic acid	0.6578 gL ⁻¹ h ⁻¹	Pharmaceutical and cosmetic applications	[91]
Cottonseed meal and corn cob residues	–	Enzymatic saccharification for CCR hydrolysate and fed-batch fermentation by <i>Sporolactobacillus inulinus</i> YBS1-5 at 37 °C	D-lactic acid	0.85 g/g glucose	Pharmaceutical and cosmetic applications	[92]
Banana peels	–	Simultaneous saccharification and cofermentation by <i>Lactobacillus paracasei</i> LA104 at 37 °C	L-lactic acid	69.38%	Pharmaceutical and cosmetic applications	[93]
Bakery waste	Incubation with <i>Aspergillus awamori</i> and <i>Aspergillus oryzae</i> for 5 days at 30 °C	Inoculation with <i>Aspergillus niger</i> UABN 210 suspension at 30 °C in a rotary shaking incubator for 5 days	Citric acid	8.2%	Cosmetics, pharmaceutical, dietary, and food supplements	[94]
Food waste hydrolysate	Pre-hydrolysis of food waste in bioreactor by consortium of enzymes	Enzymatic hydrolysis at 55 °C for 24 h; bacterial fermentation under 37 °C with external CO ₂ at pH 6.6–6.8	Succinic acid	28,335%	Precursor to polymers, resins, solvent, food, and dietary supplements	[95]
Bread waste	–	Bench-top scale fermentation at 28 °C with engineered <i>Yarrowia lipolytica</i>	Succinic acid	76%	Precursor to polymers, resins, solvent, food, and dietary supplements	[96]
Fermented pomegranate waste	Wine production by yeast fermentation	Enzymatic hydrolysis by enzyme complexes from solid-state fermentation with <i>A. awamori</i> and <i>A. oryzae</i> to produce glucose; <i>Actinobacillus succinogenes</i> fermentation to produce succinic acid	Succinic acid	55%	Precursor to polymers, resins, solvent, food, and dietary supplements	[97]
Vegetable waste	Stored in air-tight containers at 4 °C after freeze-drying followed by grinding and sieving through a 0.2-mm mesh	70 mL 6 M HCl hydrolysis at 100 °C overnight; extraction with methanol (20 mL) for 1 h at room temperature under magnetic stirring	Ellagic acid	53%	Nutraceutical applications	[98]
		Microwave heating with Amberlyst 36 catalyst at 135–150 °C for 5 min in aqueous medium	Levulinic acid	13–17 °C mol%	Pharmaceuticals	[54]

Economic feasibility

In order for the conversion processes of food and agricultural waste to be implemented industrially, their economic feasibility and process efficiencies must be analyzed. The feasibility of the process can induce investment interest in the waste to raw materials biorefinery market. Growth is expected in the bio-based market, especially focused on conversion of raw waste materials into value-added building blocks [2]. For example, the portion of the market for succinic acid produced from bio-based feedstock grew from five percent in 2009 of the total succinic acid market to half of the market in 2020 [2].

Table 5 summarizes some feasibility studies on the valorization of food waste. One such study was performed by Lam et al. [99], focusing on the production of succinic acid from 1 ton per day of bakery waste via fermentation. Simulation software SuperPro Designer[®] 8.0 was used to perform the mass and energy balances of the process, necessary to assess the economic variables affecting the feasibility [99]. This project was found to be economically feasible, with a return on investment (ROI) of 12.8%, a breakeven of the capital investment at 7.2 years, and an internal rate of return (IRR) of 15.3%. The price of succinic acid used in this study was \$9 per kilogram, which was the market price at the time of their research. A sensitivity analysis showed that the prices of the products, such as succinic acid and biomass, affected the profitability of the plant most significantly. The only issue may occur if the amount of incoming bakery waste drops below 0.26 tons per day, approximately 25% of the amount of waste the plant is designed to convert [99].

Kwan et al. [27] performed techno-economic analysis of a food waste valorisation process for three different plant scenarios: lactic acid, lactide, and PLA, each with a capacity of 10 tons of food waste powder per hour. Although all scenarios were shown to be economically feasible (Table 5), the most promising of the three scenarios was the lactic acid production process, with the highest annual net profits, highest net present value, and lowest payback period [27]. The

resulting overall conversion yields of 3.1 tons of 80% LA solution, 1.7 tons of lactide and 1.3 tons of PLA point to these processes being an efficient approach to food waste recycling. In another study, Kwan et al. [36] found that a decentralized approach to food waste recycling could also be advantageous for the bioconversion of food waste in urban areas.

Integrated biorefineries are a promising strategy of producing value from food and agricultural waste by pairing the production of value-added products with energy production. Demichelis et al. [100] performed a comparison of three different scenarios of food waste utilization for LA and biogas production. One scenario presented an integrated biorefinery which produced lactic acid and biofuels from food waste, while the other two only produced LA or biogas (Demichelis et al., 2018). This integrated biorefinery option proved to be the most profitable of the three explored, with an annual net revenue of \$879,000 for 20 tons per day of food waste utilized, and a selling price of LA of \$1360 per ton. Integrating the processes by sequential LA production via separate hydrolysis and fermentation (SHF) followed by biogas production resulted in a reduced amount of waste generated, reduced digester volume for biogas production, and enhanced value of the products [100].

The economic potential of valorizing food processing waste has also been studied. Mango processing waste biorefinery for pectin and seed oil extraction was evaluated in a study by Arora et al. [101] to be potentially profitable in case the plant had minimum 10 tons per hour capacity. It was shown that co-production of pectin and seed oil was the most optimal with IRR 34% and a payback period of 2.4 years, compared to production of only one of the products [101].

The valorisation of grape seed pomace in a biorefinery was assessed by Jin et al. [102], in which the production of a combination of seed oil, polyphenols and biochar were compared. A biorefinery approach with all three products showed the best profitability with an IRR of 34.3%, and payback period of 2.5 years. Only producing grape seed oil had the worst economic performance with a negative net present

Table 5 The results of the techno-economic feasibility studies reviewed, showing the product produced by the process investigated, amount of food waste processed, the selling price, and the annual net revenue generated

References	Product(s)	Feasibility	Food waste processed (tons/day)	Selling price	Net revenue generated (\$USD/year)
Lam et al. [99]	Succinic Acid	Yes	1	\$9/kg	\$374,041
Kwan et al. [27]	Lactic Acid	Yes	227	\$1874/ton	\$22,184,000
	Lactide		227	\$2800/ton	\$11,646,000
	Polylactic Acid		227	\$5215/ton	\$20,038,000
Demichelis et al. [100]	Lactic Acid + Biogas (integrated biorefinery)	Yes	20	€1360/ton (LA)	\$879,000

value. The sensitivity was mostly related to plant capacity and polyphenol selling price [102].

Biorefineries with sugarcane bagasse as a feedstock have been shown to be potentially profitable. Ntimani et al. [103] evaluated the production of furfural, ethanol, or co-producing the two from sugarcane bagasse in a biorefinery annexed to a sugar mill. Among the scenarios, producing furfural only was the most profitable because of lower investment costs (IRR = 12.92%), but co-producing furfural and ethanol was more feasible without energy sales (IRR = 10.30%). The fluctuations in IRR caused by the variability in chemical selling prices decreased when co-producing furfural and ethanol compared to producing only one chemical [103]. Another study assessed adding a biorefinery to an existing sugar mill to co-produce xylitol or glutamic acid with electricity. Profitability increased for both biorefinery scenarios compared to combustion, with the IRR increasing from 10.3% for just combustion to 12.3% and 31.2% for co-production with xylitol and glutamic acid, respectively [104].

One aspect of economic feasibility which connected all of these studies is that the feasibility of the processes was sensitive to the changing market prices of the platform chemicals being produced. The fluctuating selling price of the platform chemicals being produced greatly affects whether these processes can be shown to be economically feasible at an industrial scale, as indicated by the sensitivity tests of each study. Additionally, shifts in the petroleum market would also affect investors' disposition toward embracing a bio-based market. If oil prices plummet, interest in expending the capital costs needed to shift to biorefinery products may be lost.

Future perspectives

The need for increased resource recycling and a sustainable circular economy is evident. The high volatility of oil prices and their sensitivity to geopolitical issues are prompting countries to invest in alternative fuel sources [2]. The future expansion of biochemicals depends on the availability of biomass feedstock. However, the harvesting of biomass could potentially endanger food safety or cause deforestation, necessitating the development of policies to ensure sustainable practices [125]. A circular and biobased economy concept has been introduced in the EU as a policy objective, in which biorefineries are highlighted as a key technology [105].

In the EU, the collection and reuse of food waste and agricultural waste is receiving more focus, with EU directives and policies making the collection of biodegradable waste mandatory by 2023, and include food waste valorisation as a method to manage unavoidable food waste [126]. The increased collection of biodegradable waste brings

opportunities to expand and incentivize the bioeconomy in a sustainable way. The shift to a bio-based economy is expected to be gradual, and it is not expected that bio-based alternatives will phase out petrochemicals in this decade [105]. According to another report, the global bioenergy crop potentials in 2050 will be between 44 and 133 EJ/yr, while the total global primary bio-energy potentials in 2050 may vary between 160 and 270 EJ/yr [127]. From a circular economy view point, the production of energy and other value-added products (e.g. platform chemicals) from waste biomass is considered to be highly sustainable for developing countries.

The implementation of new environmental policies and carbon taxes will assist in making this industry competitive. Food waste and agricultural waste valorisation is a growing field of research with promising results and various practical applications. Most bio-based chemicals are not yet produced on an industrial scale nor are market competitive, so the optimization of chemical processes to the properties of biomass is necessary. Economic pathways in integrated biorefineries for simultaneous biofuel and platform chemical for further processing need to be defined to make integrated biorefineries compatible with fossil-based refineries [105]. Techno-economic feasibility depends on the ability to scale up these processes to an industrial scale, requiring plants with the ability to treat thousands of tons of waste per year. This requires an improvement in the handling and logistics of biomass in large quantities, and advancements in the technological aspects of industrial scale processes [18].

Conclusions

Food and agricultural waste valorisation are an increasingly growing field of research. The most common platform chemicals produced from biomass on an industrial scale are ethanol, lactic acid, succinic acid, levulinic acid, sorbitol, and 2,5-furandicarboxylic acid. The production of these chemicals has proven to be currently economically viable, and more chemical products are expected to become viable as the chemical industry transitions toward more bio-based and circular solutions. Converting food and agricultural waste into value-added chemicals is a sustainable way of waste management. Biorefineries provide the technological basis for the versatile conversion of biomass waste to chemicals by subjecting biomass to saccharification, hydrolysis, and fermentation. Technical aspects of the separation, purification, and pre-treatment of recalcitrant lignocellulosic biomass still need to be addressed, and an integrated biorefinery approach which combines biochemical and biofuel production is necessary for the practical considerations of biomass valorisation. It is expected that bio-based chemicals and fuels will play an increasingly large role in the future economy.

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