

Recycling of Food Waste into Chemical Building Blocks

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Abstract: Enormous quantities of food waste (FW) arise from global production. Roughly, one third of all food for human consumption is wasted resulting in huge costs to the world economy alongside significant environmental problems. FW is a potential reservoir of functionalized molecules, i.e. carbohydrates, proteins and lipids that can be recovered, concentrated and transformed into high value products. Conversion of renewable carbon from FW to building block chemicals can also more profitable than conventional processing methods. Recent studies have used microbial routes to recover value from FW into a number of chemical building blocks. Recycling FW into valuable chemicals directly contributes to the transition from current fossil fuel-based economies to a bioeconomy and reduced waste society. This paper reviews the potential for using FW and focuses on recent updates in second-generation valorisation methods where the bioproduction of chemical building blocks uses FW as a feedstock.

Key words: Food waste; Chemical building blocks; Succinic acid; Lactic acid; 2,3-Butanediol; Ethanol; n-Butanol

Need for waste biorefineries: International priorities to reduce fossil fuel emissions, alongside rising prices for oil derivatives are resulting in significant interest in the production of chemical building blocks from renewable sources [1, 2]. The biorefinery concept has the potential to contribute to reducing international dependency on petroleum-based industries globally. Biorefineries are integrated complexes producing marketable products and energy from the processing of biomass. Analogous to petroleum refineries, first generation biorefineries generate biofuels and biochemicals from edible sources, e.g. starch, sugar, corn, animal fats and vegetable oils. These processes are efficient, well established but are part of the food versus fuel debate. However, the high cost of fermentable sugars limits the scope of bulk chemicals manufactured economically. In addition, use of these substrates as production feedstocks is unsustainable as they are essential components within the food chain. To ensure the long-term feasibility of biorefineries, development efforts are focussing on alternative technologies capable of producing fuels and chemicals from a wide array of non-edible, agro-industrial by-products most commonly available as wastes [3, 4]. This biorefinery concept enables the valorisation of discarded substrates into feedstocks producing high value from wastes.

Food waste and more circular economies: a definition of food waste (FW) is the unconsumed, discarded or lost produce arising from any of the four stages of the food supply chain from; agriculture & processing, handling & storage, the retail market, and final consumption. Current estimates are that between one-third and a half of all food produced worldwide, i.e. approx. 1.3 billion tonnes per year is wasted with a total cost to the world economy of about \$750 billion [5, 6]. In the UK alone, FW was more than 14 million tonnes in 2013, the highest wastage rate in Europe [7, 8]. In addition to being a significant loss of valuable materials, these enormous quantities result in serious management problems, both economically and environmentally. Emission calculations indicate losses of two tonnes of

carbon dioxide per tonne of waste. FW spoils quickly due to its high nutritional and water content. This bacterial contamination provides the basis for first generation valorisation technologies including; anaerobic digestion, composting, incineration and animal feed production with residues disposed to landfills. Despite the value gained in producing energy and soil amendments from these methods, the high quantity of FW has the potential feedstock for global bioproduction of large quantities of high value chemicals. Indeed, the conversion of FW to building block chemicals can be more profitable than conventional processing methods [9]. FW is attractive in terms of its nutrient content, i.e. 30-60% starch, 5-10% proteins and 10-40% lipids. Notably, the sugar content is high in value for microbial fermentation in comparison to other bulk, crude, or renewable sources such as recalcitrant lignocellulose wastes [10]. Conversion processes, shown in Figure 1, unlock this huge potential from FW resulting in a spectrum of commodity chemicals. This integration of renewable carbon from FW within a biorefinery relies in low cost feedstocks with a reduced carbon footprint. The combination of waste recycling, production of valuable chemicals and a reduced carbon footprint aligns well with sustainable development goals and transition from a fossil fuel-based economy to a bioeconomy and low-waste society.

Bioconversion of FW into commercially important chemicals: Sourcing cheap and easily fermentable feedstocks is a major challenge for bio-based industries. FW is rich in functionalized molecules which can be recovered, concentrated and transformed into high value products [11-13], see Figure 2. The reutilization of FW as feedstocks for the bioproduction for chemicals is evident in recent innovative work where selected chemical building blocks have been successfully synthesized using FW as substrate, see Table 1. Table 2 shows the maximum theoretical potential of chemical building blocks from FW. Calculations have been determined for the sugar concentration in FW hydrolysate, reported

by Pleissner et al. [14]. The following sections discuss recent updates and the potential for bioproduction from FW of these chemical building blocks.

Succinic acid: According to US Department of Energy, succinic acid is a top platform chemical which can be produced from biomass. This platform chemical has multiple practical applications including synthesis of 1,4-butanediol, tetrahydrofuran, gamma-butyrolactone, plus as a monomer for some biodegradable polymers [15]. Biomolecules present in FW are in the form of macromolecules such as starch, cellulose, proteins and lipids etc. These need to be hydrolysed into useable forms to enable microbial growth for biochemical production. Zhang et al. [16] and Leung et al. [17] employed bakery wastes, e.g. cake, pastries and bread for microbiological succinic acid production by *Actinobacillus succinogenes*. The starch and proteins molecules in bakery and bread waste were broken down into glucose and amino acids using fungal enzymes by *Aspergillus awamori* and *Aspergillus oryzae*. The hydrolysate from fungal treatment was rich in sugars and free amino nitrogen with sufficient nutrients to support the growth of *A. succinogenes*. No additional supplements were required. The titre of succinic acid accumulated using cake, pastry and bread wastes were 24.8, 31.7 and 47.3 g/L with a yield of 0.80, 0.67 and 1.16 g/g sugars, respectively. Downstream processing was also conducted to recover succinic acid crystals with a purity level of 96-98% in the case of bakery waste. In their latest work, they made use of fruit and vegetable waste (apples, pears, orange, potatoes, cabbage, lettuce and taros) hydrolysate as feedstock and a massive succinic acid titre of 140.6 g/L was accumulated by oleaginous yeast *Yarrowia lipolytica* using this hydrolysate [18].

Lactic acid: Lactic acid is a commercially important chemical with wide ranging applications in the food, chemical, cosmetic and pharmaceutical industries. Lactic acid is a monomer that can be polymerized to yield the biodegradable plastics, polylactic acid (PLA) and poly(3-hydroxybutyrate-co-lactate). Unlike the chemical route, microbial fermentation

can yield optically pure isomers, D- and L-lactic acid. Currently, nearly all commercial lactic acid comes from microbial fermentation [19]. Kwan et al. [20] used the same strategy referred to above to produce lactic acid from mixed food leftovers of rice, noodles, meat and vegetables as well as bakery wastes including, unsold products such as cakes, breads and pastries. The fermentation of mixed food and bakery waste hydrolysate by *Lactobacillus casei* Shirota resulted in 94.0 and 82.6 g/L lactic acid with a high productivity of 2.61 and 2.50 g/L. h, respectively. The yield was the same (0.94 g/g) for both hydrolysates.

2,3-butanediol (BDO): BDO is a promising compound both as a platform chemical and as a liquid fuel. BDO has many applications in the pharmaceutical, biomedical, and other chemical industries for the production of printing inks, perfumes, fumigants, spandex, moistening and softening agents, and plasticizers, e.g., cellulose nitrate, polyvinyl chloride and polyacrylates [21]. BDO is also used as an antifreezing agent, and octane booster for petrol as is; or it can be converted to useful derivatives such as 1,3-butadiene, diacetyl and methyl ethyl ketone. In recent work, BDO was manufactured from fruit, i.e. plums, apples and pears, and mixed with vegetable wastes containing mainly broccoli (80%) using *Enterobacter ludwigii* [22]. The sugars, glucose, fructose and sucrose present in the fruit extract were fermented to BDO. The fed-batch cultivations of *E. ludwigii* resulted in a BDO concentration of 50 g/L with a yield and productivity of 0.4 g/g and 0.41 g/L. h, respectively. The vegetable waste was pre-treated with sulphuric acid (3%) to extract the sugars; glucose, fructose, xylose, galactose and arabinose, from the hemicellulosic fraction. The BDO titre obtained from mixed vegetable waste hydrolysate was 17.6 g/L with a conversion yield of 0.32 g/g and productivity of 0.39 g/L. h.

Ethanol: Ethanol is a renewable energy source and widely used as a fuel additive for partial gasoline replacement. Commercial ethanol is produced currently from fermenting sugar and starch. USA and Brazil are the major producers of ethanol in the world. Corn is the dominant

feedstock used for production in USA and sugarcane in Brazil. Ethanol is by far the most significant biofuel in the USA, accounting for all biofuel production in 2012. In recent times a number of reports on ethanol production from FW have been published. Huang et al. [23] investigated the feasibility of producing ethanol from FW at high solids content, i.e. 35%, w/w. FW was collected from a food retail store in Illinois, USA that contained mainly mashed potatoes, sweet corn and white bread. Conventional fermentation resulted in accumulation of 144 g/L. A vacuum recovery system was employed to eliminate product inhibition and thus complete consumption of glucose. Ethanol yield for vacuum and conventional fermentation was found to be 358 g/kg and 327 g/kg of FW (dry basis), respectively. Kiran and Liu [24] attempted ethanol production from waste cake. The fungal mash rich in hydrolytic enzymes was employed for obtaining glucose (127 g/L) and free amino nitrogen (1.8 g/L) from FW. Use of a hydrolysed solution as sole fermentation feedstock resulted in 58 g/L of ethanol with a yield of 0.5 g/g in 32 h.

n-Butanol: 1-Butanol or n-butanol is an attractive molecule for its multiple uses as a solvent, intermediate within the chemical industry, as well as a fuel. It also has a low vapour pressure and gasoline-like octane rating which allows it to be blended with gasoline or used as a pure fuel without modification in some vehicle engines [25]. FW contains significant amounts of sugars and starch, which can be easily metabolized into n-butanol by Clostridia, a well-known organisms for ABE fermentation. FW has also been examined as a feedstock for acetone-butanol-ethanol (ABE) fermentation with butanol as the main product. Bioconversion of FW, i.e. potatoes, sweet corn and white bread, by *Clostridium beijerinckii* accumulated 18.9 g/L ABE solvents with a productivity of 0.46 g/L. h and yield of 0.38 g/g from 81 g/L FW containing an equivalent glucose of 60.1 g/L. On the other hand, 14.2 g/L of ABE was produced from 40.5 g/L in control fermentation with a productivity and yield of 0.22 g/L. h and 0.35 g/g, respectively [26]. Similar results were obtained by Ujor et al. [27]

where batch ABE fermentations were carried out by *C. beijerinckii* using inedible dough, breadings, and batter liquid as substrates, see Table 1. ABE fermentation of FW has several advantages including lower feedstock cost, and higher productivity in comparison to costly glucose.

Future outlook: In the last two decades, the bio-based production of chemicals and polymers from renewable sources has received notable attention. The cost of feedstock is a major hurdle for the fermentative production of chemicals, accounting for up to 70% of total costs and severely influencing commercial viability. The majority of FWs are carbohydrate rich and thus a feasible feedstock alternative for fermentative production of chemicals. FW has several advantages in comparison to lignocellulosic biomass (LCB). Most FW contains significant amounts of sugars and starch, which can be easily valorised to high value products by the majority of industrially attractive microbes. In contrast, LCB requires harsh pre-treatments with a large investment in energy. In addition to sugars, FW contains functionalized molecules, i.e. proteins, fatty acids, minerals, unlike LCB. These support microbial growth eventually leading to improved metabolite production rates. The fermentative production of chemicals from most of FW does not require supplementation of expensive hydrolytic enzymes, i.e. the most expensive pre-treatment step. This is a significant economic advantage. Further, the energy content and global abundance of starchy FW makes them ideal for use as potential feedstocks for bioproduction. Recent FW valorisation studies opens a number of avenues giving hope for the bulk production of bio-based products including chemicals, fuels, bioactive compounds, biodegradable plastics, enzymes and many other molecules. The concept of the FW-based biorefinery is still in its infancy and many more efforts are required before it is evident in commercialization.

Conclusion: The generation of food waste is inevitable. This has the potential to cause significant environmental damage including the formation and emission of greenhouse gases,

as well as ground water contamination. Thus, developing more sustainable solutions for FW management is a large-scale challenge for society. However, FW is a renewable bioresource with potential to produce valuable chemicals at industrial scale, i.e. a raw material for biorefineries. The profitability of chemicals and biofuels produced from FW has the potential to stimulate investment in biorefinery chains increasing the likelihood that FW processing will move away from traditional waste management processes. The development of risk assessment methods and legislation will need to match these changes in order to stimulate and promote production of new chemical building block markets from FW biorefineries. This development will enable effective exploitation of FW with the potential for positive contributions to renewable energy, more sustainable production of raw materials, economic value and reductions in environmental impact.

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In this work, highly efficient fungal mash rich in various hydrolytic enzymes was employed for pre-treatment of mixed food waste and hydrolysate was used as feedstock for ethanol production. The study demonstrated that food waste can be successfully used as the nutrient-complete hydrolysates for the fermentative production of ethanol.

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The fermentative production of n-butanol was carried out using food waste. The fermentation was coupled with *in situ* removal using novel vacuum stripping technology to reduce n-butanol concentration in culture broth to alleviate its toxic effects. It was demonstrated that food waste is a superior feedstock for producing butanol in comparison to costly glucose.

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This report evaluates the feasibility of bioconversion of starchy food waste (inedible dough, breadings, and batter liquid) into n-butanol through ABE fermentation. It demonstrates that industrial starchy food waste is a feasible alternative substrate for fermentative production of butanol

Figure captions

Figure 1: Food waste-based biorefinery

Figure 2: Bioproduction of chemical building blocks from food waste

Tables

Table 1: Summary of bioproduction of chemicals from food waste*

Chemical	Food waste	Microorganism	Process mode	Titre (g/L)	Yield (g/g)	Productivity (g/L. h)	Reference
Succinic acid	Cake waste	<i>Actinobacillus succinogenes</i>	Batch	24.8	0.80	0.79	[16]
	Pastry waste	<i>Actinobacillus succinogenes</i>	Batch	31.7	0.67	0.87	[16]
	Bread waste	<i>Actinobacillus succinogenes</i>	Batch	47.3	1.16	1.12	[17]
	Fruit and vegetable waste	<i>Yarrowia lipolytica</i>	Fed-batch	140.6	0.47	0.43	[18]
Lactic acid	Mixed food waste (rice, noodles, meat and vegetables)	<i>Lactobacillus casei</i> Shirota	Batch	94.0	0.94	2.61	[20]
	Bakery waste (cakes, breads and pastries)	<i>Lactobacillus casei</i> Shirota	Batch	82.6	0.94	2.50	[20]
	Fruit waste (plums, apples and pears)	<i>Enterobacter ludwigii</i> FMCC 204	Fed-batch	50.1	0.40	0.41	[22]

2,3-Butanediol	Mixed vegetable waste with 80% broccoli	<i>Enterobacter ludwigii</i> FMCC 204	Fed-batch	17.6	0.32	0.39	[22]
Ethanol	Mashed potatoes, sweet corn and white bread	<i>Saccharomyces cerevisiae</i>	Batch	144.0	0.74	2.0	[23]
	Bakery waste	<i>Saccharomyces cerevisiae</i>	Batch	58.0	0.50	1.82	[24]
n-Butanol	Mashed potatoes, sweet corn and white bread	<i>Clostridium beijerinckii</i> P260	Batch	12.3 (18.9)	0.25 (0.38)	0.30 (0.46)	[26]
	Inedible dough	<i>Clostridium beijerinckii</i> NCIMB 8052	Batch	9.3 (14.4)	0.24 (0.37)	0.16 (0.24)	[27]
	Breading	<i>Clostridium beijerinckii</i> NCIMB 8052	Batch	10.5 (14.8)	0.26 (0.36)	0.14 (0.20)	[27]
	Batter liquid	<i>Clostridium beijerinckii</i> NCIMB 8052	Batch	10.0 (15.1)	0.25 (0.37)	0.21 (0.31)	[27]

*The data within brackets refers to ABE (acetone + n-butanol + ethanol).

Table 2: Yield of chemical building blocks on food waste*

Metabolite	Maximum theoretical yield on glucose (mol/mol)	Maximum theoretical yield on dry FW (g/kg)
Acetic acid	3.0	331.2
Ethanol	2.0	169.3
Lactic acid	2.0	331.2
Pyruvic acid	2.4	388.6
1,3-propanediol	1.5	210.0
3-hydroxypropionic acid	2.0	331.2
2,3-butanediol	1.1	182.2
Succinic acid	1.7	369.4
Fumaric acid	2.0	427.2
Malic acid	2.0	493.5
n-Butanol	1.0	136.2
Citric acid	1.3	470.1

*The calculations have been made using sugars concentration from FW hydrolysate reported in Pleissner et al. [14].

Figures

Figure 1

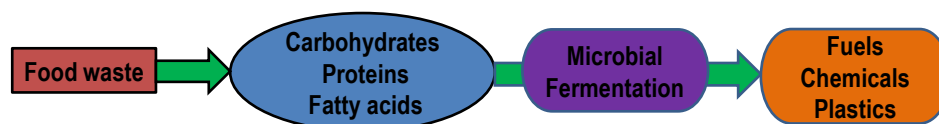
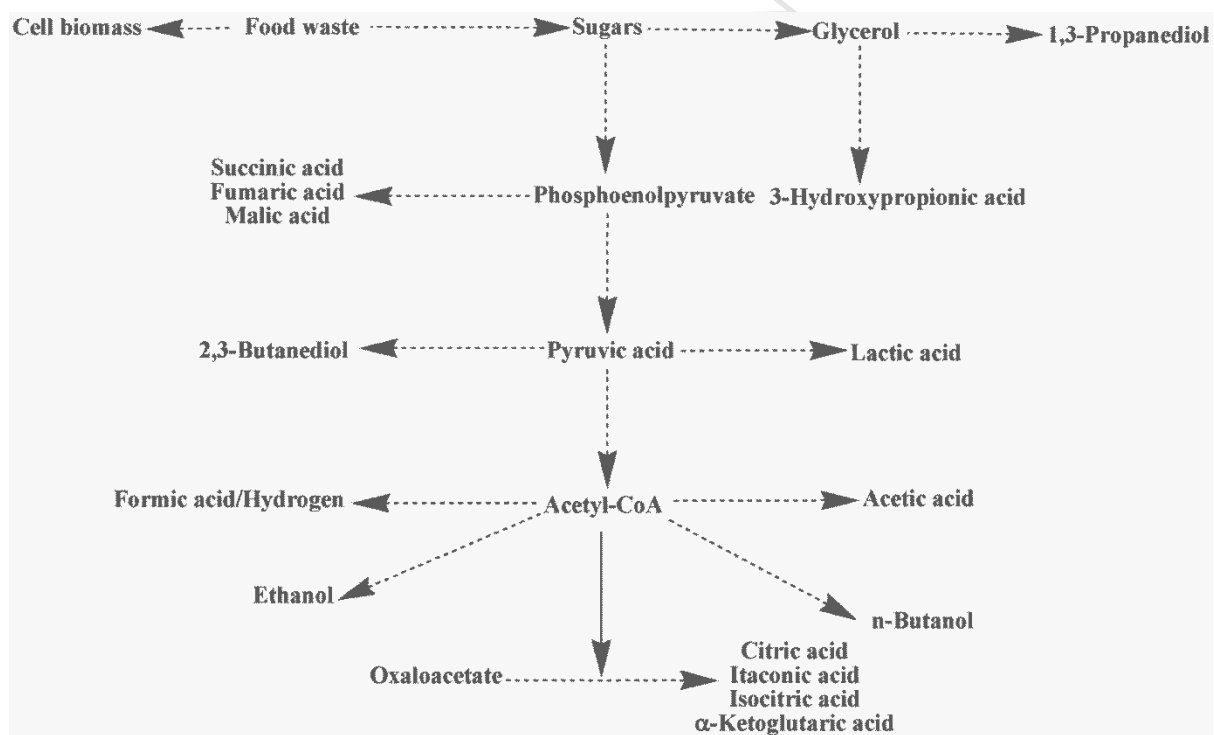


Figure 2



Recycling of food waste into chemical building blocks

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