Enzyme production from food wastes using a biorefinery concept: a review

Esra Uckun Kiran[a], Antoine P. Trzcinski[a], Wun Jern Ng[a,b] and Yu Liu[a, b]*

[a] Advanced Environmental Biotechnology Centre, Nanyang Environment & Water Research Institute, Nanyang Technological University (NTU), Singapore, 637141, Singapore

[b] School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore.

*Corresponding author.

Email: CYLiu@ntu.edu.sg

Tel: +65 67905254.

Fax: +65 6790 6813.

ABSTRACT

According to FAO, one third of food produced globally for human consumption (nearly 1.3 billion tonnes) is lost along the food supply chain. In many countries food waste are currently landfilled or incinerated together with other combustible municipal wastes for possible recovery of energy. However, these two approaches are facing more and more economic and environmental stresses. Due to its organic- and nutrient-rich composition, theoretically food waste can be utilized as a useful resource for the production of enzymes through various fermentation processes. Such conversion of food waste is potentially more profitable than its conversion to animal feed or transportation fuel. Food waste valorisation has therefore gained interest, with value added bio-products such as methane, hydrogen, ethanol, enzymes, organic acids, chemicals, and fuels. The aim of this review is to provide information on the food waste situation with emphasis on Asia-Pacific countries and the state-of-the-art food waste processing technologies to produce enzymes.

1. Introduction

Food waste (FW) is organic waste produced in food processing plants, domestic and commercial kitchens, cafeterias, and restaurants. It accounts for a considerable proportion of municipal solid waste all over the world [1]. According to FAO [2], nearly 1.3 billion tonnes of foods including fresh vegetables, fruits, meat, bakery and dairy products are lost along the food supply chain.

The amount of FW is continuing to increase due to the increase in population and economical growth, particularly in Asian countries. The annual amount of urban FW in Asian countries could rise from 278 to 416 million tonnes from 2005 to 2025 [3]. The highest absolute amount per year was in China (82.8 Million tonnes (MT) followed by Indonesia (30.9 MT), Japan (16.4 MT), Philippines (12 MT) and Vietnam (11.5 MT). However, the highest amount of FW produced per capita was in New Zealand and Australia with 280 kg/year, while it was around 120-130 kg in Southeast Asia other than Cambodia (173 kg/year). Although the absolute amount of food waste in China is the highest, the waste production per capita is the lowest (61 kg/year), while the waste production per capita is 120 and 168 kg/year in Singapore and Hong Kong, respectively [4, 5], showing that food wastage seems more prevalent in high-income states.

Food wastes can be practically dumped, landfilled, incinerated, composted, digested anaerobically and/or used as animal feed. In many Asian countries FW is still dumped with other household waste in landfills or dumpsites (Figure 1). Unfortunately, the capacity of the landfills is mostly surpassed due to a lack of waste management planning, so the environmental pollution (leachate, gas, odors, flies, vermin, and pathogens) poses serious problems [6]. Hence, there is a need for an appropriate management of FWs [7].

In order to reduce its volume, FW is traditionally incinerated with other combustible municipal wastes for generation of heat or energy, particularly in Japan and Singapore. It is generally favoured over landfilling with regard to overall energy use and emissions of gases contributing to global warming[8].However, it is an inappropriate approach for most low-income countries due to the high capital and operating costs [6]. Moreover, incineration of FW can potentially cause air pollution [9].

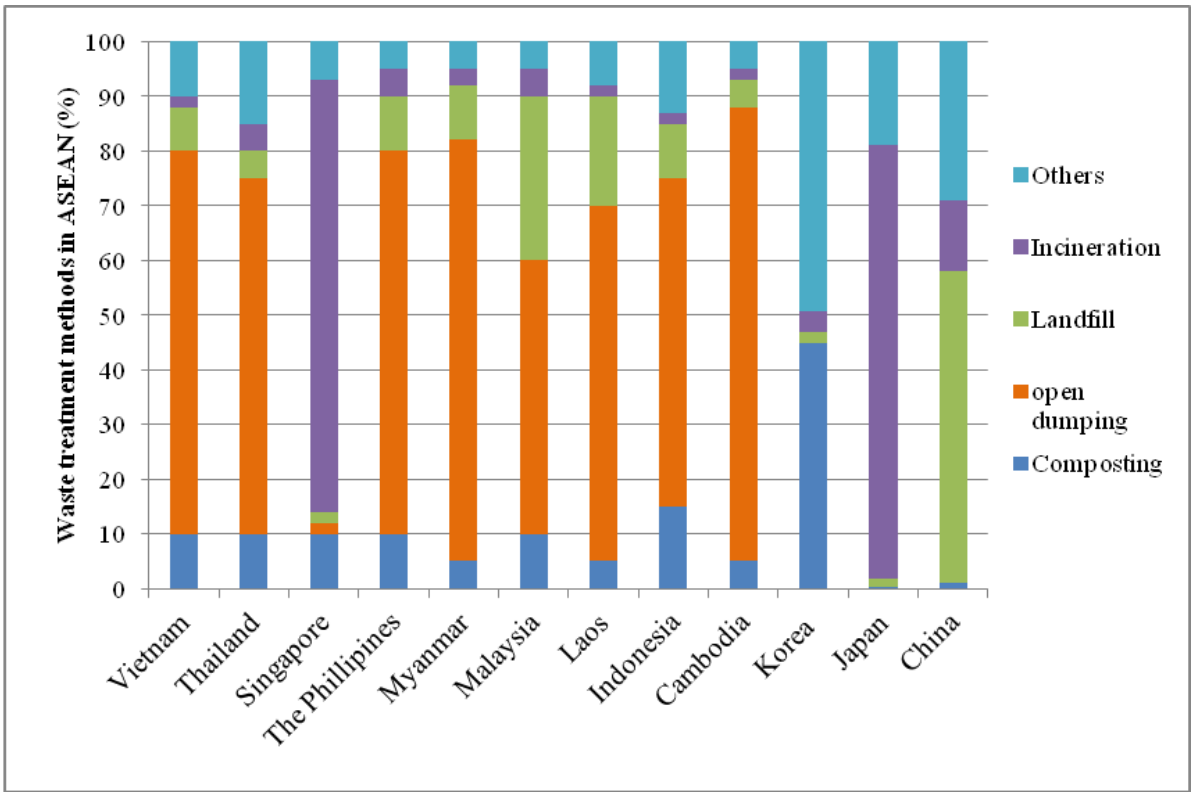

Figure 1. Waste treatment methods in some Asia-Pacific countries.

Another approach to handle biodegradable FW is composting which results in a valuable soil conditioner and fertilizer [10]. Composting facilities showed a relatively low environmental impact and a high economic efficiency compared to other treatment methods. The primary recycling method in Korea is composting (Figure 1). However, the high moisture content of FW causes remarkable levels of leachate which affects process performance by reducing

oxygen availability and weakening the pile strength [11]. In this case, high airflows for aeration or excessive carbon ingredients are necessary for process control, which increase the operational costs. Indeed, compost is more expensive than commercial fertilizers and the available market for compost is not big [12].

Anaerobic digestion is another alternative which yields methane and carbon dioxide as metabolic end products and therefore could be feasible from an economic and environmental point of view because methane is used as an energy source [8]. Hirai, Murata [13] evaluated the environmental impacts of FW treatment and found that utilising a methane fermentation process prior to incineration reduces approximately 70 kg CO_2eq/tonne waste of the global warming potential, due to the substitution effect. The disadvantages of using FW as animal feed are the variable composition and the high moisture content, which favors microbial contamination [14]. To prevent this, animal feed is generally dried but greenhouse gas emission increases depending on the energy usage during the drying process, which is related to the water content of FW [9].

FW is mainly composed of carbohydrate polymers (starch, cellulose and hemicelluloses), lignin, proteins, lipids, organic acids (Table 1). Total sugar and protein contents in FW are in the range of 35.5-69% and 3.9-21.9%, respectively. Due to its inherent chemical complexity, alternative treatment methods are currently studied and attention is being directed to production of high value-added products such as biofuels, biodiesel, platform chemicals and enzymes [15-23]. As a comparison, fuel applications ($200-400/ ton biomass) and organic acids, biodegradable plastics & enzymes applications ($1000/ton biomass) are usually creating more value compared to generating electricity ($60-150/ton biomass) and animal feed ($70-200/ton biomass) [24].

97

98 **TabTable 1.** Characteristics of mixed food waste.

Origin	pH	Moisture	Total solid	VS/TS	Total sugar	Starch	Cellulose	Lipid	Protein	Ash	References
Dining hall	NR	79.5	20.5	95.0	NR	NR	NR	NR	21.9	NR	Han and Shin [15]
Cafeteria	5.1	84.1	15.9	15.2	NR	NR	NR	NR	NR	NR	Kim, Oh [25]
Cafeteria	5.1	80.0	20.0	93.6	NR	NR	NR	NR	NR	1.3	Kwon and Lee [26]
MSW	NR	85.0	15.0	88.5	NR	NR	15.5	8.5	6.9	11.5	Rao and Singh [27]
Cafeteria	4.6-5	79.1	20.9	93.2	NR	NR	NR	NR	NR	NR	Ramos, Buitron [28]
Cafeteria	NR	75.9	24.1	NR	42.3	29.3	NR	NR	3.9	1.3	Ohkouchi and Inoue [29]
NR	NR	87.6	12.4	89.3	NR	NR	NR	NR	NR	NR	Kim, Oh [30]
Residents	4.9	80.8	19.2	92.7	NR	15.6	NR	NR	NR	NR	Pan, Zhang [21]
Dining hall	NR	80.3	19.7	95.4	59.8	NR	1.6	15.7	21.8	1.9	Tang, Koike [31]
Dining hall	NR	82.8	17.2	89.1	62.7	46.1	2.3	18.1	15.6	NR	Wang, Ma [32]
Restaurant	3.9	80.0	20.0	95.0	70.0	NR	NR	10.0	13.0	NR	Zhang, He [33]
Dining hall	5.6	82.8	17.2	85.0	62.7	46.1	2.3	18.1	15.6	NR	Ma, Wang [34]
Cafeteria	NR	61.3	38.7	NR	69.0	NR	NR	6.4	4.4	1.2	Uncu and Cekmecelioglu [35]
Food court	NR	64.4	35.6	NR	NR	NR	NR	8.8	4.5	1.8	Cekmecelioglu and Uncu [36]
Canteen	NR	81.7	18.3	87.5	35.5	NR	NR	24.1	14.4	NR	He, Sun [23]
Restaurant	NR	81.5	18.5	94.1	55.0	24.0	16.9	14.0	16.9	5.9	Vavouraki, Angelis [22]
Restaurant	NR	81.9	14.3	98.2	48.3	42.3	NR	NR	17.8	NR	Zhang and Jahng [37]

99 Total Solid, Total sugar, Starch, Cellulose, Lipid, Protein and Ash Contents were given in wt% on the basis of dry weight. Volatile solid contents were given as the
100 %VS ratio on total solid basis. NR: not reported.

101

102 The critical stage of biomass bioconversion is saccharification, which hampers its
103 commercial use. For an efficient biomass conversion, carbohydrate components of FW
104 should be hydrolyzed to yield high concentrations of oligosaccharides and monosaccharides,
105 which are amenable to fermentation. Hence, there is an increasing interest on the production
106 of biomass saccharifying enzymes, mainly amylases and cellulases [38].

107

Commercial enzyme utilization increases the operational cost due to the purchase of these enzymes on a regular basis. In addition, commercial enzymes are generally sold singly. Therefore, mixtures of enzymes would have to be prepared from separate sources. Each commercial enzyme requires different operating conditions for the hydrolysis of their specific substrates. Therefore, the process would either operate sub-optimally with a mix or take a long time to carry out each enzyme step sequentially. However, the cost of enzyme production could be reduced either by using low-cost raw materials and/or developing economical processing technologies. There are remarkable amount of publications on the lab-scale production of various industrial enzymes such as proteases, amylases, lignocellulosic enzymes and lipases using different types of FW. Therefore, this review summarizes and discusses recent industrial enzyme production studies from FW.

2. Enzyme Production

Enzymes are commonly used in many industrial applications due to their great selectivity for the substrates and their biodegradabilities. Besides they act under mild and environmentally friendly conditions. Hence, enzyme production is one of the most important applications, which serves to various industries. Research is continuing on the production of different enzymes in solid-state fermentation (SSF) with the ultimate aims to obtain high activity enzymes at lesser cost using low cost substrates and/or by improving economical processing technologies. There are remarkable amount of publications on the production of various enzymes using different agro-industrial waste [39-42]. However, the main problem is the recalcitrant nature, which resulted in low enzyme yields and expensive enzyme production. The recalcitrant nature can be mitigated by some pre-treatment steps while the enzyme yields can be enhanced by developing suitable fermentation conditions or by using genetically modified microbial strains [43]. On the other hand, the enzyme production costs can be

reduced by developing suitable fermentation processes using FW, which has easily digestible components. There are some publications reporting the production of different enzymes from FW by using both solid and submerged fermentation systems (Tables 2 to 6). Various kinds of FWs were used to produce different enzymes such as proteases, cellulases, amylases, lipases and pectinases particularly by using solid-state fermentation (SSF). SSF has several advantages over submerged fermentation (SmF) as it requires less capital, lower energy, a simple fermentation medium; it has superior productivity and produces less wastewater [44]. Moreover, an easy control of bacterial contamination and lower costs of downstream processing make it more attractive. Dos Santos, Gomes [45] have evaluated SSFs efficiency for producing enzymes. It is appropriate for the production of enzymes, especially because of the higher enzyme yields that can be obtained compared to submerged fermentation [46-48]. SSF provides a similar environment to the microorganism's natural environment which provides better conditions for its growth and enzymes production [48] . However, there are only a few reports on SSF bioreactor design in the literature. The large scale production of enzymes using SSF is challenging because pH, temperature, aeration, oxygen transfer and moisture content is difficult to control [44, 49].

2.1. Amylases

The amylase family has two major classes, namely α-amylase (EC 3.2.1.1) and glucoamylase (GA) (EC 3.2.1.3). α-amylase hydrolyses starch into maltose, glucose and maltotriose by cleaving the 1,4-α-D-glucosidic linkages between adjacent glucose units in the linear amylose chain [51] while glucoamylase hydrolyses the non-reducing ends of amylose and amylopectin to glucose [52]. Amylases have been widely used in the food, fermentation, textiles and paper industries [51]. They are also used for the pre-treatment of the agroindustrial and organic by-products to improve the bioproduct yield in subsequent processes. Thereby, there is an

158 increasing interest on the production of amylases using cheap feedstocks [49]. High activity
159 amylases can be produced from various kinds of FWs such as kitchen refuse [49], potato peel
160 [47, 53], coffee waste [54] and tomato pomace [55] via the optimization of fermentation
161 using different microbial strains. However, it is not easy to compare the efficiency of the
162 processes as the produced enzymes' activities are defined differently (Table 2). The main
163 advantages of FW utilization for enzyme production are that fermentations do not require
164 harsh pre-treatments and extra nutrient supplements.
165
166 **Table 2.** Amylase production from food wastes.

Residual materials	**Microorganism**	**Pretreatment method**	**Fermentation mode & vessel type**	**Fermentation conditions**	**Duration** (day)	**Achievements**
Potato peel	*Bacillus subtilis*	Dried, ground, sieved	SSF-250 mL flasks	40ºC, pH 7, 65% MC, 10% (v/w) inoculum	2	α-amylase (600 U
Potato peel	*Bacillus licheniformis*	Dried, ground, sieved	SSF-250 mL flasks	40ºC, pH 7, 70% MC, 10% (v/w) inoculum	2	α-amylase (270 U
Coffee waste	*Neurospora crassa* CFR 308	Ground, steamed	SSF-250 mL flasks	28ºC, pH 4.6, 60% MC, 1 mm PS, 10^7 spores/g ds,	5	α-amylase (6342
Potato peel	*Bacillus firmus* CAS 7	Dried, ground, sieved	SmF-250 mL flasks	35ºC, pH 7.5, 1% S	2	α-amylase (676 U
Tomato pomace	*Aspergillus awamori*	Dried, milled, sieved	SSF-plate-type SSF bioreactor	28ºC, pH 5	5	α-amylase (10.9 I
Bread waste	*Bacillus caldolyticus DSM 405*	NR	SmF- 1L flask with 100 ml working vol	30ºC, pH 7	1	α-amylase (6.7 U/
Pea pulp	*Bacillus caldolyticus DSM 405*	None	SmF- flasks	70ºC, 150 rpm	6	α-amylase (8.6 U/m
Food waste	*Aspergillus niger* UV-60	None	SmF-250 mL flasks	30ºC, pH 5, 120 rpm, 5% I/S	4	GA (137 U/mL)
Bread waste	*Aspergillus oryzae*	None	SSF-petri plates	30ºC, MC:1.8 (w/w, db), PS:20 mm, 10^6spore/gdS	6	GA (114 U/gdS)

S: substrate, SSF: solid state fermentation, SmF: submerged fermentation, I/S: Inoculum to substrate ratio, ds: dry substrate, MC: moisture content, PS: particle size, ds: dry solid, GA: glucoamylase

Wang, Wang [49] investigated the production of glucoamylase from FW by *Aspergillus niger* UV-60 using SmF. They reported that the nutrient supplementation including yeast extract, $(NH_4)_2SO_4$, KH_2PO_4, $MgSO_4.7H_2O$, $FeSO_4.7H_2O$ and $CaCl_2$ and particle size reduction had no significant influence on the glucoamylase production. Maximum glucoamylase activity of 137 U/mL was obtained using 3.75% FW and 5% (v/w, 10^6 spores/mL) inoculum at 30°C, 120 rpm for 96h. A reducing sugar concentration of 60.1 g/L could be produced from 10% FW (w/v), within 125 min using the produced crude glucoamylase. Shukla and Kar [47] produced high activity α-amylase from potato peels by SSF using two thermophilic isolates of *Bacillus licheniformis* and *Bacillus subtilis*. Under optimal conditions (40°C, pH 7, using potato peels having 1000 µm particle size with 65-70% moisture content). Alpha-amylase activities obtained by using *B. licheniformis* and *B. subtilis* were 270 and 600 U/mL, respectively. In another study, α-amylase production from potato peels was conducted by SmF using thermophilic isolate of alkaline tolerant *Bacillus firmus* CAS7 strain [53]. Under the optimal conditions (at 35°C, pH 7.5 using 1% of substrate concentrations), 676 U/mL of α-amylase which was optimally active at 50°C and pH 9 was obtained. Murthy, Madhava Naidu(check the references style) [54] used coffee wastes as sole carbon source for the synthesis of α-amylase in SSF using a fungal strain of *Neurospora crassa* CFR 308. α-amylase activity of 4324 U/g dry substrate was obtained using 1 mm particle size, 10^7 spores/g dry substrate, 60% moisture content at 28°C, pH 4.6. Steam pre-treatment improved the accessibility of coffee waste and the α-amylase activity of 6342 U/g dry substrate was obtained.

FW can be used to produce high activity amylases by using suitable microbial strains. In some of the lactic acid production studies from FW, a saccharification step using commercial amylases was conducted prior to the fermentation in order to improve and ease the

fermentation process [59, 60]. If the enzyme production step can be integrated to the fermentation system, the process costs could be lowered. In a study of Leung, Cheung [61], waste bread was used as sole feedstock in a biorefinery concept for the production of succinic acid (SA), one of the future platform chemicals of a sustainable chemical industry. Waste bread was used in the SSF of *Aspergillus awamori* and *Aspergillus oryzae* to produce enzyme complexes rich in amylolytic and proteolytic enzymes. The resulting fermentation solids were added directly to a bread suspension to generate a hydrolysate rich in glucose and free amino nitrogen. The bread hydrolyzate was used as the sole feedstock for *A. succinogenes* fermentations, which led to the production of 47.3 g/L succinic acid with 1.16 g SA/g glucose yield, which is the highest succinic acid yield compared from other FW-derived media reported to date. This consolidated process could be potentially utilised to transform no-value FW into succinic acid.

2.2. Lignocellulolytic enzymes

Lignocellulolytic enzymes are mainly produced by several fungi and are composed of cellulases, xylanases and ligninases, which degrade the lignocellulosic materials. Cellulases have many applications in various industries including food, animal feed, brewing and wine making, agriculture, biomass refining, pulp and paper, textile, and laundry [62]. The bioconversion of cellulose to fermentable sugars requires the synergistic action of complete cellulase system comprising of three enzyme classes: endoglucanases (EC 3.2.1.4) which act randomly on soluble and insoluble cellulose chains, exoglucanases (cellobiohydrolases; EC 3.2.1.91) which liberate cellobiose from the reducing and non-reducing ends of cellulose chains, and β-glucosidases (EC 3.2.1.21) which liberate glucose from cellobiose [63]. Xylanases have many applications in food, feed, pulp and paper, brewing, wine making and textile industries with or without concomitant use of cellulases [64]. The hydrolysis of xylans

mainly requires the action of endo-β-1,4-xylanase and β-xylosidase. However, the presence of other accessory enzymes is needed to hydrolyse substituted xylans [65]. Lignin is an undesirable polymer for biofuel production as it prevents the accessibility of plant derived polysaccharides. However, lignin derived materials can be used to develop valuable products such as dispersants, detergents, drilling mud thinner, surfactants, coagulants and flocculants (for sewage and waste water treatment), adhesives, graft polymers including polyurethanes, polyesters, polyamines and epoxies and rubbers [66, 67]. In order to degrade lignin polymers ligninolytic enzyme systems composed by laccases, lignin peroxidases and Mn-peroxidase are utilized.

These enzymes are also used for the pre-treatment of the agroindustrial and organic by-products to improve the bioproduct yields in subsequent processes [68, 69]. Recent studies on lignocellulosic enzyme production using different FWs and the achieved enzyme activities are summarized in Table 3. Since the enzyme activity definitions are different in each study, it is not an easy task to compare the achievements and detect the best method. However, generally fungal SSF is the most preferred method due to its advantages over SmF [68-73]. Krishna [71] reported that the total cellulase production from banana waste was 12 fold higher in SSF than that obtained using SmF. However, Díaz, de Ory [74] reported that the SmF resulted in higher xylanase production in comparison to SSF due to better aeration. Umsza-Guez, Díaz [55] demonstrated a clear positive effect of aeration on xylanase and carboxymethyl cellulase (CMCase) production using SSF in a plate-type bioreactor.

Table 3. Lignocellulosic enzyme production from food wastes.

Residual materials	**Microorganism**	**Pretreatment method**	**Fermentation mode & vessel type**	**Fermentation conditions**	**Duration** (day)	**Achievements**
Banana wastes	*Bacillus subtilis* (CBTK106)	Dried, ground, acid and alkali pretreatment	SSF-250 mL flasks	35°C, pH 7, 400 µm PS, 70% MC, 15% (v/w) I/S ratio	3	FPAse (2.8 IU/ds) (9.6 IU/g ds), Cel IU/g ds)

Grape pomace	*Aspergillus awamori*	Dried, milled, sieved	SSF- petri dishes	30ºC, 10 g S, 5×10^5 I/S, 60% MC	7	Xylanase (40.4 IU Cellulase (9.6IU/g
Apple pomace	*Trichoderma sp.*	Dried, crushed, sieved	SSF-250 mL flasks	32ºC, 70% MC, 10^8 spores/flask	6	Cellulase (5.8 U/g
Banana peel	*Trichoderma viride* GIM 3.0010	Dried, crushed, sieved	SSF-250 mL flasks	30°C, 65% MC, 10^9 spores/flask	6	FPA(5.6U/g ds), C U/g ds), β-glucosi ds)
Tomato pomace	*Aspergillus awamori*	Dried, milled, sieved	SSF-plate-type SSF bioreactor	28ºC, pH 5	5	Xylanase (195.9 I CMCase (19.7 IU
Carrot, orange, pineapple, potato peels, wheat bran	*Aspergillus niger* NS-2	Acid/base pretreatment	SSF-250 mL flasks	30ºC, pH 7, 1:1.5 to 1:1.75 S/M ratio	4	CMCase (310 U/g U/gds), β-glucosid U/gds) using alka wheat bran
Apple pomace	*Aspergillus niger* NRRL-567	Drying, crushing, sieving	SSF-500 mL flasks	30ºC, 1.7-2 mm PS, 75% MC, 10^7 spores/g dS	7	FPase (113.7 IU/g (172.31 IU/gds), β (60.1IU/gds), Xyl IU/gds)
Grape pomace and orange peel	*Aspergillus awamori*	Dried, milled and sieved	SSF-petri dishes	30ºC, pH 5, 70% MC, 4.5×10^8 spores/g S.	15	Exo-PG (3.8 IU/g (32.7 IU/gds), Ce IU/gds)
Potato peel	*Aspergillus niger*	Dried, ground	SSF	30ºC, 10^7 spores/ g dS, 50% MC	3	FPase (0.015 U/m (0.023 U/mL), Xy U/mL)
Mango Peel	*Trichoderma reesei*	Alkaline pretreatment	SmF-250mL flasks	30ºC, pH 7, 200 rpm	6	Cellulase (7.8 IU/
Passion fruit waste	*Pleurotus pulmonarius*	Dried, milled.	SSF-250 mL flasks	28ºC in complete darkness	14	MnP (0.22 U/mL) (4.76 U/mL), β-G (2.96 U/mL), β-ga (6.21 U/mL)
Passion fruit waste	*Macrocybe titans*	Dried, milled.	SSF-250 mL flasks	28°C in complete darkness	14	Laccase (10.2 U/m (1.72 U/mL), End (0.27 U/mL)

S: substrate, SSF: solid state fermentation, SmF: submerged fermentation, I/S: Inoculum to substrate ratio, DS: dry substrate, S/M: substrate to moisture ratio, MC: moisture content, PS: particle size, ds: dry solid,PG: polygalacturonase, CMCase: carboxymethylcellulase, MnP: Manganese peroxidise, NR: Not reported.

The effects of process parameters such as incubation temperature, pH, moisture content, particle size of the substrates, nutrient supplementation, inoculum size and different substrate pre-treatment methods on enzyme production have been investigated. In general, the optimum conditions in SSF depend not only on the microorganism employed, but also greatly on the type of substrate. The incubation time, pH, temperature, particle sizes and water content of the medium should be optimized when the substrate and microorganisms are chosen. Some FWs require extra nutrients [55, 70, 72], while some others can be used as sole

nutrient to produce high titers of cellulases [68, 73, 75]. Dhillon, Kaura [70] analysed the effects of different inducers on cellulase and hemicellulase production by *Aspergillus niger* NRRL-567 using apple pomace as a substrate. The higher filter paper cellulase (FPA) and β-glucosidase activities of 133.68 ± 5.44 IU/gram dry substrate (gds) and 60.09 ± 3.43 IU/gds, respectively were observed while using $CuSO_4$ and veratryl alcohol. Similarly, higher xylanase activity of 1412.58 ± 27.9 IU/gds was observed with veratryl alcohol after 72 h of fermentation time while the higher CMCase activity of 172.31 ± 14.21 IU/g ds was obtained with lactose after 48 h of incubation period. Sun, Ge [72] have also reported that the cellulase production using SSF was markedly improved by supplementing lactose and corn-steep solid to the apple pomace.

The effects of nutrients and other process parameters on cellulase production from banana waste by *Bacillus subtilis* (CBTK 106) was also evaluated by Krishna [71]. The optimal FPAse of 2.8 IU/g dry substrate, CMCase activity of 9.6 IU/g dry substrate and cellobiase activity of 4.5 IU/g dry substrate were obtained at 72 h incubation with media containing heat pretreated banana fruit stalk, $(NH_4)_2SO_4$, $NaNO_3$ and glucose. Saravanan, Muthuvelayudham [69] investigated the cellulase production from mango peel using *Trichoderma reesei* and reported that avicel, soybean cake flour, KH_2PO_4, and $CoCl_2{\cdot}6H_2O$ have positive influences on cellulase production. Cellulase activity was to 7.8 IU/mL using the optimum nutrient concentrations of 25.3 g/L avicel, 23.53 g/L soybean cake flour, 4.9 g/L KH_2PO_4 and 0.95 g/L $CoCl_2$ $6H_2O$ which was determined by response surface methodology.

Díaz, de Ory [74] reported that the cellulase production was inhibited at high concentration of reducing sugars when grape pomace was used as substrate. They avoided this problem by adjusting the nutrients composition of grape pomace by supplementing orange peel, which is

a pectin, cellulose and hemicellulose rich substrate inducing cellulase production. The synthesis of xylanase and cellullase increased using the mixed type substrate compared to whole grape pomace. Umsza-Guez, Díaz [55] have reported that the xylanase production from tomato wastes using SSF system is activated by Mg^{2+}, but strongly inhibited by Hg^{2+} and Cu^{2+}.

The effects of substrate pre-treatments on cellulase and xylanase production have been studied [69, 71]. Bansal, Tewari [68] studied the effects of acid and base pre-treatment on cellulase production from different FWs including carrot peelings, orange peelings, pineapple peelings, potato peelings and wheat bran using SSF. The pretreated substrates are well suited for the organism's growth, producing high titers of cellulases after 96 h without the supplementation of additional nutritional sources. Yields of cellulases were higher in alkali treated substrates compared to acid treated and untreated substrates except in wheat bran. Of all the substrates tested, untreated wheat bran induced the maximum production of enzyme components followed by alkali treated composite kitchen waste and potato peelings. Krishna [71] investigated the effects of acid, alkaline and heat pre-treatment on cellulase production from banana waste using *Bacillus subtilis*. Although cellulase production was not affected by alkali or acid treatment, it increased by 6.84 fold using pressure-cooking under controlled pH. Pressure cooking of plant materials at a controlled pH could result in greater substrate accessibility for microbial growth. Moreover, it did not result in the formation of monosaccharide degradation products, such as furfural and hydroxymethyl furfural, which otherwise inhibit the cellulases [77].

Besides cellulases and xylanases, ligninases were also produced from FWs by white rot fungi. Zilly, dos Santos Bazanella [76] studied the oxidative and hydrolytic enzymes

303 production by SSF of yellow passion fruit waste using white-rot fungi *Pleurotus ostreatus*,
304 *Pleurotus pulmonarius*, *Macrocybe titans*, *Ganoderma lucidum*, and *Grifola frondosa*. Under
305 the conditions used, the main enzymes produced by the fungi were laccases, pectinases, and
306 aryl-β-D-glycosidases (β-glucosidases, β-xylosidases, and β-galactosidases). The yellow
307 passion fruit waste was as good as wheat bran, which is the most commonly used substrate
308 for white-rot fungi cultivation.
309
310 Biorefineries need to develop their indigenous enzyme production processes along with their
311 existing processes as commercial enzyme production systems are still expensive to
312 incorporate in biorefineries [78]. As can be seen from the studies above, some strains are
313 producing different lignocellulosic enzymes from food wastes simultaneously. These enzyme
314 cocktails can be used to hydrolyse biomass effectively at low cost for their conversion to
315 biofuels, platform chemicals and biodegradable films. To further improve the hydrolysis,
316 different strains can be used to produce enzyme solutions with different hydrolytic acivities.
317 Besides, some engineered strains can be used to improve the saccharification yield.
318 **2.3 Pectinolytic enzymes**
319 Pectinolytic enzymes, i.e. pectinases degrade pectin polymers in a sequential and synergic
320 way, by depolymerisation and deesterification reactions. Complete degradation of pectin
321 requires endo- and exo-acting polygalacturonases and pectin- and pectate lyases as well as
322 enzymes that cleave the rhamnogalacturonan chain, the rhamnogalacturonases [79].
323 Pectinases are widely used in food industry particularly for juice and wine production and
324 many other conventional industrial processes, such as textile, plant fiber processing, tea,
325 coffee, oil extraction, treatment of industrial wastewater [46, 80, 81]. The production of
326 pectinases is mainly conducted via fungal SSF particularly by using *Aspergillus* strains [79].
327 For industrial implementation, pectinases can be produced from pectin-containing wastes,

such as citrus and orange wastes [82-84], apple pomace [85, 86], grape pomace [75] and many other fruit residues [87] without any harsh pre-treatment owing to the nature of these substrates and the low moisture content [80, 87]. Hours, Voget [86] investigated the pectinase production from apple pomace by SSF using *Aspergillus foetidus*. The medium composition, temperature and type of apple pomace used affected the enzyme production. After 36h culture at 30^{o}C with organic nitrogen supplemented apple pomace medium, an enzyme activity of 1,300 U/g was obtained (Table 4).

Table 4. Pectinolytic enzyme production from food wastes.

Residual materials	**Microorganism**	**Pretreatment method**	**Fermentation mode & vessel type**	**Fermentation conditions**	**Duration** (day)	**Achievements**
Apple pomace	*Aspergillus foetidus* NRRL 341	None	SSF- petri dishes	30^{o}C, pH 4, 10^3 I/S	2	Pectinase (1300 U
Citrus waste	*Aspergillus foetidus* NRRL 341	None	SSF- petri dishes	30^{o}C	2	Pectinase (1641 U
Apple pomace	*Aspergillus niger*	None	SSF- 15L horizontal solid state stirred tank reactor	35^{o}C	3	900 AJDA U/mL
Grape pomace	*Aspergillus awamori*	Milled, sieved	SSF- petri dishes	30^{o}C, 60% MC	1	Exo-PG(40U/g S) U/g S)
Orange bagasse	*Botryosphaeria rhodina MAMB-05*	Dried, ground	SSF-125 mL flask	28^{o}C	6	Pectinase (32 U/m Laccase (46 U/mL
Orange waste	*Aspergillus giganteus* CCT3232	NR	SmF-Flask	30^{o}C, pH 6, 120 rpm, 1.10^7 spores/mL	3.5	Exo-PG (48.5 U/m
Fruit residues (apple, lemon peel, grape skin & tamarind kernel)	*Aspergillus flavipes FP-500*	Dried, milled, sieved	SmF-Flask	37^{o}C, pH 3.5-5.5, 150 rpm, 1.10^6 spores/mL	3	Endopectinase (6 Pectinlyase (5 U/m Exopectinase (4.8 Rhamno-galacturo U/mL)
Fruit residues (apple, lemon peel, grape skin & tamarind kernel)	*A. terreus FP-370*	Dried, milled, sieved	SmF-Flask	37^{o}C, pH 3.5-5.5, 150 rpm, 1.10^6 spores/mL	3	Endopectinase (3 Pectinlyase (33 U Exopectinase (4.8 Rhamno-galacturo U/mL)
Tomato pomace	*Aspergillus awamori*	Dried, milled, sieved	SSF-plate-type SSF bioreactor	28^{o}C, pH 5	5	Exo-PG (36.2 IU/

Lemon peel pomace	*Aspergillus niger* Aa-20	Dried, ground	SSF- column-tray bioreactor	30ºC, 70% MC, 194 mL/min AFR, 2–0.7 mm PS	4	Pectinase (2.18 U
Passion fruit waste	*Macrocybe titans*	Dried, milled.	SSF-250 mL flasks	28°C in complete darkness	14	Pectinase (1.72 U
Orange peel	*Aspergillus niger* URM5162	Dried, ground	Fixed bed bioreactor	25ºC, 3.105 spores/mL	7	Endo-PG (1.18 U/ Exo-PG (4.11 U/r

S: substrate, SSF: solid state fermentation, SmF: submerged fermentation, I/S: Inoculum to substrate ratio, AFR: air flow rate, DS: dry substrate, MC: moisture content, PS: particle size, ds: dry solid, PG: polygalacturonase, CMCase: carboxymethylcellulase, NR: Not reported.

In another study, pectinolytic enzyme production from citrus waste was studied using *Aspergillus foetidus* for SSF [83]. Yeast extract and mineral salt addition improved the activity up to 1,600-1,700 U/g after 36 h of culture. Berovic and Ostroversnik [85] reported that the pectolytic enzyme production from apple pomace using SSF with *Aspergillus niger* was induced and/or improved by supplementing the media with other cheap nutrients such as soya flour, wheat bran, wheat corn and whey. They also mentioned that the highest activity was obtained using 38% moisture content and moisture content is very important in enzyme production. Whereas, Ruiz, Rodriguez-Jasso [46] reported that the 70% moisture content gave the highest pectinase activity using lemon peel pomace. Botella, Diaz [80] evaluated the feasibility of grape pomace for the production of exo-polygalacturonase by *Aspergillus awamori* in SSF fermentation. The particle size of the substrate did not influence the enzyme production like it was reported by Hours, Voget [86] while the addition of extra carbon sources and the initial moisture content of the grape pomace were found to have a marked influence on the enzymes yields. In another study, Giese, Dekker [84] carried out the production of pectinases from orange waste by *Botryosphaeria rhodina* MAMB-05 using both SSF and SmF with and without adding nutrients. Orange bagasse with a solid concentration of 16% (w/v) provided good microbial growth and the highest pectinase titre (32 U/mL) was obtained using SSF without adding extra nutrients.

Aeration is another important parameter affecting the pectinase production. Umsza-Guez, Díaz [55] reported that the forced aeration has negative effects on exo-PG synthesis, reducing to half of its activity in multi-layer packed bead reactor. MacIel, Ottoni [89] obtained the maximum endo- and exo-PG activities of 1.18 U/mL and 4.11 U/mL, respectively, using the reactors without aeration. A system without aeration is advantageous since it is easier to implement and economical.

The pH value of the medium can also affect the pectinase production. Martínez Sabajanes, Yáñez [87] investigated the effect of different substrates (apple, lemon peel, grape skin & tamarind kernel) and fungi (*Aspergillus flavipes* FP-500 and *Aspergillus terreus* FP-370) on the production of pectinases. The highest activities were obtained using lemon peel. In both strains, acidic pH values and high carbon source concentration favoured exopectinase and endopectinase production, while higher pH values and low carbon source concentration promoted pectin lyase and rhamnogalacturonase production.

In summary, fruit wastes are superior substrates to produce high titers of pectinolytic enzymes using either SSF or SmF. Process parameters including medium pH, temperature, composition, inoculum size, moisture content and particle size of the substrate and aeration highly depend on the utilized substrate and microbial strain. Statistical experimental designs can be employed to optimize the fermentation conditions by evaluating the effects and interactions of the different parameters that rule a biochemical system.

There is no industrial scale FW biorefinery facility currently in operation. However, there are some studies reporting the technical advances and engineering challenges of orange and lemon waste biorefineries [90, 91]. Direct utilization of citrus peel as animal feed is the

simplest option, requiring little infrastructure or investment, while increasing the value of the waste material significantly [91]. However, citrus peel contains many high value compounds such as pectin and D-limonene [92]. Pectin is frequently used in food processing, while D-limonene is an important essential oil for cosmetics, foods and pharmaceutical industries. D-limonene can be extracted using suitable solvents. The biomass left over after limonene extraction, mainly consists of pectin and lignocellulose, is an excellent source for pectinolytic and lignocelluloytic enzyme production and for the growth of microorganisms to generate high value products such as industrial enzymes, ethanol, methane and single cell proteins. Moreover, the residual biomass i.e. lignin can be used as an energy source.

2.4. Proteases

Proteases are also one of the most important commercial enzyme groups because of their wide range use in food, pharmaceutical, detergent, dairy and leather industries [39, 41, 93, 94]. Some fungal strains such as *Aspergillus, Penicillium* and *Rhizopus* and bacteria of genus *Bacillus* have been reported as the active producers of proteases [39, 57, 95]. Although the protease production from agro-industrial wastes has been studied in detail using both SSF and SmF, the investigations on the utilization of FWs has not been comprehensive. The studies reporting protease production from several FWs are listed in Table 5. Khosravi-Darani, Falahatpishe [95] used a newly isolated alkalophilic *Bacillus* sp. in SmF of date wastes without any pre-treatment. High activity protease production (57420 APU/mL) was obtained at pH 10, 37^{o}C and the enzyme was reported to be thermostable, indicating its possible utilization in industrial applications. Afify, Abd El-Ghany [96] investigated the production of proteases from potato waste in a submerged system using *S. cerevisiae* and studied the utilization of remained solid waste as a biofertilizer for plant development. The highest enzyme activity (360 U/mg) was obtained using a fermentation medium containing 15 g

potato waste, at initial pH 6.0, 20°C for 72 h. There are some studies reporting the production of high activity proteases using fishmeal and shrimp wastes. In a study of Gupta, Prasad [93], fishmeal from sardine and pink perch were evaluated as a sole carbon and nitrogen sources in the medium for alkaline protease production by *Bacillus pumilus* MTCC 7514. The protease obtained in medium containing only fish meal (4,914 U/mL) was nearly two times higher than that using basal medium (2,646 U/mL). The protease production was enhanced to 6,966 U/mL and 7,047 U/mL when scaled up from flask to 3.7 and 20 L fermenters, respectively, using fish meal as the sole source (10 g/L). The crude protease was found to have dehairing ability in leather processing, which is bound to have great environmental benefits in leather industry. In another study, a powder was prepared from shrimp wastes and tested as growth substrate for the production of protease by *P. aeruginosa* MN7 [97]. *P. aeruginosa* MN7 was found to grow and over-produce proteolytic enzymes (15,000 U/mL) in media containing only SWP as microbial growth substrate. Although there are few reports on protease production from FW, the appreciable protease activities obtained on different FW residues highlighted the potential of these wastes.

Besides its potential utilization in many industrial applications, proteases produced from FW can be also used for biorefining different biomasses. Koutinas, Malbranque [98] evaluated an oat-based biorefinery for the production of lactic acid as well as other value-added by-products, such as β-glucan and antioxidant-rich oil bodies using *Rhizopus oryzae*. During the process, *Rhizopus oryzae* produced a range of enzymes (glucoamylase, protease, phosphatase) during the hydrolysis of complex macromolecules in oat. The utilization of waste biomass and in-situ produced enzyme cocktails in such a biorefining strategy could lead to significant operating cost reduction as compared to current industrial practices for lactic acid production from pure glucose achieved by bacterial fermentations.

435 **Table 5.** Protease production from food wastes.

Residual materials	Microorganism	Pretreatment method	Fermentation mode & vessel type	Fermentation conditions	Duration (day)	Achievements	References
Date waste	*Bacillus sp*. 2-5	Heat treatment & filtration	SmF-125 mL flask	37°C, pH 10, 125 rpm	2	57420 APU/mL	[95]
Potato waste	*Saccharomyces cerevisiae*	NR	SmF- 250 ml flask	28°C	5	360 U/mg	[96]
Fish meal	*Bacillus pumilus* MTCC 7514	None	SmF-20L bioreactor	30°C, pH 7.5	2	7.05 U/mL	[93]
Waste bread	*Aspergillus oryzae*	None	SSF-petri plates	30°C, MC:1.8 (w/w, db), PS:20 mm, 10^6 spore/gdS	6	83.2 U/gdS	[58]
Cuttlefish by-products	*Vibrio parahaemolyticus*	Heat treatment, pressing, grinding, drying at 80°C o/n, powdering	SmF- 250 mL flasks	37°C, pH 8.7, 200 rpm	1	2487 U/mL	[99]
Shrimp waste	*Pseudomonas aeruginosa MN7*	Heat pretreatment (100°C, 20 min), drying, grinding	SmF- 250 mL flasks	37°C, 200 rpm	<1	15000 U/mL	[97]

436 SmF: submerged fermentation, SSF: solid state fermentation, MC: moisture content, PS: particle size, S: substrate, o/n: overnight, NR: Not reported.

2.5. Lipases

After proteases and carbohydrases, lipases (EC 3.1.1.3) are considered as the third largest group based on total sales volumes [100]. They are widely used for several applications in food, detergent, cosmetics, organic synthesis and pharmaceutical industries. They are catalysing the hydrolysis of triacylglycerols to di- and mono- acylglycerols, fatty acids and glycerol [42, 101, 102]. They are also able to catalyze alcoholysis, acidolysis,aminolysis, esterification and transesterification under certain conditions [103]. Phospholipases are a sub class of lipases that catalyse the hydrolysis of one or more ester and phosphodiester bonds of glycerophospholipids. They vary in site of action on phospholipid which can be used for the modification/production of new phospholipids for some applications in oil refinery, health, food manufacturing, dairy and cosmetics industries [104].

Most of the research has been concentrated on high activity extracellular lipase production by using both SmF and SSF via a wide variety of microorganisms including bacteria, fungi, yeast and Actinomyces [42, 102, 105, 106]. Several strains of commercial lipase producing fungi are quite dominant, including *Rhizopus, Rhizomucor, Aspergillus, Geotrichum, Yarrowia* and *Penicillium* species [107]. Recently, the production of lipase investigated by several researchers using different FWs as substrates [101] or by supplementing FWs as inducer [108, 109]. Alkan, Baysal [101] investigated the production of lipase from melon waste by SSF using *Bacillus coagulans.* The highest lipase production (78.1 U/g) was achieved after 24 h of cultivation with 1% olive oil enrichment at 37ºC and pH 7.0 by supplementing sodium dodecyl sulphate (Table 6). The best results were obtained by supplementing starch and maltose (148.9 and 141.6 U/g, respectively), whereas a rather low enzyme activity was found in cultures grown on glucose and galactose (approximately 118.8 and 123.6 U/g, respectively). Enzyme was inhibited by Mn^{2+} and Ni^{2+} by 68% and 74%,

462 respectively. By contrast, Ca^{2+} enhanced enzyme production by 5%. In a study of
463 Dominguez, Deive [108] investigated the biodegradation of waste cooking oil and its
464 application as an inducer in lipase production by *Yarrowia lipolytica* CECT 1240. The
465 addition of waste cooking oil to the medium led to a significant augmentation in extracellular
466 lipase production by yeast, compared to oil-free cultures. Papanikolaou, Dimou [109]
467 explored the effects of different *Aspergillus* and *Penicillium* strains on lipid accumulation and
468 lipase production using the waste cooking oil as substrate. In carbon-limited medium, the
469 highest amount of biomass (18 g/L) with a lipid content of 64% was obtain using *Aspergillus*
470 *sp*. ATHUM 3482, while the highest extracellular lipase activity (645 U/mL) was obtained by
471 *Aspergillus niger* NRRL 363. The studies above have indicated the possibility of FWs
472 utilization either as substrates or inducers for lipase production. Lipase production can be
473 further improved using mutant or engineered strains.
474
475 Lipases are also used for biodiesel production from crude oil and fats [112] either in free or
476 immobilized form. Lipase production processes from FW can be integrated in a biodiesel
477 biorefining process to decrease the transesterification cost. Besides lipases, phospholipases
478 are used for oil degumming and improving the efficiency of fatty acid yields [113]. Although
479 there is no report on phospholipase production using FWs, a process for the production of
480 various types of phospholipases from FWs can be developed using suitable strains.
481
482

Table 6. Lipase production from food wastes.

Substrate	Microorganism	Pretreatment method	Fermentation mode & vessel type	Fermentation conditions	Duration (day)	Achievements	References
Banana waste, melon waste, watermelon waste	*Bacillus coagulans*	None	SSF-Flasks	37ºC, pH 7	1	148.9 U/g S from melon waste	[101]
Waste cooking oil	*Y.lipolytica* CECT 1240	None	SmF- 5L stirred tank bioreactor with 3L working vol, fb	30ºC, 400 rpm	6	0.93U/mL	[108]
Waste cooking olive oil	*Aspergillus* and *Penicillium* strains	Filtration	SmF-250 mL flasks	28ºC, pH 6, 200 rpm	3	645 U/ mL	[109]
Olive oil cake	*Y.lipolytica* NRLL Y-1095	Alkaline pretreatment (3% NaOH) 20ºC o/n	SSF-150 mL Erlenmeyer flasks	30ºC, pH 7, 55% MC	4	40IU/g S	[114]
Tri-substrate (wheat bran, wheat rawa and coconut oil cake)	*A.niger* MTCC2594	None	SSF-3*1kg tray type bioreactor	30ºC, 60% MC	4	745.7 IU/gdS	[115]
Seafood processing waste	*Bacillus altitudinis*	Drying (80ºC o/n)	SSF-Flasks	50ºC, pH 8, 80% MC	3	2U/gdS (Esterase)	[116]
Tuna by-products	*Rhizopus oryzae*	Heat pretreatment (100ºC 20 min) and filtration	SmF- 1L flasks	30ºC, pH 6, 150 rpm	3	23.5 IU/mL	[117]
Wheat bran with 2% olive oil	*Aspergillus flavus*	None	SSF-Flasks	29ºC, pH 7, 65% MC	4	121.4 U/gdS	[118]
Wheat bran with 2% olive oil	*Aspergillus niger* J1	None	SmF- 500 mL flasks	30ºC, pH 6, 100 rpm	8	1.46 U/mL	[119]
Wheat bran with 2% olive oil	*Aspergillus niger* J1	None	SSF- flasks	30ºC, pH 6, 65% MC	7	1.46 U/mL	[119]

S: substrate, ds: dry substrate, SSF: solid state fermentation, SmF: submerged fermentation, fb: fed-batch, *Y. lipolytica:Yarrowia lipolytica*, MC: moisture content, o/n:overnight.

3. Conclusions

The management of FWs has posed a serious economic and environmental concern. The publications discussed above indicated that a wide range of high titres industrial enzymes can be produced from various FWs The produced enzymes can be used for some industrial applications. Moreover, these enzyme production processes can be consolidated with other value-added product development processes to create FW biorefineries.

So far, all developed biorefinery processes for the conversion of FW into ethanol and other value-added products have only been achieved at bench-top and pilot levels. There is no industrial scale FW biorefinery facility currently in operation. Therefore, it is not possible to conduct an economical analysis for the proposed biorefinery systems. However, considering the cost of defined medium preparation in current commercial enzyme processes, the utilization of low or no cost waste biomass for biorefining could lead to significant reductions in operating costs. However, difficulties and costs associated with the collection/transportation of FW should also be taken into account. Optimization and scale up studies need to be carried out in order to exploit for large-scale applications.

ACKNOWLEDGEMENTS

We would like to thank the National Environment Agency (NEA, Singapore) for financial support of this research (Grant no: ETRP 1201 105).

REFERENCES

1. Lundqvist, J., C. de Fraiture, and D. Molden, *Saving water: From field to fork – curbing losses and wastage in the food chain*, in *SIWI Policy Brief*. 2008, Stockholm International Water Institute Stockholm, Sweden.

2. FAO, *Towards the future we want: End hunger and make the transition to sustainable agricultural and food systems*. 2012, Food and agriculture organization of the United Nations Rome.
3. Melikoglu, M., C.S.K. Lin, and C. Webb, *Analysing global food waste problem: pinpointing the facts and estimating the energy content.* Cent. Eur. J. Eng. , 2013. **3**(2): p. 157-164.
4. National-Environment-Agency. *http://app2.nea.gov.sg/topics_wastestats.aspx*. 2011 [cited 2013 3 February].
5. Lin, C.S.K., et al., *Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective.* Energy and Environmental Science, 2013. **6**(2): p. 426-464.
6. Ngoc, U.N. and H. Schnitzer, *Sustainable solutions for solid waste management in Southeast Asian countries.* Waste Management, 2009. **29**: p. 1982–1995.
7. Ma, H., et al., *The utilization of acid-tolerant bacteria on ethanol production from kitchen garbage.* Renewable Energy 2009. **34**(6): p. 1466–1470.
8. Othman, S.N., et al., *Review on life cycle assessment of integrated solid waste management in some Asian countries.* Journal of Cleaner Production, 2013. **41**: p. 251-262.
9. Takata, M., et al., *The effects of recycling loops in food waste management in Japan: Based on the environmental and economic evaluation of food recycling.* Science of the Total Environment, 2012. **432**: p. 309-317.
10. Gajalakshmi, S. and S.A. Abbasi, *Solid waste management by composting: State of the art.* Critical Reviews in Environmental Science and Technology, 2008. **38**(5): p. 311-400.
11. Cekmecelioglu, D., et al., *Applicability of optimized in-vessel food waste composting for windrow systems.* Biosystems Engineering, 2005. **91**: p. 479-486.
12. Aye, L. and E.R. Widjaya, *Environmental and economic analysis of waste disposal options for traditional markets in Indonesia.* Waste Management, 2006. **26**: p. 1180-1191.
13. Hirai, Y., et al., *Life cycle assessment on food waste management and recycling.* Waste Manag Res, 2001. **12**(5): p. 219-228.
14. Esteban, M.B., et al., *Evaluation of fruit, vegetable and fish wastes as alternative feedstuffs in pig diets.* Waste Management, 2007. **27**: p. 193-200.
15. Han, S.K. and H.S. Shin, *Biohydrogen production by anaerobic fermentation of food waste.* International Journal of Hydrogen Energy 2004. **29**(6): p. 569 – 577.
16. Sakai, K. and Y. Ezaki, *Open L-lactic acid fermentation of food refuse using thermophilic Bacillus coagulans and fluorescence in situ hybridization analysis of microflora.* Journal of Bioscience and Bioengineering, 2006. **101**(6): p. 457-463.
17. Yang, S.Y., et al., *Lactic acid fermentation of food waste for swine feed.* Bioresource Technology, 2006. **97**(15): p. 1858–1864.
18. Zhang, C., et al., *The anaerobic co-digestion of food waste and cattle manure.* Bioresource technology, 2013. **129**: p. 170-176.
19. Zhang, M., et al., *Improved bioethanol production through simultaneous saccharification and fermentation of lignocellulosic agricultural wastes by Kluyveromyces marxianus 6556.* World J. Microbiol. Biotechnol. , 2010. **26**(6): p. 1041-1046.
20. He, Y., et al., *Recent advances in membrane technologies for biorefining and bioenergy production.* Biotechnology advances, 2012. **30**(4): p. 817-858.
21. Pan, J., et al., *Effect of food to microorganism ratio on biohydrogen production from food waste via anaerobic fermentation.* International Journal of Hydrogen Energy, 2008. **33**(23): p. 6968-6975.
22. Vavouraki, A.I., E.M. Angelis, and M. Kornaros, *Optimization of thermo-chemical hydrolysis of kitchen wastes.* Waste Management, 2014. **34**(1): p. 167-173.
23. He, M., et al., *Influence of temperature on hydrolysis acidification of food waste* Procedia Environmental Sciences, 2012. **16**: p. 85-94.

24. Sanders, J., et al., *Bio-refinery as the bio-inspired process to bulk chemicals.* Macromolecular Bioscience, 2007. **7**(2): p. 105-117.
25. Kim, J.K., et al., *Statistical optimization of enzymatic saccharification and ethanol fermentation using food waste.* Process Biochemistry, 2008. **43**(11): p. 1308-1312.
26. Kwon, S.H. and D.H. Lee, *Evaluation of Korean food waste composting with fed-batch operations I: using water extractable total organic carbon contents (TOCw)* Process Biochemistry 2004. **39**(10): p. 1183–1194.
27. Rao, M.S. and S.P. Singh, *Bioenergy conversion studies of organic fraction of MSW: kinetic studies and gas yield–organic loading relationships for process optimisation.* Bioresource Technology 2004. **95**(2): p. 173–185.
28. Ramos, C., et al., *Effect of the initial total solids concentration and initial pH on the bio-hydrogen production from cafeteria food waste.* International Journal of Hydrogen Energy, 2012. **37**(18): p. 13288-13295.
29. Ohkouchi, Y. and Y. Inoue, *Direct production of L(+)-lactic acid from starch and food wastes using Lactobacillus manihotivorans LMG18011.* Bioresource Technology, 2006. **97**: p. 1554–1562.
30. Kim, J.K., et al., *Effects of temperature and hydraulic retention time on anaerobic digestion of food waste.* Journal of Bioscience and Bioengineering, 2006. **102**(4): p. 328-332.
31. Tang, Y.Q., et al., *Ethanol production from kitchen waste using the flocculating yeast Saccharomyces cerevisiae strain KF-7.* Biomass and Bioenergy 2008. **32** (11): p. 1037–1045.
32. Wang, Q., et al., *Ethanol production from kitchen garbage using response surface methodology.* Biochemical Engineering Journal, 2008. **39**(3): p. 604-610.
33. Zhang, B., et al., *Anaerobic digestion of kitchen wastes in a single-phased anaerobic sequencing batch reactor (ASBR) with gas-phased absorb of CO2.* Journal of Environmental Sciences, 2005. **17**(2): p. 249-255.
34. Ma, H., et al., *Optimization of the medium and process parameters for ethanol production from kitchen garbage by Zymomonas mobilis.* International Journal of Green Energy 2008. **5**(6): p. 480-490.
35. Uncu, O.N. and D. Cekmecelioglu, *Cost-effective approach to ethanol production and optimization by response surface methodology.* Waste Management, 2011. **31**(4): p. 636-643.
36. Cekmecelioglu, D. and O.N. Uncu, *Kinetic modeling of enzymatic hydrolysis of pretreated kitchen wastes for enhancing bioethanol production* Waste Management 2013. **33**(3): p. 735-739.
37. Zhang, L. and D. Jahng, *Long-term anaerobic digestion of food waste stabilized by trace elements.* Waste Management, 2012. **32**(8): p. 1509-1515.
38. Teeri, T.T., *Crystalline cellulose degradation: new insight into the function of cellobiohydrolases.* Trends in Biotechnology, 1997. **15**: p. 160-167.
39. Chutmanop, J., et al., *Protease production by Aspergillus oryzae in solid-state fermentation using agroindustrial substrates.* Journal of Chemical Technology and Biotechnology, 2008. **83**(7): p. 1012-1018.
40. De Castro, A.M., et al., *Valorization of residual agroindustrial cakes by fungal production of multienzyme complexes and their use in cold hydrolysis of raw starch.* Waste and Biomass Valorization, 2011. **2**(3): p. 291-302.
41. Prakasham, R.S., et al., *Alkaline protease production by an isolated Bacillus circulans under solid-state fermentation using agroindustrial waste: Process parameters optimization.* Biotechnology progress, 2005. **21**(5): p. 1380-1388.
42. Vaseghi, Z., et al., *Production of active lipase by Rhizopus oryzae from sugarcane bagasse: Solid state fermentation in a tray bioreactor.* International Journal of Food Science and Technology, 2013. **48**(2): p. 283-289.

43. Pandey, A., et al., *Biotechnological potential of agro-industrial residues. I: Sugarcane bagasse.* Bioresour Technol, 2000. **74**(1): p. 69-80.
44. Couto, S.R. and M.A. Sanromán, *Application of solid-state fermentation to food industry-A review.* Journal of Food Engineering, 2006. **76**(3): p. 291-302.
45. Dos Santos, T.C., et al., *Optimisation of solid state fermentation of potato peel for the production of cellulolytic enzymes.* Food Chemistry 2012. **133**: p. 1299–1304.
46. Ruiz, H.A., et al., *Pectinase production from lemon peel pomace as support and carbon source in solid state fermentation column-tray bioreactor.* Biochemical Engineering Journal, 2012. **65**: p. 90-95
47. Shukla, J. and R. Kar, *Potato peel as a solid state substrate for thermostable alpha amylase production by thermophilic Bacillus isolates.* World Journal of Microbiology & Biotechnology 2006. **22**(5): p. 417–422.
48. Thomas, L., C. Larroche, and A. Pandey, *Current developments in solid-state fermentation.* Biochemical Engineering Journal, 2013. **81**: p. 146-161.
49. Wang, Q., et al., *Glucoamylase production from food waste by Aspergillus niger under submerged fermentation.* Process Biochemistry 2008. **43**(3): p. 280–286.
50. Kawa-Rygielska, J., W. Pietrzak, and A. Czubaszek, *Characterization of fermentation of waste wheat-rye bread mashes with the addition of complex enzymatic preparations.* Biomass Bioenergy 2012. **44**: p. 17-22.
51. Pandey, A., et al., *Advances in microbial amylases.* Biotechnology and Applied Biochemistry, 2000. **31**(2): p. 135-152.
52. Anto, H., U.B. Trivedi, and K.C. Patel, *Glucoamylase production by solid-state fermentation using rice flake manufacturing waste products as substrate.* Bioresour Technol, 2006. **97**(10): p. 1161-1166.
53. Elayaraja, S., et al., *Thermostable alpha-amylase production by Bacillus firmus CAS 7 using potato peel as a substrate.* African Journal of Biotechnology 2011. **10**(54): p. 11235-11238.
54. Murthy, P.S., M. Madhava Naidu, and P. Srinivas, *Production of α-amylase under solid-state fermentation utilizing coffee waste.* Journal of Chemical Technology Biotechnology 2009. **84**(8): p. 1246–1249.
55. Umsza-Guez, M.A., et al., *Xylanase production by Aspergillus awamori under solid state fermentation conditions on tomato pomace.* Brazilian Journal of Microbiology, 2011. **42**(4): p. 1585-1597.
56. Jamrath, T., et al., *Amylase and protease production by B. caldolyticus.* Food technology and biotechnology, 2012. **50**(3): p. 355–361.
57. Jamrath, T., et al., *Production of amylases and proteases by Bacillus caldolyticus from food industry wastes.* Food Technology and Biotechnology 2012. **50**(3): p. 355-361.
58. Melikoglu, M., C.S.K. Lin, and C. Webb, *Stepwise optimisation of enzyme production in solid state fermentation of waste bread pieces.* Food and Bioproducts Processing, 2013. **91**(4): p. 638-646.
59. Kim, K.I., et al., *Production of lactic acid from food wastes.* Applied Biochemistry and Biotechnology - Part A Enzyme Engineering and Biotechnology, 2003. **107**(105-108): p. 637-647.
60. Sakai, K., et al., *Making plastics from garbage: A novel process for poly-L-lactate production from municipal food waste.* Journal of Industrial Ecology, 2004. **7**(3-4): p. 63-74.
61. Leung, C.C.J., et al., *Utilisation of waste bread for fermentative succinic acid production.* Biochemical Engineering Journal, 2012. **65**: p. 10-15.
62. Kuhad, R.C., R. Gupta, and A. Singh, *Microbial cellulases and their industrial applications.* Enzyme Research, 2011. **2011**(1): p. 10.
63. Jørgensen, H., J.B. Kristensen, and C. Felby, *Enzymatic conversion of lignocellulose into fermentable sugars: challenges and opportunities.* Biofuels Bioproducts Biorefinery, 2007. **1**(2): p. 119–134.

64. Khandeparkar, R.D.S. and N.B. Bhosle, *Isolation, purification and characterization of the xylanase produced by Arthrobacter sp. MTCC 5214 when grown in solid-state fermentation.* Enzyme and Microbial Technology, 2006. **39**(4): p. 732-742.
65. Uçkun Kiran, E., O. Akpinar, and U. Bakir, *Improvement of enzymatic xylooligosaccharides production by the co-utilization of xylans from different origins.* Food and Bioproducts Processing, 2013. **91**(4): p. 565-574.
66. Effendi, A., H. Gerhauser, and A.V. Bridgwater, *Production of renewable phenolic resins by thermochemical conversion of biomass: A review.* Renewable and Sustainable Energy Reviews, 2008 **12**(8): p. 2092-2116.
67. Menon, V. and M. Rao, *Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept.* Progress in Energy and Combustion Science, 2012. **38**(4): p. 522-550.
68. Bansal, N., et al., *Production of cellulases from Aspergillus niger NS-2 in solid state fermentation on agricultural and kitchen waste residues.* Waste Management 2012. **32**(7): p. 1341–1346.
69. Saravanan, P., R. Muthuvelayudham, and T. Viruthagiri, *Application of statistical design for the production of cellulase by Trichoderma reesei using mango peel.* Enzyme Research, 2012. **2012**: p. 157643-157649.
70. Dhillon, G.S., et al., *Potential of apple pomace as a solid substrate for fungal cellulase and hemicellulase bioproduction through solid-state fermentation.* Industrial Crops and Products, 2012. **38**(1): p. 6–13.
71. Krishna, C., *Production of bacterial cellulases by solid state bioprocessing of banana wastes.* Bioresource Technology 1999. **69**(3): p. 231-239.
72. Sun, H., et al., *Cellulase production by Trichoderma sp. on apple pomace under solid state fermentation.* African Journal of Biotechnology, 2010. **9**(2): p. 163-166.
73. Sun, H.Y., et al., *Banana peel: A novel substrate for cellulase production under solid-state fermentation.* African Journal of Biotechnology, 2011. **10**(77): p. 17887-17890.
74. Díaz, A.B., et al., *Enhance hydrolytic enzymes production by Aspergillus awamori on supplemented grape pomace.* Food and Bioproducts Processing 2012. **90**(1): p. 72-78.
75. Botella, C., et al., *Hydrolytic enzyme production by Aspergillus awamori on grape pomace.* Biochemical Engineering Journal, 2005. **26**(2-3): p. 100–106.
76. Zilly, A., et al., *Solid-state bioconversion of passion fruit waste by white-rot fungi for production of oxidative and hydrolytic enzymes.* Food Bioprocess Technology 2012. **5**(5): p. 1573–1580.
77. Weil, J., et al., *Cellulose pretreatments of lignocellulosic substrates.* Enzyme and Microbial Technology, 1994. **16**(11): p. 1002-1004.
78. Chandel, A.K., et al., *The realm of cellulases in biorefinery development.* Critical Reviews in Biotechnology, 2012. **32**(3): p. 187-202.
79. Kashyap, D.R., et al., *Applications of pectinases in the commercial sector: A review.* Bioresource technology, 2001. **77**(3): p. 215-227.
80. Botella, C., et al., *Xylanase and pectinase production by Aspergillus awamori on grape pomace in solid state fermentation.* Process Biochemistry 2007. **42**(1): p. 98–101.
81. Pedrolli, D.B., et al., *Pectin and pectinases: Production, characterization and industrial application of microbial pectinolytic enzymes.* Open Biotechnology Journal, 2009. **3**: p. 9-18.
82. Afifi, M.M., *Effective technological pectinase and cellulase by Saccharomyces cerevisiae utilizing food wastes for citric acid production.* Life Science Journal 2011. **8**(2): p. 405-413
83. Garzon, C.G. and R.A. Hours, *Citrus waste: An alternative substrate for pectinase production in solid-state culture.* Bioresource Technology 1992. **39**(1): p. 93-95.
84. Giese, E.C., R.F.H. Dekker, and A.M. Barbosa, *Orange bagasse as substrate for the production of pectinase and laccase by Botryosphaeria rhodina MAMB-05 in submerged and solid state fermentation.* BioResources, 2008. **3**(2): p. 335-345.

85. Berovic, M. and H. Ostroversnik, *Production of Aspergillus niger pectolytic enzymes by solid state bioprocessing of apple pomace.* Journal of Biotechnology, 1997. **53**(1): p. 47–53.
86. Hours, R.A., C.E. Voget, and R.J. Ertola, *Some Factors Affecting Pectinase Production from Apple Pomace in Solid-State Cultures.* Biological Wastes 1988. **24**(2): p. 147-157.
87. Martínez Sabajanes, M., et al., *Pectic oligosaccharides production from orange peel waste by enzymatic hydrolysis* International Journal of Food Science and Technology, 2012. **47**(4): p. 747-754.
88. Pedrolli, D.B., et al., *Studies on productivity and characterization of polygalacturonase from Aspergillus giganteus submerged culture using citrus pectin and orange waste.* Applied Biochemistry and Biotechnology, 2008. **144**(2): p. 191-200.
89. MacIel, M., et al., *Production of polygalacturonases by Aspergillus section Nigri strains in a fixed bed reactor.* Molecules, 2013. **18**(2): p. 1660-1671.
90. Rivas-Cantu, R.C., K.D. Jones, and P.L. Mills, *A citrus waste-based biorefinery as a source of renewable energy: Technical advances and analysis of engineering challenges.* Waste Management and Research, 2013. **31**(4): p. 413-420.
91. Ángel Siles López, J., Q. Li, and I.P. Thompson, *Biorefinery of waste orange peel.* Critical Reviews in Biotechnology, 2010. **30**(1): p. 63-69.
92. Lohrasbi, M., et al., *Process design and economic analysis of a citrus waste biorefinery with biofuels and limonene as products.* Bioresource Technology, 2010. **101**(19): p. 7382-7388.
93. Gupta, R.K., et al., *Scale-up of an alkaline protease from Bacillus pumilus MTCC 7514 utilizing fish meal as a sole source of nutrients.* Journal of Microbiology and Biotechnology, 2012. **22**(9): p. 1230–1236.
94. Potumarthi, R., S. Ch, and A. Jetty, *Alkaline protease production by submerged fermentation in stirred tank reactor using Bacillus licheniformis NCIM-2042: Effect of aeration and agitation regimes.* Biochemical Engineering Journal 2007. **34**(2): p. 185–192.
95. Khosravi-Darani, K., H.R. Falahatpishe, and M. Jalali, *Alkaline protease production on date waste by an alkalophilic Bacillus sp. 2-5 isolated from soil.* African Journal of Biotechnology 2008. **7**(10): p. 1536-1542.
96. Afify, M.M., T.M. Abd El-Ghany, and M.M. Alawlaqi, *Microbial utilization of potato wastes for protease production and their using as biofertilizer.* Australian Journal of Basic and Applied Sciences, 2011. **5**(7): p. 308-315.
97. Jellouli, K., et al., *Purification, biochemical and molecular characterization of a metalloprotease from Pseudomonas aeruginosa MN7 grown on shrimp wastes.* Applied Microbiology and Biotechnology, 2008. **79**(6): p. 989-999.
98. Koutinas, A.A., et al., *Development of an oat-based biorefinery for the production of L(+)-lactic acid by rhizopus oryzae and various value-added coproducts.* Journal of Agricultural and Food Chemistry 2007. **55**(5): p. 1755-1761.
99. Souissi, N., et al., *Preparation and use of media for protease-producing bacterial strains based on by-products from cuttlefish (Sepia officinalis) and wastewaters from marine-products processing factories.* Microbiological Research, 2008. **163**(4): p. 473-480.
100. Contesini, F.J., et al., *Aspergillus sp. lipase: Potential biocatalyst for industrial use.* Journal of Molecular Catalysis B: Enzymatic, 2010. **67**(3-4): p. 163-171.
101. Alkan, H., et al., *Production of lipase by a newly isolated Bacillus coagulans under solid-state fermentation using melon wastes.* Applied Biochemistry and Biotechnology 2007. **136**(2): p. 183-192.
102. Li, N.W., M.H. Zong, and H. Wu, *Highly efficient transformation of waste oil to biodiesel by immobilized lipase from Penicillium expansum.* Process Biochemistry 2009. **44**(6): p. 685–688.
103. Saxena, R.K., et al., *Purification and characterization of an alkaline thermostable lipase from Aspergillus carneus.* Process Biochemistry, 2003. **39**(2): p. 239-247.

104. Ramrakhiani, L. and S. Chand, *Recent progress on phospholipases: Different sources, assay methods, industrial potential and pathogenicity.* Appl Biochem Biotechnol, 2011. **164**: p. 991-1022.
105. Gupta, N., V. Shai, and G. R, *Alkaline lipase from a novel strain Burkholderia multivorans: Statistical medium optimization and production in a bioreactor.* Process Biochemistry, 2007. **42**(2): p. 518-526.
106. Rehman, S., et al., *Optimization of process parameters for enhanced production of lipase by Penicillium notatum using agricultural wastes.* African Journal of Biotechnology 2011. **10**(84): p. 19580-19589.
107. Colen, G., R.G. Junqueira, and T. Moraes-Santos, *Isolation and screening of alkaline lipase-producing fungi from Brazilian savanna soil.* World Journal of Microbiology and Biotechnology, 2006. **22**(8): p. 881-885.
108. Dominguez, A., et al., *Biodegradation and utilization of waste cooking oil by Yarrowia lipolytica CECT 1240.* European Journal of Lipid Science and Technology 2010. **112**(11): p. 1200–1208.
109. Papanikolaou, S., et al., *Biotechnological conversion of waste cooking olive oil into lipid-rich biomass using Aspergillus and Penicillium strains.* Journal of Applied Microbiology 2011. **110**(5): p. 1138–1150.
110. Zhang, R., et al., *Characterization of food waste as feedstock for anaerobic digestion.* Bioresource technology, 2007. **98**(4): p. 929-935.
111. Du, G., L.X.L. Chen, and J. Yu, *High-efficiency production of bioplastics from biodegradable organic solids.* Journal of Polymers and the Environment, 2004. **12**(2): p. 89-94.
112. Bajaj, A., et al., *Biodiesel production through lipase catalyzed transesterification: An overview.* Journal of Molecular Catalysis B: Enzymatic, 2010. **62**(1): p. 9-14.
113. Dijkstra, A.J., *Enzymatic degumming.* European Journal of Lipid Science and Technology, 2010. **112**(11): p. 1178-1189.
114. Moftah, O.A.S., et al., *Adding value to the oil cake as a waste from oil processing industry: Production of lipase and protease by Candida utilis in solid state fermentation.* Applied Biochemistry and Biotechnology, 2012. **166**(2): p. 348-364.
115. Edwinoliver, N.G., et al., *Scale up of a novel tri-substrate fermentation for enhanced production of Aspergillus niger lipase for tallow hydrolysis.* Bioresource Technology, 2010. **101**: p. 6791–6796.
116. Esakkiraj, P., et al., *Solid-state production of esterase using fish processing wastes by Bacillus altitudinis AP-MSU.* Food and bioproducts processing, 2012. **90**: p. 370-376.
117. Sellami, M., et al., *Optimization of marine waste based-growth media for microbial lipase production using mixture design methodology.* Environmental Technology, 2013. **34**(15): p. 2259-2266.
118. Toscano, L., et al., *Lipase production through solid-state fermentation using agro-industrial residues as substrates and newly isolated fungal strains.* Biotechnology & Biotechnological Equipment, 2013. **27**(5): p. 4074-4077.
119. Falony, G., et al., *Production of Extracellular Lipase from Aspergillus niger by Solid-State Fermentation.* Food Technol. Biotechnol., 2006. **44**(2): p. 235-240.