Valorising agricultural residues as biorefinery feedstocks: current advancements and challenges

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Abstract

Biological pretreatment using microorganisms have been identified as a promising approach to degrade lignocellulosic structure extracellularly, thus increasing the sugar conversion rate of the agricultural biomass. They have several attractive traits such as eco-friendly and simple operation, low capital cost, low energy requirement, and no chemical requirement. Major drawbacks are long pretreatment time and strict microbial growth conditions. The direct use of ligninolytic enzymes extracted from microorganisms on lignocellulosic biomass emerges as an alternative approach to eliminate the above problems. Besides, the application of advanced biotechnologies to extract enzymes is expected to genetically enhance the lignin-degrading properties suitable for industrial practice. Advanced biotechnologies could help to reduce the current bottleneck (cost of enzyme extraction and purification) of biological pretreatments. The capability to recover and reuse enzymes from the pretreatment process can reduce the overall expenditure. Effective separation and recovery of energy products (e.g. ethanol and methane) from the conversion process will also contribute to increasing the cost-effectiveness. This chapter aims to present a succinct overview of the status of technologies for agricultural residues to produce and recover bioenergy and biochemicals from the conversion of their lignocellulosic components. It is envisioned that further technical improvements will allow agricultural residue biorefinery to become a domain sector in the sustainable harvesting of green energy and biochemicals.

Keywords: Agricultural residue; Pretreatment; Biogas; Biofuel; Anaerobic digestion; Ligninolytic enzyme

Contents

1. Introduction

Agricultural residues as alternative feedstocks for energy and biochemical production have emerged as a promising solution to social issues of fossil fuel depletion and environmental degradation (García-Torreiro et al., 2016; Ravindran et al., 2018; Vu et al., 2020). Holocelluloses (i.e. polysaccharides) are the main components of agricultural residues, which can be converted into monomer sugars (e.g. glucose) and further processed into value-added products (e.g. biofuels) (Romaní et al., 2016; Song et al., 2014). Millions of tons of agricultural wastes (e.g. plant straws, peels, skins, and bagasse) are generated annually, with most being burned or discarded improperly (Paul and Dutta, 2018; Vargas et al., 2015). This can contribute to greenhouse gas emission, air, and water pollution. Thus, effective valorisation of these abundant agricultural wastes can facilitate profitable biorefinery, reduce negative environmental impacts, eliminate food versus fuel competition and land requirement for growing new plants or food crops (GHD, 2019; Vu et al., 2020).

Biogas, liquid biofuels (i.e. bioethanol) and a range of biochemical (e.g. enzymes, biopolymers, and organic acids) are valuable commodities that can be obtained from the bioconversion of agricultural residues (Vu et al., 2020). The capability to replace fossil fuels and products with these sustainable bioenergy and biochemical will bring about tremendous socioeconomic impacts and ensure future resource security (GHD, 2019). The industrialisation of this biorefinery concept will likely create a new wave of employment opportunities, with major facilities being built and operated globally (GHD, 2019; Vu et al., 2020). However, there remain some techno-economic challenges in recovering high-quality biofuels and biochemical from biorefinery processes of agricultural residues. These challenges include high utility demand, toxicity, high operational cost, activity loss (e.g. enzyme) and physical-chemical changes (e.g. lignin) that might hinder the economic value and downstream valorisation (Kim et al., 2019; Ragauskas et al., 2014; Surra et al., 2019). Several strategies have been investigated to overcome the problems and optimise the biorefinery of agricultural residues such as using hybrid technologies for synergistic performance, employing metabolic and genetic engineering for targeted strains, and effective biomass pretreatment to enhance bioconversion efficiency (Kim et al., 2019; Saini et al., 2020).

Biological approach utilising microorganism and enzymes has emerged as an effective, simple, and environmentally friendly pretreatment technique for agricultural residues (Rouches et al., 2016; Sharma et al., 2019). Lignocellulolytic microorganisms (e.g. white-rot fungi and bacteria) produce enzymes laccase and cellulase that can depolymerise the lignocellulosic structure of agricultural wastes, thus enhancing sugar conversion to value-added products. Developments in genetic engineering have allowed industrially important enzymes (e.g. cellulase) to be isolated from microorganisms and synthesised at high enzymatic activity and broad selectivity (Chen et al., 2020; Liu and Qu, 2019). Enzyme cost is currently a bottleneck, but further progress in enzyme recycling and efficiency will enable the large-scale application of biological treatment for the biorefinery of agricultural residues.

This chapter is a review of biorefineries of agricultural residues, focusing on the current advancements and challenges in conversion and recovery of value-added products, as well as the sustainable approach to biomass treatment using microbes and enzymes. This chapter also emphasizes the strategies to enhance the bioenergy and biochemical production from agricultural residues at a reduced cost and minimal environmental impacts. These strategies are essential to facilitate the large-scale valorisation of agricultural residues.

2. Agricultural residue characteristics

Agricultural residues are available in huge volume globally (Kosinkova et al., 2017). In Canada, 69 million dry tons of agricultural crop residues are produced annually (Paul and Dutta, 2018). Spain as the fifth largest world producer of barley can accumulate up to 4.5 million tons of barley straws per year (Vargas et al., 2015). In Australia, millions of tons of agricultural wastes are also generated from the fruit and energy crop industry such as banana, pineapple, and sugarcane. The majority of this non-avoidable agricultural waste is being discarded or burned, contributing to the release of greenhouse gases (Hassan et al., 2019). It, however, is a valuable and cheap source of lignocellulosic raw material that can be utilised for second-generation biofuel production. The abundant annual production of agricultural wastes ensures a constant supply of feedstocks for commercial applications.

The main chemical building blocks of agricultural residues are lignocellulose complexes, which include cellulose (35-50 wt%), hemicellulose (20-35 wt%), and lignin (15-20 wt%) (Haghighi Mood et al., 2013). This composition is varied and influenced by the cultivation conditions, geographical location, and the type of plants (Pérez et al., 2002) (Table 1). Cellulose is the main constituent of lignocellulose complex, and currently the most promising and abundant source of renewable energy. It can be broken down into sugar monomers, which are then converted to biofuels and biochemicals through several biotechnologies. Cellulose contains linear chains of D-glucose linked to each other by β-(1,4)-glycosidic bonds. The cellulose molecules form rigid and crystallised structure of fibrils through intra- and intermolecular hydrogen bonds (Haghighi Mood et al., 2013). Cellulose fibrils are covered by hemicellulose. Hemicellulose is an amorphous and heterogenous biopolymer with low molecular weight. It consists of different monosaccharides such as pentoses (β-D-xylose, α-L-arabinose), hexoses (β-D-mannose, β-D-glucose, α-D galactose), and sugar acids (Gírio et al., 2010). Hemicellulose can be readily hydrolysed and is another major carbon source for biofuel production. It also acts as the crosslinks between cellulose fibrils and the lignin matrix. Lignin is an amorphous heteropolymer network of phenyl propane located in the plant cell walls (Hendriks and Zeeman, 2009). It provides structural support and an impermeable barrier to microbial attack and oxidative stress on plant tissues. The tough and tightly packed lignocellulose complexes are formed by the hydrophobic and covalent interactions between lignin and the carbohydrates. This recalcitrant structure hinders the hydrolysis and conversion of agricultural residues into bioproducts. This problem can be overcome by effective removal of lignin and the breakdown of hemicellulose during biomass pretreatment. This process increases enzyme accessibility to cellulose fibrils, thus enhancing the digestibility of agricultural residues in biorefinery (Irmak, 2017; Maurya et al., 2015).

Table 1: Chemical composition of various agricultural residues.

Agricultural residues	**Composition (% dry weight)^a**			**Refs**
	Cellulose	**Hemicellulose**	**Lignin**	
Corn straw	49.3	28.8	7.5	(Song et al., 2014)
Oat straw	37.1	23.3	21.29	(Romaní et al., 2016)
Rice straw	31.1	22.3	13.3	(Chen et al., 2011)
Sugarcane bagasse	43.1	31.1	11.4	(Martín et al., 2007)

Wheat straw	35.9	23.9	19.3	(Kaparaju et al., 2009)
Banana bunch stem	60 – 65	6 – 8	7.9	(Guimarães et al., 2009; Kosinkova et al., 2017)
Barley straw	35.1	26.5	19.7	(Vargas et al., 2015)
Garlic skin	46	18	26	(Moreno et al., 2020)

[a] In addition to polysaccharides and lignin, lignocellulosic biomass also contains some inert materials (< 10 wt%) (da Silva et al., 2020; Rego et al., 2019).

3. Bioenergy and biochemical production from pretreated agricultural residues

The production chain to convert agricultural residues to value-added products includes technologies that are already mature e.g. anaerobic digestion, and fermentation (Fig. 1). However, it remains necessary to improve current pretreatment and conversion methods to enhance biomass digestibility and conversion to bioproducts at an industrial level.

[FIGURE 1]

Figure 1: Production pathways to produce bioenergy and biochemical from agricultural residues.

3.1. Biogas and biofuels

Agricultural residues are decomposed in the absence of oxygen during anaerobic digestion to produce biogas, which consists of 50-70% biomethane (CH_4), 30-50% carbon dioxide and 0-3% nitrogen and hydrogen sulphide (Angelidaki et al., 2018). Raw biogas is useful for heating, cooking and electrical applications (Kapoor et al., 2020). Meanwhile, biomethane is an important fuel gas which causes 80-90% less greenhouse gas emissions compared with natural gas (Andersen et al., 2020). Rice straw, corn stover, and wheat straw are representative feedstocks for biogas production (Dell'Omo and Spena, 2020; Mustafa et al., 2016; Nguyen et al., 2019; Song et al., 2014). Their theoretical methane yield is high at 414, 415, and 426 mL CH_4/g-VS for corn stover, rice straw and wheat straw, respectively (Kaparaju et al., 2009;

Teghammar et al., 2012). However, these values have not been achieved practically due to the rigid lignocellulosic structure of agricultural residues which prevents the complete degradation of carbohydrates to biomethane (Li et al., 2016). Implementation of effective pretreatment is a strategy to increase the anaerobic digestibility of biomass, thus working towards achieving the maximum theoretical methane or biogas yield (Li et al., 2020; Mustafa et al., 2016; Schroyen et al., 2014). Co-digestion of agricultural residues with other feedstocks (e.g. sewage sludge and animal manure) to optimise the ratio of carbon and nitrogen also helps to improve methane yield (Wang et al., 2018). Germany, the United Kingdom, the United States, and China are leading countries driving the industrialisation of this sector, with a large number (10,000-100,000) of both small agricultural units and large-scale centralised plants (Carlu et al., 2019).

Liquid biofuel (e.g. ethanol and diesel) production is another major global market where agricultural residues can be exploited more effectively. The biomass is subjected sequentially to pretreatment, hydrolysis, fermentation, and distillation to produce > 99% bioethanol, a sustainable substitute to fossil fuels. The hydrolysate of processed agricultural residues can also be converted to lipid for biodiesel production using oleaginous yeasts or black soldier fry larvae (Elsayed et al., 2020; Karlsson et al., 2017; Miao et al., 2020). Extensive investigations to produce biofuels from agricultural residues have recognised that pretreatment is a necessary step to maximise the sugar yield from these feedstocks (Asgher et al., 2013; Kaparaju et al., 2009; Vargas et al., 2015; Vu et al., 2020). Biological pretreatment is particularly attracting interests due to its eco-friendliness and low generation of inhibitors (Wang et al., 2013). For example, corn stover pretreated with white-rot fungus *Irpex lacteus* increased the biomass digestibility by 103% and yielded 102 mg ethanol per g dry biomass (García-Torreiro et al., 2016). Nonetheless, biofuel production from agricultural residues has reached industrial level with several notable commercial-scale plants (GHD, 2019). The POET-DSM Advanced Biofuels plant in South Dakota, USA produces 80 ML of bioethanol annually from corn stover. The Raizen plant in Brazil produces 8 ML/year of ethanol from bagasse.

3.2. Biochemicals

The increasing demand for environmentally friendly chemicals and polymers to replace petroleum-based products has led to the production of biochemicals using agricultural residues. Important enzymes (e.g. cellulases, xylanases, and α-amylases), organic acids (e.g. acetic and lactic acids), bioactive compounds (e.g. phenylpropanoids), and biopolymers (e.g. polyhydroxyalkanoates) can be generated through the processing of agricultural residues and its primary products (i.e. bioethanol and biomethane) (Pieja et al., 2017; Ravindran et al., 2018; Rosales-Calderon and Arantes, 2019; Sindhu et al., 2016) (Fig. 1). Lignin, which constitutes up to 30% of the biomass dry weight, is in particular an important but underutilised biopolymer. Large-scale biomass biorefineries have traditionally burned lignin to generate heat and electricity (Ragauskas et al., 2014). However, lignin poses great potential for advanced applications in biochemical production (e.g. phenol, guaiacol, vanillin, ethylated kraft lignin glycols, plastics, carbon fibres, and adipic acids) (Johnston et al., 2020; Linger et al., 2014; Vardon et al., 2015). Production and recovery of biochemicals and polymers from agricultural residue processing is still under development and represents great opportunities to optimise the commercial value of agricultural residue biorefinery (Section 5).

4. Biological approach to sustainably pre-treat agricultural residues

Biological pretreatment using microorganisms and enzymes can degrade lignocellulosic structure extracellularly, thus increasing the sugar conversion rate of the agricultural residues (Sharma et al., 2019) (Fig. 2). They have several attractive traits such as eco-friendly and simple operation, low capital cost, low energy requirement, and no chemical requirement (Maurya et al., 2015; Rouches et al., 2016). Major drawbacks are long pretreatment time and strict microbial growth conditions. The extraction of lignin-degrading enzymes from microorganisms to be used directly on the biomass emerges as an alternative approach to eliminate the above problems. However, efforts in reducing the cost of enzyme production are necessary to make it a viable process.

4.1. Cellulolytic and ligninolytic microorganisms

Commonly used bacteria and filamentous fungi (e.g. ascomycetes and basidiomycetes) for biological pretreatment are found ubiquitous in soil, living plants, and lignocellulosic waste materials (Vats et al., 2013; Zabed et al., 2018). There are three classified groups of fungi including brown-rot, white-rot, and soft-rot fungi. Ligninolytic fungi (e.g. white-rot) secrete enzymes that are capable of selectively degrade lignin (Nguyen et al., 2020). Cellulolytic bacteria secrete cellulase that can hydrolyse cellulose and hemicellulose (Sharma et al., 2019). The performance of these species in pretreating agricultural residues has been extensively studied (Table 2).

Table 2: Selected examples of microorganisms capable of degrading lignin, hemicellulose, and cellulose contents of various agricultural residues (MC: moisture content)

Group	**Microorganism**	**Feedstock**	**Operation conditions**	**Effects**	**Ref.**
White-rot fungus	*Pleurotus ostreatus*	Rice straw	20 days 28 °C 75% MC	Degraded 33.4% of lignin content Methane yield increased by 120%	(Mustafa et al., 2016)
	Trametes gibbosa	Wheat straw	7 days 25 °C	Degraded 52% of lignin content in enriched medium	(Knežević et al., 2017)
	Echinodontium taxodii	Corn straw	15 days 25 °C	Degraded 29.5% of lignin content and 7.6% of cellulose Increased sugar yield by 50.7%	(Yu et al., 2010)
Soft-rot fungus	*Trichoderma reesei*	Rice straw	20 days 28 °C 75% MC	Degraded 23.6% of lignin content Methane yield increased by 78.3%	(Mustafa et al., 2016)
Brown-rot fungus	*Gloeophyllum trabeum*	Wheat straw	10 days 25 °C	Preferentially degraded 26.4% of hemicellulose; No quantifiable lignin degradation; Increased glucose yield by 26.1%	(Hermosilla et al., 2018)
Bacterium	*Cupriavidus basilensis* B-8	Acid-pretreated rice straw	3 days 30 °C	Enzymatic digestibility increased 35–70% and 173–244% compared to acid-pretreated only and raw biomass, respectively	(Yan et al., 2017)
Mixed microbes	*P. chrysosporium* *C. versicolor* *T. viride* *A. niger* *G. trabeum* *B. circulans* *P. aeruginosa* *S. badius*	Corn straw	14 days 30 °C	Degraded 44.4%, 34.9% and 39.2% of hemicellulose, cellulose and lignin, respectively; Increased the methane content by 22% in the anaerobic fermentation process	(Li et al., 2020)

White-rot fungi are particularly notable for their effective performance in pretreating lignocellulosic materials such as agricultural residues (Knežević et al., 2017; Mustafa et al., 2016; Yu et al., 2010). Some representative species are *Pleurotus* sp.*, Trametes versicolor*, *Phanerochaete chrysosporium,* and *P. chrysosporium*. Most white-rot fungi secrete lignin-degrading enzymes (e.g. laccase, lignin peroxidases, and manganese peroxidases) during their growth (Hatakka, 1994; Plácido and Capareda, 2015). By inoculating white-rot fungi with agricultural residues, these enzymes can cause the cleavage of lignin aromatic rings through oxidation processes (Chan et al., 2020). This leads to the rupture of lignocellulose complexes, liberating cellulose and hemicellulose components (Vu et al., 2020). The hydrolysis of cellulose into glucose is thus enhanced. Some white-rot fungi (e.g. *P. chrysosporium, C. subvermispora,* and *Echinodontium taxodii* 2538) produce cellulolytic enzymes which exhibit specificity for cellulose hydrolysis, thus increasing its enzymatic digestibility (Narayanaswamy et al., 2013). Cellulolytic enzymes, however, can consume polysaccharides for fungal growth and cause a considerable sugar loss (Zabed et al., 2019). An ideal fungal strain for biological pretreatment should have a selectivity value > 1.0 for lignin breakdown (i.e. the ratio of lignin loss to cellulose loss) (Kamcharoen et al., 2014; Zhang et al., 2007). Vasco-Correa and Shah (Vasco-Correa and Shah, 2019) reported a sugar production cost of $1.60/kg from corn stover pretreated with white-rot fungi. Their production capacity was 75,700 m^3 fermentable sugars per year. This value remains higher than the cost of conventional methods (e.g. acid and alkaline pretreatment), which is < $1/kg (Vasco-Correa and Shah, 2019).

Biological pretreatment requires no chemical addition and low energy demand (i.e. sustainable) but it necessitates long treatment time and sterilised conditions. The duration can be reduced by incorporating microorganisms into the seasonal biomass storage on the field (i.e. ensiling) (Vu et al., 2020). The pretreatment efficiency can be enhanced by using a combination of microorganisms instead of a single species to induce synergistic metabolic activities (Ma and Ruan, 2015; Zabed et al., 2019). Ma and Ruan (Ma and Ruan, 2015) co-cultivated *Coprinus comatus* with *Trichoderm reesei* and achieved 2.6-fold increase in laccase activity (i.e. lignin degradation) within three days compared to *C. comatus* monoculture. Microbial consortia are an approach to consolidated bioprocessing of agricultural residues i.e. simultaneous enzymatic degradation, hydrolysis, and fermentation for direct conversion to biofuels (Bayer et al., 2009; Minty et al., 2013; Zuroff et al., 2013).

4.2. Ligninolytic enzymes

Ligninolytic enzymes can be extracted from microorganisms and purified for direct applications on lignocellulosic agricultural residues (Zabed et al., 2018). This eliminates the long growing phase of microorganisms, thus significantly reducing the total pretreatment time from 15-40 days to 6-24 h (Chan et al., 2020; Hosseini Koupaie et al., 2019). Laccase, lignin peroxidase (LiP), manganese peroxidase (MnP) and versatile peroxidase (VP) are major ligninolytic enzymes that have been investigated for biomass delignification (Vu et al., 2020; Zabed et al., 2018) (Table 3). Laccase, in particular, is readily available as a commercial product from major enzyme companies such as DuPont (Wilmington, USA), Novozymes (Bagsvaerd, Denmark) and DSM (Delft, the Netherlands) (Zerva et al., 2019). Enzymatic pretreatment can be performed using an enzyme cocktail or system (i.e. a combination of several ligninolytic enzymes) to mimic the synergistic metabolic activities in nature (Asgher et al., 2013; Schroyen et al., 2015) (Table 3). The capability to screen out high-performing, stable ligninolytic enzymes from microorganisms and synthesise cost-effective enzyme systems is essential for the large-scale feasibility of this pretreatment method (Chan et al., 2020; Zabed et al., 2018).

Table 3: Selected studies of the effects of ligninolytic enzymes on agricultural residues

Enzyme (s)	**Source**	**Feedstock**	**Processing conditions**	**Effects**	**Ref(s)**
Laccase	*Trametes versicolor*	Corn stover	30 °C, 24 h Continuous shaking HBT^a as a mediator	25% increase in methane production	(Schroyen et al., 2014)
		Ensiled corn stover	40 °C, 48 h, 90 rpm HBT^a as a mediator	30% increase in cellulose conversion	(Chen et al., 2012)
	Sclerotium sp.	Steam-exploded wheat straw	1.3 MPa, 5 min 50 °C, 24 h	84% cellulose conversion	(Qiu and Chen, 2012)
	Trametes villosa	Sugar bagasse Rice husk	28 °C, 48 h, 130 rpm Tween 80 or SAB^b as mediators	10-fold increase in sugar yield	(Matei et al., 2020)
MnP	*Phanerochete chrysosporium* PC-1	Corn stover	45 °C, 48 h, 150 rpm Followed by washing	50% increase in sugar yield	(Plácido and Capareda, 2015; Wang et al., 2013)

Laccase MnP LiP	Pleurotus ostreatus IBL-02	Sugar bagasse	35 °C, 48 h Followed by washing	33.5% delignification 72% cellulose conversion	(Asgher et al., 2013)
Laccase VP	*Trametes versicolor* *Bjerkandera adusta*	Corn stover Wheat straw	30 °C, 24 h, 60 rpm Enzyme additives (HBT[a] & Tween 80)	1.5-fold increase in delignification	(Schroyen et al., 2015)

[a] 1-hydroxybenzotriazole; [b] Sodium acetate buffer

Pretreatment of agricultural residues using ligninolytic enzymes has several advantages over methods such as acid and alkaline pretreatment. This process does not require chemical additions and the enzymes are naturally sourced, thus posing minimal environmental impacts (Vu et al., 2020; Woolridge, 2014). The breakdown of lignin by ligninolytic enzymes provides cellulase with better access to exposed cellulose. It also prevents the adsorption of cellulase by lignin (i.e. more cellulase available for cellulose hydrolysis) (Binod et al., 2019). In addition, enzymes such as laccase and peroxidase are capable of selectively degrading lignin while keeping cellulose intact (Qiu and Chen, 2012; Wang et al., 2013). The HPLC analysis performed by Wang et al. (Wang et al., 2013) showed that a much lower concentration of monomer sugars and microbial inhibitors (e.g. acetic acid and furfural) was released into the medium by enzyme pretreatment compared to acid pretreatment (Wang et al., 2013). This allows enzyme-pretreated biomass to produce higher yields of sugars and ethanol than those pretreated with acid or alkali in subsequent processes (i.e. hydrolysis and fermentation) (Asgher et al., 2013; Wang et al., 2013).

4.3. Advances in enzyme production

The major bottleneck of utilising enzymes for biomass pretreatment and hydrolysis is the high production cost (Binod et al., 2019; Ravindran et al., 2018). Several strategies have been developed and adopted to reduce the cost of enzymes such as (i) improve enzyme producing abilities of microorganisms through genetic and metabolic engineering, (ii) produce multi-enzyme mixtures directly or from engineered microorganisms to synergistically treat biomass, and (iii) in-house enzyme production via solid-state fermentation (SSF) (Binod et al., 2019; Masran et al., 2016; Nguyen et al., 2020; Ravindran et al., 2018). These approaches are essential to enhance the economic feasibility of lignocellulosic biorefinery.

4.3.1. Solid-state fermentation

Agricultural residues as the substrates for SSF have emerged as the sustainable and low-cost approach to produce industrially important enzymes from microorganisms (e.g. fungi and bacteria) (Ravindran et al., 2018; Salim et al., 2017). The abundance of fermentable sugars in agricultural residues (Section 2) can be used in SSF as a carbon source to enhance microbial growth and enzyme production (Salim et al., 2017). Compared to submerged fermentation, SSF shows a much higher resemblance to microorganisms' natural growth conditions (i.e. adequate moisture content but still in solid phase) (Ravindran et al., 2018; Singhania et al., 2009). This process also possesses several advantages such as low capital cost, higher end-product concentration, and easy operation (Hölker et al., 2004). Kaur et al. (Kaur et al., 2020) reported the cost to produce 100 FPU of cellulase-hemicellulase consortium from SSF of *Aspergillus niger* with rice straw to be US $ 0.00186. Thus, SSF is favourable for microbial growth and shows higher productivity of value-added products (e.g. biopolymers and enzymes) (Salim et al., 2017; Singhania et al., 2009). Cellulase, laccases, α-amylases, and xylanases are examples of lignocellulolytic enzymes which have been produced from SSF using cultures containing agricultural residue (Fernández Núñez et al., 2017; Salim et al., 2017) (Table 4). These enzymes are highly specific, safe, and useful for applications in various industries (e.g. biofuels, pharmaceuticals and food) (Mei-Ling et al., 2020; Salim et al., 2017). Crude enzymes obtained from SSF of microorganisms can be used for enzymatic pretreatment of agricultural residues to produce biofuels at a low cost and minimal environmental impacts (Zhao et al., 2020).

Table 4: Selected examples of enzyme production from SSF of microorganisms with agricultural residues as the substrate.

Substrate	Microorganism	SSF operating conditions	Enzyme product (s)	Maximum enzyme activity (U/g substrate)	Ref. (s)
Maize straw Wheat bran	*Trichoderma viride*	25 °C 3 days	CMCase	11	(Zhao et al., 2020)
			β-glucosidase	4.9	
			Xylanase	864	
Rice straw	*Aspergillus niger* P-19	28 °C 5 days	CMCase	126	(Kaur et al., 2020)
			FPase	36	
			β-glucosidase	47	
			Xylanase	693	
			Mannanase	57	

Wheat bran	*Rhizopus oligosporus*	30 °C 6 days	α-amylase	392.5	(Fernández Núñez et al., 2017)
Wheat bran	*Pleurotus ostreatus*	29 °C 7 days	Laccase	4,610	(El-Batal et al., 2015)

Co-culture or mixed culture in SSF is a beneficial strategy to overcome the limitations of single culture fermentation (Binod et al., 2019; Lodha et al., 2020). Enzyme preparations from SSF of a single organism may be inadequate for biomass hydrolysis due to the low enzyme concentration and specific enzyme range of each organism (Binod et al., 2019). For example, *T. reesei* produces high titre of endoglucanases and cellobiohydrolases but lacks β-glucosidase which is essential for effective cellulose conversion (Binod et al., 2019). Meanwhile, *Asergillus* sp. is a fungus with high β-glucosidase content. Thus, co-culture of *T. reesei* and *Aspergillus* sp. in SSF can lead to the preparation of an enzyme system sufficient in β-glucosidase, endoglucanases, and cellobiohydrolases. The combination of these enzymes reduces cellobiose inhibition and induces a synergistic effect on the hydrolysis of lignocellulose (Gruno et al., 2004). A co-culture of *T. reesei* and *Penicillium citrinum* in SFF with wheat bran also showed high titer of enzyme expressions (i.e. 71.526, 3.268, and 50.696 IU/g of CMCase, FPase, and ß-glucosidase, respectively) (Lodha et al., 2020). SSF of microbial co-cultures using low-cost agricultural wastes is therefore a promising strategy to optimise the techno-economic viability of enzyme production for biomass conversion.

4.3.2. Genetic engineering

Advances in genetic engineering, metabolic engineering and strain improvement have allowed for a better understanding of cellular pathways, thus enhancing the techno-economic viability of lignocellulolytic enzyme production from microorganisms (Binod et al., 2019). For example, fungus *Trichoderma reesei* is a well-known hyper-producer of cellulase, an essential enzyme for the hydrolysis of cellulose into glucose (Chen et al., 2020; Kubicek et al., 2009). By engineering the transcription factors (i.e. proteins that control the process of converting DNA into messenger RNA) through gene mutation, researchers were able to regulate and optimise cellulase gene expressions in *T. reesei* strains (Derntl et al., 2013; Shida et al., 2015; Wang et al., 2019). Similarly, the deletion or mutation of transcription factors (e.g. *creA* and *creB*) in fungi *Trichoderma orientalis* and *Aspergillus oryzae* improved their cellulase, xylanase, α-amylase, and β-glucosidase activities (Ichinose et al., 2014; Ichinose et al., 2018;

Long et al., 2018). Overexpression of heterogenic accessory enzymes (e.g. cellobiohydrolase, β-xylosidase, and xylanase) in microbial hosts has also been reported to boost the saccharification efficiency (Li et al., 2017; Ye et al., 2017). This can be done through chemical mutagenesis (e.g. inserting a specific enzyme-encoding gene from *A. oryzae* into *T. reesei* to improve *T. reesei*'s lignocellulolytic enzyme expressions) (Manavalan et al., 2017). Development in DNA technology also leads to the knowledge of the complete genome sequence of important organisms (e.g. *T. reesei*) (Le Crom et al., 2009). This increases the organism's susceptibility to targeted improvement in lignocellulolytic enzyme production by genetic and metabolic engineering (Chen et al., 2020; Kubicek et al., 2009). This approach is an important strategy to reduce the cost of enzymes and increase the efficacy of enzyme treatment in large-scale biorefinery.

Attempts to optimise lignocellulolytic enzyme systems have also been made through genetic engineering. Enzyme mixtures can be supplemented or reconstituted to include exogenous components that are capable of boosting lignocellulose conversion (Liu and Qu, 2019). Lytic polysaccharide monooxygenases (LPMOs) are an example of exogenous proteins that can synergistically work with cellulolytic enzymes to improve the saccharification of agricultural residues (Agrawal et al., 2020; Eibinger et al., 2014). The addition of xylanase (e.g. an enzyme for hemicellulose hydrolysis) in a cellulase system could also increase the accessibility of cellulose to cellulases, thus enhancing the biomass hydrolysis efficiency (Kong et al., 2018; Song et al., 2016; Xiao et al., 2019). Cellic® CTec3 is a new-generation commercial enzyme from Novozymes resulted from this genetic engineering approach. Compared to the original enzyme preparations, Cellic® CTec3 contains significantly more LPMOs, arboxymethyl cellulase, cellobiohydrolase 1, BG, xylanase and β-xylosidase (Sun et al., 2015). The supplementation of these proteins and enzymes is likely to enhance the performance of Cellic® CTec3 as well as reducing the inhibition of different sugars on cellulases (Liu and Qu, 2019).

5. Current challenges in resource recovery

5.1. Biofuel recovery

Bioethanol recovery and purification steps are necessary to convert the diluted (5-20 wt. %) and impure ethanol stream obtained from the biomass fermentation broth into high concentration, fuel-grade ethanol (99.6 wt. %) (Torres-Ortega and Rong, 2016) (Fig. 2). The key challenge of bioethanol recovery arises from the azeotropic nature of ethanol-water mixture (i.e. a mixture of 95 wt. % ethanol and 5 wt. % water has a minimum boiling point of 78.2 °C, strong hydrogen bond between ethanol and water) (Huang et al., 2008; Saini et al., 2020). This characteristic causes the conventional distillation process to become expensive as high reflux ratios are required when the ethanol stream is concentrated to more than 85 wt. % (i.e. near the azeotropic point of 95 wt. %) (Huang et al., 2008). Thus, research interest has shifted towards hybrid processes involving distillation and other emerging technologies such as membrane separation and adsorption to achieve 99.6 wt. % bioethanol more efficiently (Huang et al., 2008; Saini et al., 2020). These processes possess various advantages and disadvantages (Table 5). Further research to improve the viability of these technologies and to identify suitable combinations of separation processes is essential for the large-scale application in biorefineries.

[Figure 2]

Figure 2: Biofuel production and value chain using agricultural residues as the feedstocks

Table 5: The advantages and disadvantages of ethanol recovery technologies

Process	Separation mechanisms	Advantages	Disadvantages	Ref. (s)
Conventional distillation	Different boiling points of ethanol (78.2 °C) and water	Recover up to 95 wt. % ethanol High technology readiness	Energy-intensive Expensive to achieve fuel-grade ethanol	(Saini et al., 2020)
Azeotropic distillation	Addition of a volatile entrainer to change the separation factor of azeotrope mixture	Direct purification of diluted stream to >99 wt. % ethanol	Energy-intensive High capital cost Hazardous entrainers (e.g. benzene)	(Huang et al., 2008; Saini et al., 2020)
Extractive distillation	Addition of a selective high boiling agent to increase the separation factor	Wide range of agents e.g. solvents, salts, ionic liquids, polymers, or their combinations.	High energy requirement Some agents are expensive (e.g. ionic liquids and hyper-branched polymers)	(Huang et al., 2008; Saini et al., 2020)

Membrane pervaporation	The concentration gradient between the feed and permeate side of the membrane	Energy-saving Cost-effective Environmental friendly	Membrane fouling i.e. short membrane life time High maintenance cost	(Huang et al., 2008; Saini et al., 2020; Zentou et al., 2019)
Adsorption	Molecular separation using absorbents with specific pore size and selectivity	Not energy-intensive Some absorbents are bio-based and renewable	Low separation capacity (bio-based absorbent) Absorbents can be expensive	(Huang et al., 2008; Saini et al., 2020)

Biogas upgrading into biomethane is a necessary step to broaden the scope of valorisation of individual components of biogas. Without upgrading, raw biogas utilisation is limited to low grade applications (i.e. cooking and lighting) due to carbon dioxide reducing the calorific value and transportability of biogas (Kapoor et al., 2020) (Fig. 2). By separating and upgrading the components of biogas, high quality (> 96% v/v) biomethane and carbon dioxide are obtained and employed for useful applications in transport fuels, natural gas grid, and chemical production (Kapoor et al., 2020; Lombardi and Francini, 2020) (Fig. 2). Commercial technologies for biogas upgrading include water scrubbing, chemical scrubbing, pressure swing adsorption, membrane, and cryogenic separation (Kapoor et al., 2020; Lombardi and Francini, 2020; Surra et al., 2019). Water and chemical scrubbing can simultaneously remove harmful components (e.g. hydrogen sulphide and ammonia) and recover >96% v/v biomethane (Surra et al., 2019). However, these processes are energy intensive, toxic (i.e. amine usage) and require additional equipment for dewatering, compression and pH control, thus increasing the overall cost (Surra et al., 2019; Ullah Khan et al., 2017). Membrane separation is cost effective, safe, and environmentally friendly but multiple membrane steps are required to achieve high purity biomethane. Membrane surface may also be subjected to acid formation caused by volatile organic compounds, hydrogen sulphide and ammonia (Surra et al., 2019). Emerging technologies using biological approach or combination of two or more well-known processes could overcome the current challenges and improve the viability of biogas upgrading as well as biomethane valorisation.

5.2. Enzyme recovery

On-site enzyme recovery is a simple approach that has been adopted along with genetic engineering and SSF to reduce the cost of enzymes in biorefineries (Binod et al., 2019; Kim et al., 2019). Enzymes such as cellulases can be recovered in the liquid phase from the hydrolysate and reused on fresh biomass. This approach significantly reduces enzyme usage, but hydrolysis efficiency may be compromised. For example, three consecutive recycling of 20 FPU of fungal cellulase/g glucan for 2% (w/v) alkali pretreated wheat straw led to a saving of 60 FPU enzyme but a 12.8% reduction in glucose yield (Qi et al., 2011). Similarly, three consecutive recycling of 15 FPU of Spezyme CP/g glucan for 5% (w/v) ammonia pretreated corn stover saved 45 FPU enzyme but losing 26.8% glucose yield (Steele et al., 2005).

Several challenges associated with enzyme recovery from lignocellulose biorefineries include the loss of enzyme activities, the non-productive binding of enzymes to insoluble biomass fractions, and enzyme inhibition by glucose (Binod et al., 2019; Kim et al., 2019; Tu et al., 2009). Kim et al. (Kim et al., 2019) observed significant drops in glucose yield after three rounds of cellulase (40 FPU/g) recycling for high solid loading (20%) empty fruit bunches pretreated hydrothermally. The glucose yields for first, second and third round enzymatic hydrolysis were 96.7, 19.3 and 5%, respectively (Kim et al., 2019). This reduction could be due to the inhibition of cellulases by residual glucose in the reused hydrolysate (Xiao et al., 2004). Removal of end-products (i.e. glucose) by ultrafiltration had been shown to improve the hydrolysis of recycled hydrolysate containing cellulases (Xiao et al., 2004). In addition, the non-productive binding of β-glucosidase onto residual lignocellulosic biomass (i.e. lignin fraction) resulted in a significant loss of β-glucosidase activity, thus limiting the conversion of cellobiose into glucose in recycling rounds (Haven and Jørgensen, 2013; Kim et al., 2019; Ko et al., 2015). Polyethylene glycol is a non-ionic surfactant that has been used for lignin blocking and cellulose hydrolysis enhancement (Kim et al., 2019; Kristensen et al., 2007; Yang et al., 2017). The addition of polyethylene glycol before enzymatic hydrolysis of empty fruit bunches increased the glucose yield of second round of hydrolysis using recycled hydrolysate by 3.1 times (Kim et al., 2019). Suitable pretreatment of agricultural residues (e.g. using ligninolytic organisms and enzymes) is necessary to break down lignin and prevent lignin from interfering with enzymes during biomass hydrolysis.

5.3. Lignin recovery for biochemical production

Lignin recovery and valorisation is a promising strategy to increase the profitability of agricultural residue biorefinery. The greatest challenge of lignin recovery from biorefinery is to design a process that not only reduces biomass recalcitrance through lignin removal but also enable downstream lignin valorisation (Ragauskas et al., 2014). Common lignocellulosic pretreatment techniques (e.g. acidic, alkaline, ionic liquids, and hydrothermal) can cause different degrees of saturation or changes to the physical and chemical structures of lignin, making it more difficult to produce lignin-derived chemicals (Beckham et al., 2016; Ragauskas et al., 2014). Given this challenge, microbial treatment has emerged as a viable approach to break down lignin aromatic rings and convert them to value-added products through microbial catabolic pathways (Beckham et al., 2016). *Pseudomonas* sp., *Rhodococcus* sp. and *Acinetobacter baylyi* are among the promising microbes for biological lignin processing and upgrading of aromatic compounds to targeted molecules (Linger et al., 2014; Salvachúa et al., 2015; Vardon et al., 2015). White-rot fungi secreting ligninolytic enzymes have proven to be effective at breaking down lignin (Section 4), but its capability to catabolise aromatic compounds and convert lignin to valuable biochemical still requires further development in metabolic engineering (Beckham et al., 2016).

6. Future research

Developments in biological treatment of agricultural residues using microorganisms and enzymes are a great approach to enhance the techno-economic viability of biomass biorefinery. This can be achieved through advancements in metabolic engineering, genetic engineering and strain improvement of targeted species (e.g. white-rot fungi). Ideal engineered microorganisms should possess rapid growth rate and secret a broad range of lignocellulolytic enzymes with high activities (e.g. cellulase, laccase, and peroxidases). Microbial and enzymatic treatments are simple and environmentally friendly techniques to break down the recalcitrant structure of agricultural wastes for enhanced bioconversion. They are also useful techniques to recover biochemical (e.g. lignin) from biomass biorefinery for further applications in bioproduct synthesis (e.g. plastics and carbon fibres).

Resource recovery is an important aspect of agricultural waste biorefinery. This approach can increase the scope of valorisation of individual components of the feedstock, thus maximising the economic benefits of the biorefinery. Primary products (i.e. biofuels) of agricultural residue biorefinery require recovery and upgrading processes to achieve fuel grade quality, but these processes are often expensive and energy intensive. A promising strategy to overcome the current challenges is using hybrid systems combining conventional (e.g. distillation) and emerging technologies. The success in identifying a suitable combination of upgrading technologies with minimal utility usage and cost will significantly improve the large-scale viability of agro-waste biorefinery. In addition, the capability to recycle enzymes used for biomass treatment and recover lignin from treated biomass for biochemical production is essential to reduce the overall cost and environmental impacts. The addition of surfactants and effective pretreatment (e.g. biological) to remove lignin can enable enzyme recycling with low activity loss, and production of lignin-derived polymers. Lab- and pilot-scale investigations are encouraged to validate the process efficiency of these technologies. Advancements in resource recovery will contribute to the commercial valorisation of agricultural residues.

7. Conclusion

Full-scale biorefineries of agricultural residues have seen progress in technical capacity, but the high investment and operation cost remains a bottleneck. This is attributed to the energy-intensive and somewhat complex processes used to break down the recalcitrant structure of agricultural residues and recover value-added products (i.e. biofuels and enzymes) from the process. This chapter presents biological treatment using lignocellulolytic organisms and enzymes as a sustainable and effective approach to enhance sugar conversion and lignin recovery from processing agricultural residues. Further development in genetic and fermentation technology will enable engineered microorganisms or microbial consortium to produce high enzyme concentration and activity useful for agricultural residue bioconversion. In addition, resource recovery (i.e. primary products and waste products) is necessary to maximise the economic outlook and beneficial applications of agricultural residues. Hybrid conventional and membrane system is promising for recovering fuel-grade ethanol and methane. Enzyme recycling should be reinforced to reduce the cost, but more research is required to overcome current challenges (e.g. activity loss and non-productive binding with biomass). At last, the recovery of lignin, a significant natural polymer, from the biorefinery processes will broaden the valorisation of agricultural residue in value-added bioproduct manufacturing.

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