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Challenges and perspectives of green-like lignocellulose pretreatments selectable for low-cost biofuels and high-value bioproduction

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Mild pretreatments for near-complete saccharification of desirable lignocelluloses.
- Integrated green-like biomass pretreatments to achieve maximum cellulosic ethanol.
- Green-like pretreatments selectable for generation of nanomaterials and nanocarbon.
- Distinct pretreatment mechanisms accounting for biomass recalcitrance reduction.
- A novel strategy for cost-effective biofuels and functional materials at high value.

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ABSTRACT

Lignocellulose represents the most abundant carbon-capturing substance that is convertible for biofuels and bioproduction. Although biomass pretreatments have been broadly applied to reduce lignocellulose recalcitrance for enhanced enzymatic saccharification, they mostly require strong conditions with potential secondary waste release. By classifying all major types of pretreatments that have been recently conducted with different sources of lignocellulose substrates, this study sorted out their distinct roles for wall polymer extraction and destruction, leading to the optimal pretreatments evaluated for cost-effective biomass enzymatic saccharification to maximize biofuel production. Notably, all undigestible lignocellulose residues are also aimed for effective conversion into value-added bioproduction. Meanwhile, desired pretreatments were proposed for the generation of highly-valuable nanomaterials such as cellulose nanocrystals, lignin nanoparticles, functional wood, carbon dots, porous and graphitic nanocarbons. Therefore, this article has proposed a novel strategy that integrates cost-effective and green-like pretreatments with desirable lignocellulose substrates for a full lignocellulose utilization with zero-biomass-waste liberation.

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Review





1. Introduction

Expanding consumption of finite fossil fuels becomes a potential threat to economic sustainability and environmental safety (Tan and Nielsen, 2022). As a promising solution, renewable biofuels are considered as the perfect additive into petrol-fuels. By unique photosynthesis, plants capture atmospheric carbon to produce the most abundant lignocelluloses on the earth (Dahmen et al., 2019; Flexas et al., 2021). Although lignocellulose has been implemented for conversion into biofuels and biochemicals, its natural recalcitrant inevitably decides a costly biomass process with potential secondary waste liberate into the environment (Zoghlami and Paes, 2019). Hence, advanced technology for biomass pretreatments has been attempted to reduce lignocellulose recalcitrance in bioenergy crops, which is not only aimed for cost-effective biofuels and value-added biomaterials, but also for full utilization of biomass resource with zero-biomass-waste release.

Lignocellulose recalcitrance arises from complicated structures and diverse functions of plant cell walls (Wang et al., 2021). As the primary target substrate of bioconversion, cellulose microfibrils are deposited as highly-ordered crystalline scaffolding framework with alternated amorphous cellulose chains that may deeply associate with hemicelluloses (Herburger et al., 2020; Wang et al., 2016c). Meanwhile, hemicellulose works as an inter-linker for cellulose and lignin assembly (Giummarella et al., 2019). As lignin is a major barrier against cellulose enzymatic hydrolysis, the lignocellulose recalcitrance is therefore accountable by cellulose crystallinity, hemicellulose interplay, and lignin deposition in plant cell walls.

Provided that biomass pretreatment is effective to reduce lignocellulose recalcitrance, the optimal pretreatment technology is fundamentally dependent on lignocellulose specificity and biomass resource (Mankar et al., 2021; Wang et al., 2021). Thus, this review article firstly elucidated the principle of biomass pretreatment process for improving lignocellulose recalcitrance in major types of lignocellulose substrates of both grassy crops and woody plants, which includes biomass feedstock size reduction at microscale level, cell wall layer broken and delaminated at cellular level, lignocellulose matrix disruption at ultrastructural level, and cell wall polymers destruction at molecular level (Fig. 1). Then, this study sorted out the optimal biomass pretreatments selectable for near-complete enzymatic saccharification towards maximum biofuel production. Furthermore, this study updated more-recently-achieved technology about the pretreatments that enable to generate highly-valuable nanomaterials. An applicable strategy is thus raised for a full utilization of lignocellulose by co-producing biofuels and nanomaterials under a cost-effective and green-like style.

2. Distinct pretreatments to reduce lignocellulose recalcitrance

Since various physical, chemical, and biological pretreatments have been conducted with diverse lignocellulose substrates in bioenergy crops, we initially attempted to classify all major pretreatments for their distinct roles on lignocellulose recalcitrance by highlighting positive and negative parameters of wall polymers as described below (Fig. 2).

2.1. Reduced biomass size and disrupted cell wall structure by physical pretreatments

For collection of raw biomass materials, mature bioenergy crops firstly require physical pretreatment to reduce particle size. The particle size reduction could increase the specific surface area and heat transfer capacity of lignocellulose substrates (Park et al., 2016). Particularly, irradiation techniques are a group of promising alternatives for biomass pretreatments such as microwave, ultrasonic and electron beam irradiation (Zhou and Tian, 2022). As a typical non-ionizing electromagnetic radiation, microwave induces explosions within the particles of biomass materials and thus facilitates the disruption of recalcitrant structures (Li et al., 2016a), whereas ultrasound is the acoustic energy that travels as waves with frequencies over the hearing range and it could release high temperatures and high pressure for biomass deconstruction (Luo et al., 2014; Sun et al., 2022). Despite those physical pretreatments could disrupt plant cell walls for enhanced biomass enzymatic saccharification, concerns with cost, energy intensity, and practicality limit its application as a viable pretreatment approach.



Fig. 1. The principle of diverse biomass pretreatments for distinctively lessening lignocellulose recalcitrance.

2.2. Deconstruction of lignin barrier by chemical and biological pretreatments

As lignin provides strength and hydrophobicity in plant cell walls (Zhang and Naebe, 2021), its deposition acts as a physical barrier against enzyme accession and loading onto cellulose surface. To deconstruct lignin barrier, chemical and biological pretreatments have been applied by using alkaline, organosolv, deep eutectic solvents (DES) and fungi invasion. In general, alkali pretreatment is effective to remove lignin with partial hemicellulose co-extraction by using kraft (Na₂S and NaOH) (Crestini et al., 2017), sulfite (NaOH and Na₂SO₃) (Aro and Fatehi, 2017) and soda (NaOH alone). The alkali pretreatment mainly distinguishes chemical linkages like ester bonds (Woiciechowski et al., 2020) and hydrogen bonds (Si et al., 2015) between lignin and carbohydrates, and meanwhile disrupts lignin structure. Although dilute so dium hydroxide pretreatment is also effective for feedstocks that are of relatively low lignin levels, its cost-effectiveness has not been thoroughly evaluated (Woiciechowski et al., 2020; Zhu et al., 2020).

Organosolv pretreatment is like organosolv pulping, but the degree of its delignification is limited. In some cases of those pretreatments, the main components of biomass can be effectively fractionated with each component potentially used for value-added products (Hassanpour et al., 2020; Thoresen et al., 2020). In general, the alkaline organosolv pretreatment is favored for lignin solubility to achieve higher cellulose digestibility and less polysaccharides deconstruction (Yuan et al., 2018). In particular, DES represents a new green solvent that selectively extracts high-purity lignin and enhances biomass digestibility (Guo et al., 2019; Sai and Lee, 2019; Guo et al., 2020; Xu et al., 2020; Wang and Lee, 2021).

Most biological pretreatments utilize certain classes of ligninsolubilizing microorganisms, being more amenable for enzymatic saccharification than native biomass (Sharma et al., 2019a). Among microorganisms, white-rot fungi have been well examined to produce lignin-degrading enzymes (Kainthola et al., 2021). However, for biological pretreatment process, lignocellulose residue is inoculated with appropriate fungal cultures for several weeks, and thus almost all biomass pretreatments are time-consuming with limited lignocellulose deconstruction.

2.3. Disassociation of hemicellulose interplay by physical and chemical pretreatments

As hemicellulose is covalently bound with lignin, and also crosslinked with cellulose microfibrils (Tarasov et al., 2018), recent progress suggests that the side chains of hemicellulose may be highly interacted with amorphous cellulose chains to maintain plant cell wall integrity (Wang et al., 2016c). Due to the bridging flexible structure, hemicellulose is more susceptible to pretreatment processes. For example, dilute acid pretreatment is one of the most applied biomass process technologies (Woiciechowski et al., 2020), and it generates protons that have a quick diffusion through the amorphous parts of lignocellulose such as hemicellulose and amorphous cellulose chains. Even though most dilute acid pretreatments utilize sulfuric acid, the peracetic (Kundu et al., 2021), ascorbic (Sheng et al., 2021) or citric acid (Qiao et al., 2019) has recently been investigated as cost-effective acid pretreatment.

Steam explosion pretreatment has been practiced for nearly a century to mainly extract hemicellulose of all lignocellulose substrates examined (Sarker et al., 2021), but it also leads to releasing the organic acids that are generated from acetyl functional groups associated with hemicellulose for partial lignin co-extraction (Deng et al., 2020). Hence, the addition of acid catalysts with steam explosion has improved the yield of released carbohydrates by reducing sugar degradation (Wang et al., 2016b). Another physical pretreatment such as liquid hot water has been developed for raising hemicellulose hydrolysis at relatively low temperatures and pressure (Sun et al., 2021), but cellulose hydrolysis could be blocked by re-formed spherical lignin droplets (Ko et al., 2015). Although co-supply with acid could enhance hemicellulose extraction by adjusting pH value (Imman et al., 2021; Suriyachai et al., 2020), the toxic compounds are raised that inhibit yeast fermentation from both steam explosion and liquid hot water pretreatments.

2.4. Alteration of cellulose crystallinity and polymerization by all pretreatments

Cellulose crystalline index (CrI) has been defined to account for cellulose crystallinity, which is determined by cellulose degree of polymerization (DP) and its interaction with other wall polymers. As the most biomass pretreatments could extract partial wall polymers and/or



Fig. 2. The hierarchy map accounting for lignocellulose recalcitrance reduction by distinct biomass pretreatments.

disrupt polymer interlinkages, the cellulose CrI is applied as the key parameter negatively accounting for biomass pretreatment effectiveness and enzymatic digestibility (Wang et al., 2016c). Moreover, both cellulose CrI and DP values are increasingly applied as two correlated parameters to evaluate biomass pretreatments and to predict sequential enzymatic saccharification.

Among all biomass pretreatments, the cellulose-dissolving solvents such as ionic liquids (ILs) have been examined as the most effective technology for reducing cellulose crystallinity (Li et al., 2017b; Usmani et al., 2020; Alayoubi et al., 2020). Meanwhile, the acid pretreatment has a strong level-off degree of polymerization effect of cellulose amorphous chains, leading to significantly reduced cellulose DP examined (Alam et al., 2019). In addition, the cellulose DP is decreased to some degree in the lignocellulose residues obtained from physical pretreatments such as steam explosion and liquid hot water (Deng et al., 2020; Wu et al., 2019).

3. Optimal pretreatments for near-complete biomass enzymatic saccharification

The biomass saccharification is defined by measuring hexose/ glucose yield (% cellulose) released from enzymatic hydrolysis of pretreated lignocellulose residue. Even though it remains a challenge to achieve near-complete biomass enzymatic saccharification, recent advance has provided a practical strategy for hexoses yields at>95 % by integrating optimal pretreatments with desirable lignocellulose substrates as described below.

3.1. Classic chemical pretreatments

While lignocellulose recalcitrance is lessened in desirable bioenergy crops, genetic mutants and transgenic plants, mild chemical pretreatments are sufficient for near-complete biomass enzymatic saccharification as shown in Table 1. Notably, specific site-mutation of genes involved in biosynthesis of plant cell walls could not only maintain plant normal growth and biomass yield, but also remarkably reduce lignocellulose recalcitrance, which simply causes a near-complete biomass enzymatic saccharification upon mild chemical pretreatment (Li et al., 2017a). In addition, the transgenic rice straw overproducing *Trichoderma reesei* β -1,4-D-glucosidase, or *endo*- β -1,4-glucanase is of near-complete enzymatic saccharification due to significantly reduced cellulose CrI and DP values (Li et al., 2018; Li et al., 2019d).

3.2. Green-like pretreatments

With the sustainable development trend on waste-to-energy nexus, green-like pretreatments have been conducted with lignocelluloses in major bioenergy crops (Sharma et al., 2020). These mainly include nonchemical and chemical-recyclable pretreatments as shown in Table 1. As typical non-chemical processes, steam explosion and liquid hot water pretreatments remain high energy consumption and limited enhancements for enzymatic hydrolyses. However, the pretreatment of 20 min liquid hot water has been recently found to enable for near-complete enzymatic saccharification with the desirable brittle stalk of corn mutant (Wu et al., 2019). Furthermore, alkali chemicals such as CaO and

Table 1

Mild chemical and green-like pretreatments with common and desirable lignocelluloses for distinctively enhanced biomass saccharification and bioethanol productivity.

Pretreatment	Biomass type	Condition	Sugars and ethanol	Assessment	Reference		
I: Classic mild pretreatments							
NaOH	Rice straw editing	1 % NaOH, 50 $^\circ\mathrm{C}$ for 2 h	Near-complete saccharification	Effective, low temperature	Zhang et al.,		
	OsCAD2				2021a		
NaOH or H_2SO_4	Rice straw	1 % NaOH, 50 °C for 2 h; 1	Hexose yields of 100 %, ethanol yield of 21	and pressure, but cause	Li et al.,		
	0verexpress17BGL	[%] H ₂ 5O ₄ , 121 C 101 20 IIIII	18 %	secondary pollution	2018		
NaOH	Osfc16 mutant rice	4 % NaOH, 50 °C for 2 h	Near-complete saccharification		Li et al.,		
	straw				2017a		
NaOH	MYB103 RNAi rice	1 % NaOH, 50 $^\circ\mathrm{C}$ for 2 h	Hexose yields of 95 %		Wu et al.,		
DUD	straw				2021		
РНР	wheat straw	PHP $(H_3PO_4 + H_2O_2)$	Hexose yields of 100 %		2019 van et al.,		
H ₂ SO ₄	Wheat straw	0.4 % H ₂ SO ₄ with 10 g/L	Glucose yield of 92.9 %; Glucose yield of		Tang et al.,		
		humic acid; 0.4 % H ₂ SO ₄	89.0 %		2021		
II: Green-like pre	treatments						
Liquid hot	Corn brittle stalk	200 °C, 20 min	Glucose yield of 96 %, bioethanol yields of	No chemicals used and little	Wu et al.,		
water	** 1 * 1 * .	000 005 050 055 00 10	19%	inhibitors generation, but needs high	2019		
Dry explosion	Hybrid pennisetum	200, 225, 250, 275 °C; 10, 20 min	Enhanced fuel property	energy input	Cai et al., 2020		
Steam	Miscanthus	2.5 MPa, 180 s	Glucose yield of 77 %		Sun et al.,		
explosion					2017		
NH ₃ ·H ₂ O or	Rice straw overexpress	12.5 % NH ₃ ·H ₂ O or 10 %	Near-complete saccharification, ethanol $>$	Cheap price but lower effective	Ai et al.,		
CaO	AtCesA6	CaO, 50 °C for 48 h	20 %	· · · · · · · · · · · · · · · · · · ·	2021		
Green liquor	Miscanthus	TTA 32.77 %, 150 °C, 23.18	Glucose yield of 87 %; bioethanol yield of	Re-use industrial waste liquids	Alam et al.,		
Sulfolane	Willow	Sulfolane/water (50:50), 4	Delignification vield of 94 %	Renewability, low toxicity, and high	Zhong et al		
		% NaOH		thermos-chemical stability	2020		
γ -Valerolactone	Hybrid poplar wood	GVL/water (95:5), CHF of	Glucose yield of 84.84 %		Yang et al.,		
_		54.99			2020		
Cyrene	Populus	Cyrene/water (1:2), 120 °C, 60 min	Almost-complete saccharification		Meng et al.,		
DES	Bamboo	Choline chloride/LA (1:4)	Glucose & xylose vields of 76.9 % & 81.3 %	Less hazardous, biodegradable, and	Lin et al		
				affordable	2020		
ILs	Rice straw	10 % [Emim]Cl, pH 9, 70 °C	Reducing sugar yield of 87 %	Non-flammable, recyclable, non-	Maleki et al.,		
				volatile, but high cost	2022		
White-rot fungi	Corn cobs	Trametes orientalis, 28 °C,	Glucose yield of 83 %	No pollution and energy input, but	Wang et al.,		
		25 u, Formopsis princold,		ume-consuming	2017		

 $NH_3 \cdot H_2O$ are also applied for green-like pretreatments (Ai et al., 2021), due to being recyclable and simply collective, whereas green liquor pretreatment often uses the alkali wastes derived from industry (Alam et al., 2020). Despite such green-like pretreatments lead to relatively less enhanced saccharification than that of classic chemical pretreatments, they are applicable for the desirable lignocellulose substrates. For example, desirable *Miscanthus* accessions are selectable for almostcomplete enzymatic saccharification even though under mild greenlike pretreatments conducted (Alam et al., 2020).

Recently, new organic reagents have been applied as green-like pretreatments, due to being renewability, low toxicity, and high thermos-chemical stability. For instances, by performing Sulfolane pretreatment with willow biomass, a high rate of lignin extraction is achieved (Wang et al., 2016a; Zhong et al., 2020). Moreover, y-Valerolactone (GVL) and Cyrene are two renewable organic solvents newly used in lignin extraction (Meng et al., 2020; Yang et al., 2020), and particularly, the GVL combined with p-TsOH is applicable to pretreat hybrid poplar, resulting in lignin removal of 86 % and enzymatic digestibility of 84 % (Yang et al., 2020). Ionic liquids have been identified as promising green solvents due to being non-flammable, recyclable, non-volatile and high boiling point, but the high cost and difficult synthesis make them impractical for large-scale applications. However, DES has been proposed as an alternatively green solvent, because it is less hazardous and more biodegradable and affordable (Chen et al., 2019a; Wang et al., 2020a). In addition, white-rot fungi invasion is usually considered as the greenest biomass pretreatment, but almost all biological pretreatments are time-consuming and low-efficient (Wang et al., 2017).

3.3. Integrated pretreatments

As cost-effective and green-like manner has been regarded as the optimal biomass process to maximize biofuel production, integrating different types of green-like pretreatments with desirable lignocellulose substrates is one of the most promising solutions as shown in Table 2. Two or more synergistic pretreatments are often conducting in a reactor

Table 2

Integrated green-like pretreatments to maximize enzymatic saccharification and biofuel production.

to enhance enzymatic saccharification for maximum biofuel production. For example, an effective ball milling activation mixed with metal salt has been applied to pretreat sugarcane bagasse (Zhang et al., 2019b). Furthermore, as physical pretreatment provides mechanical or irradiation energy to disrupt cell wall matrix for raised porosity, it could facilitate chemicals to extract and disrupt wall polymers. For instances, while steam explosion is applied to extract hemicellulose-rich polymers, the alkali chemical could effectively remove lignin and reduce cellulose DP, leading to a synergistic enhancement on biomass enzymatic saccharification (Mihiretu et al., 2019). Notably, the microwave-assisted DES pretreatment leads to achieving sugar yields of 99 % glucose and 85 % xylose, being twice as much as conventional DES pretreatment (Isci et al., 2020). In addition, ultrasound-induced cavitation could also assist to accelerate chemical pretreatments involving acid (Rios-Gonzalez et al., 2021), alkali (Li et al., 2016b), DES (Sharma et al., 2021) and ionic liquids (Vishal et al., 2019; Wang et al., 2018), leading to maximizing biomass enzymatic saccharification.

Sequential pretreatments, also known as two-step pretreatments, usually include two-step processes conducted in different reactors, but they could frequently combine the benefits of two independent greenlike pretreatments (Table 2). For the most cases, steam explosion pretreatment is first conducted to remove hemicellulose, and the sequential alkali pretreatment is thus effective to extract lignin and remaining hemicellulose by using CaO (Deng et al., 2020) or green liquids (Gao et al., 2021), which enables to achieve near-complete biomass enzymatic saccharification. It is thus predictable that the second-step biological pretreatment should be more efficient and less time-consuming once using the steam-exploded lignocellulose residues. Recent reports have indicated that two-step liquid hot water and DES pretreatments could lead to 90 % cellulose digestion of poplar lignocellulose (Xu et al., 2021). In addition, two-step pretreatments by DES-H₂O₂ (Chen et al., 2019b) or DES-bacterial (Liu et al., 2018) have shown effective lignin removals for remarkably enhanced enzymatic saccharification. Thereby, integrating two green-like pretreatments could also cause a nearcomplete biomass enzymatic saccharification to achieve maximum biofuel production.

Biomass type	Pretreatment I	Pretreatment II	Sugars and ethanol	Reference
I: Synergistic pretreatments				
Sugarcane bagasse	Ball milling, 50 $^\circ\text{C}$, 60 min	AlCl ₃	Saccharification of 79.7 %	Zhang et al., 2019b
sugarcane trash and aspen wood	Steam explosion: 204 $^\circ\text{C}$, 10 min	Impregnated with 5 % NaOH	Saccharification of 92 % and 81 %, respectively	Mihiretu et al., 2019
Pinus bungeana Zucc	Microwave, 800 W, 8 min	DES: ChCl:LA (1:10)	Enzymatic conversion of 81.90 %	Li et al., 2019a
Wheat straw	Microwave, 360 W, 8 min	DES: ChCl:FA (1:3)	Glucose yield of 99 %, xylose yield of 85 %	Isci et al., 2020
Eucalyptus sawdust	Microwave, 375 W, 6 min	Ionic liquid: 12.5 % [TBA][OH]	Sugar yield of 410.67 mg/g	Hou et al., 2019
Rice straw	Microwave, 400 W, 5 min	Ionic liquid: [Bmim]Cl	Glucan conversion at 61.14 %	Sorn et al., 2019
Eucalyptus sawdust	Ultrasound, 360 W, 30 min	Ionic liquid: 12.5 % [TBA][OH]	Reducing sugar yield of 426.61 mg/g	Wang et al., 2018
Sugarcane bagasse	Ultrasound, 100 W, 60 min	Ionic liquid: [Bmim]Cl	Reducing sugar yield of 254 mg/g	Sharma et al., 2019b
Sugarcane bagasse	Ultrasound, 40 W, 20 min	DES: ChCl/Glycerol (1:10)	Reducing sugar yield of 277 mg/g	Sharma et al., 2021
II: Sequential pretreatments				
Bamboo, One-year old	Steam explosion, 213.3 °C, 2.5 Mpa, 5 min	Green-liquor: 31.01 % TTA 28.01 min 166.41 °C	Near-complete saccharification, ethanol of 20.3 %	Gao et al., 2021
Rapeseed stalks	Steam explosion, 213.3 °C, 2.5 Mpa, 5 min	5 % CaO, 50 °C, 48 h	Near-complete saccharification	Deng et al., 2020
Rice straw	DES ChCl:LA (1:5) 8 h, 120 °C	Pandoraea sp. B-6, 30 °C, 3 d	Polysaccharide digestibility of 73.1 %	Liu et al., 2018
Switchgrass	DES ChCl:LA (1:2) 30 min, 130 °C	H ₂ O ₂ , pH of 11.5, 60 °C, 3 h	Glucose yield of 94.1 %	Chen et al., 2019b
Rice straw	0.02 M FeCl ₃ , 1.5 M H ₂ O ₂ (25 °C, 2 h)	Cupriavidus basilensis B-8	Reducing sugar yield of 442 mg/g	Zhang et al., 2018
Poplar wood	LHW, 180 °C, 30 min	DES, [MEAHCl][MEA], 110 °C, 3 h	Cellulose digestibility of 90.4 %	Xu et al., 2021
Grain stillage	Hydrothermal, 120 W, 3.5 min	Phanerochaete chrysosporium, 6 d	Saccharification of 66.28 %	Ren et al., 2020
Corn fiber	LHW (25 % solids), 180 $^\circ\text{C},$ 10 min	Three cycles of disk milling	Glucose yield of 94.9 %	Juneja et al., 2021

4. Selectable pretreatments for diverse bioproduction

Given the optimal pretreatments are sufficient for near-complete biomass enzymatic saccharification in the desirable lignocellulose substrates, undigested lignin-rich residues remain to explore for valueadded bioproducts. On the other hands, as most lignocellulose substrates are not completely digestible even though under extreme pretreatment conditions, it thus proposes to generate functional nanomaterials and highly-valuable nanocarbons by performing suitable pretreatments as described below.

4.1. Cellulose nanocrystals

Nanomaterials scaled at less than 100 nm could be generated from renewable lignocelluloses, which has much advantage for industrialization due to large surface and high density. Cellulose nanocrystals (CNCs) have been characterized as optimal intermediates for diverse nanomaterial production as shown in Table 3. In principle, there are two major steps for generation of CNCs from lignocellulose: delignification as the initial step and sequential alkali or acid process for non-cellulosic polymer removal and amorphous cellulose chain extraction. Although sulfuric acid process is a commonly used method for CNCs production, due to increased electrostatic stability of colloidal solution, other greenlike methods are increasingly explored by using mineral acids and organic dicarboxylic acids such as maleic (Lin et al., 2021; Seta et al., 2020) or oxalic acids (Jia and Liu, 2019). As high-quality CNCs are of reduced sizes (Salazar et al., 2012), attempts have been made to explore advanced technology by performing green-like pretreatments such as electron beam irradiation (Lee et al., 2018), ball milling (Amin et al., 2015), sonication (Zhou et al., 2018), and enzymatic hydrolyses (de Aguiar et al., 2020). In addition, by using desirable lignocellulose substrates from genetic mutants and transgenic lines, the green-like pretreatment under mild condition is often sufficient to generate highquality CNCs as described in Table 3.

4.2. Cellulose nanofibrils

Cellulosic nanofibrils (CNFs) have micrometers' length and a few nanometers' diameters with a high aspect ratio (Nechyporchuk et al., 2016). Unlike the CNCs as described above, CNFs could maintain most axial cellulose amorphous regions to stretch its flexible orientation. In general, multiple mechanical shearing actions via homogenizer or microfluidizer are often employed with crude cellulose suspension to generate CNFs (Table 3; Noremylia et al., 2022). Due to the mechanical pretreatment with high energy consumption, integrating mild chemical pretreatment with sequential enzymatic hydrolysis has been used to produce CNFs (do Nascimento et al., 2019; Bian et al., 2019). To further reduce chemical cost and energy consumption, advanced technology is employed to simultaneously generate CNFs and other value-added products (Table 3). For examples, while solid dicarboxylic acids are applied to produce CNC, the remained unhydrolyzed fibrous solid residue can be mechanically fibrillated to carboxylate CNFs with much less energy input. The acid-catalyzed alcohols have been recently used to pretreat sugarcane bagasse to produce CNFs-containing lignin with tailored properties such as hydrophilicity and dispersion stability (Liu et al., 2022c). More recently, the desirable lignocellulose substrate of rice mutant straw has been directly applied for high enzymatic saccharification, and undigested lignocellulose is thus favor for highquality CNFs production (Peng et al., 2022).

4.3. Lignin nanoparticles

Lignin nanoparticles (LNPs) have emerged as highly-valuable and green-like nanomaterials due to their non-toxicity, corrosion resistance, UV resistance and other exceptional properties. Typically, the LNPs possess a spheres or hollow spheres morphology with a hundred nanometers' diameter (Chen et al., 2021). The production of LNP mainly involve in two steps: crude lignin extraction and sequential nanoparticle synthesis (Gao and Fatehi, 2019). The crude lignin extraction methods

Table 3

Diverse	pretreatments	selectable for	producing	g nanomaterials	and	functional	materials
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Biomass type	Pretreatment	Nanomaterials	Performance	Reference
Moso bamboo	Ball milling; Maleic acid hydrolysis, 3 h, 110 $^\circ\mathrm{C}$	CNCs	Length of 105.6-223.8 nm	Seta et al., 2020
Sugarcane bagasse	Carboxylic acids (oxalic acid, citric acid, tartaric acid, formic acid) with ultrasonication	CNCs	Pure carboxylic CNCs with 60 % yield	Luo et al., 2021
Sugarcane	Ethanol: H ₂ O (1:1) 190 °C, 90 min	LCNCs	Crystallinity from 65 % to 80 %; Aspect ratios from 18.0 to 30.1	Bilatto et al., 2020
Hardwood	DES: ChCl and carboxylic acid (lactic acid, formic acid, acetic acid, malonic acid, oxalic acid, citric acid)	CNFs	Yields of 72–88 % and DPs of 300–500; CNF- strengthened polylactic acid composites	Liu et al., 2021a
Cypress wood	1 % NaClO ₂ in 80 °C, 6 h	CNFs	Nanocomposites with high selectively separate water	Zhang et al., 2021b
Moso bamboo	60 % maleic acid, 120 °C, 3 h; acidified NaClO ₂ , 75 °C, 1 h; 2 % KOH, 90 °C, 2 h	CNFs and LCNFs	Diameter of 20-40 nm, higher hydrophobicity	Zhang et al., 2020
Softwood	1 % $\rm H_2SO_4$ with KMnO_4, 50 °C, 2 h	CNFs	High yield of 96 %; Transmittance above 80 %, haze reaching 97.45 %	Liu et al., 2021b
Rice straw	Ethanol–water (65:35, v/v) contained 0.5 % HCl; microwave 400 W, 10 min	LNPs	Highly monodisperse and stable	Si et al., 2018
Aspen, eucalyptus, lodgepole pine, corn stover	LHW, steam pretreatment; DMSO, 4 h, 100 $^\circ\text{C}$	LNPs	Yields from 17.5 to 29.4 %, sizes from 20 to 100 nm	Chen et al., 2020c
Poplar wood, pine wood, moso bamboo	Hydrothermal; DES (ChCl and lactic acid)	LCNFs and LNPs	LCNFs: high aspect ratio of 150; LNSs: diameter of 223 nm	Tian et al., 2022
Bamboo	High-pressure steam (140 $^\circ\text{C},$ 8 min); 2.5 M NaOH and 0.4 M Na_2SO_3, 12 h	Lightweight strong bamboo	Specific strength at 777 MPa $\rm cm^3~g^{-1}$	Li et al., 2020
Poplar wood	DES: ChCl and oxalic acid; 5 $\%~\text{NaClO}_2$	Lignocellulosic bioplastic	High tensile strength of 128 MPa, excellent water stability, UV resistance & thermal stability	Xia et al., 2021
Norway spruce	Acetic:H ₂ O ₂ (1:1) 80 °C, 6 h	Laminate composite wood	Tensile properties to 40 Gpa; 200 MPa in tensile stiffness & strength	Frey et al., 2021
Pine, birch, ash wood	1 % NaClO ₂ (pH 4.6), 80 °C	Transparent Wood	Transmittance of 83 %, haze of 75 %	Li et al., 2017c
Balsa wood	$Na_2SiO_3,$ NaOH, MgSO_4, diethylallyltriaminepenta acetic acid, H_2O_2, 70 $^\circ\text{C},$ 1 h	Transparent Wood	High optical transmittance & very low haze	Höglund et al., 2020

are dependent on lignocellulose composition and lignin types in raw biomass, and the LNP synthesis is mainly determined by the amphiphilic property of lignin, which comprises hydrophobic structures (aromatic rings, aliphatic chains) and hydrophilic groups (hydroxyl, carboxyl groups). The hydrophobic groups of lignin could self-assemble as the core for LNPs formation, whereas the hydrophilic part should turn towards their surface (Poursorkhabi et al., 2020). Due to largely varied sizes, LNPs have wide applications in human care (10-200 nm), drug delivery (70-250 nm) and other purposes (Schneider et al., 2021), but smaller-size LNPs should be of higher quality and values (Wang et al., 2019; Zhang et al., 2019a). In terms of the solvent consumption, environmental safety and processing cost, advance technology is further explored for LNPs synthesis by using green solvent (levulinic acid) (Melro et al., 2020) and/or biological pretreatment such as fungi invasion (Juikar and Vigneshwaran, 2017). For instance, two fungal laccases, Trametes hirsuta and Melanocarpus albomyces are incubated to reinforce LNPs dispersibility by laccase-catalyzed cross-linking reactions (Mattinen et al., 2018). Therefore, the desirable lignocellulose substrates should be of the advantage for size-reduced LNPs even though under cost-effective and green-like process.

4.4. Functional woods

Given the green-like pretreatments are effective for generation of highly-valuable nanomaterials as described above, they are restricted for the lignocellulose substrates that are of great crystallinity and lignification in woody plants. As wood-derived lignocellulose process requires a complicated extraction procedure with much energy input, advanced nanotechnology has been practiced to produce functional materials (Table 3). For instance, while the in-situ delignification of bulk wood is used by strong chemical pretreatment, it leads to exposure of cellulose nanofibrils assembly of plant cell walls for much raised biomass porosity and surface areas. A rubber-like elastic hydrogel wood could be obtained to sustain a large compression and a substantially repeated compression with negligible deformation (Chen et al., 2020a). Meanwhile, a hot-pressing physical pretreatment could create high mechanical tensile strength of woody materials by using superior specific pressures of 422 MPa·cm⁻³·g⁻¹ and 777 MPa·cm⁻³ g⁻¹ (Li et al., 2020; Song et al., 2018). For complete delignification by extreme physical and chemical pretreatments, the functional woody materials could be generated for a transparency and haze tunable smart window (Höglund et al., 2020) or for extremely low thermal conductivity (Li et al., 2019b) or for other exceptional applications (Table 3).

4.5. Carbon quantum dots

Carbon quantum dots (CQDs) are the new type of zero-dimensional fluorescent nanomaterials with widespread applications in bioimaging, biosensors, composite materials, and other fields (Fernando et al., 2015). As a comparison with other fluorescent materials, the CQDs have the advantages of better water solubility, higher fluorescence stability and well biocompatibility. While the utilization of lignocellulose as a precursor of CQDs provides a potential large-scale platform, advanced pretreatments have been implemented with diverse lignocelluloses including hydrothermal, microwave and chemical oxidation (Table 4). Particularly, hydrothermal pretreatment is the most common method for production of diverse CQDs as the green and simple technology (Song et al., 2022). After the hydrothermal pretreatment is conducted for CQDs production, the remaining residue could be further used to generate high-value nanocellulose and other nanomaterials. As a further comparison, the microwave-assisted hydrothermal pretreatment is more efficient to generate CQDs with relatively higher yield of CQDs. More recently, microwave-assisted CQDs preparation has been explored using ionic liquids at 160, 200, and 250 $^\circ\text{C},$ respectively, leading to the CQDs yields of 23 % applicable for large-scale production (Liu et al., 2015). In addition, CQDs are obtained by using hydrothermal carbonization with

chemical oxidation (Peng and Travas-Sejdic, 2009). Overall, it remains to explore desirable lignocellulose substrates to obtain high-yield and high-quality CDQS by performing cost-effective and green-like pretreatments in near future.

4.6. Biomass-derived porous and graphitic nanocarbons

The lignocellulose substrates rich at carbon element have been broadly applied for a scalable synthesis of carbon materials with excellent properties such as high thermal and electrical conductivities and well chemical and environmental stabilities (Lan et al., 2021). Particularly, the porous and graphitic nanocarbons are mostly explored due to their superperfect performances and huge applications. Over the past years, a variety of approaches have been attempted to process diverse lignocellulose substrates for generation of desired porous and graphitic nanocarbons including pyrolysis, catalytic graphitization, chemical activation and coupled activations (Table 4). However, due to diversity of lignocellulose composition and structure, it remains a technique difficulty to generate identical and high-quality nanocarbons. As a promising solution, selection of identic lignocellulose is expected for producing high-quality nanocarbons by using genetic mutants or transgenic lines or specific germplasm accessions of bioenergy crops and plants. With respect to the identic lignocellulose substrates, optimal physical and chemicals pretreatments are thus required to separate three major wall polymers, and sequential effective catalysis of carbonization and graphitization also remains to explore for generation of highlyporous and well-graphitic nanocarbons, which should have broad applications in environment remediation, energy storage and batteryelectrocatalysis. In particular, lignin is chemically inert for producing nonporous carbon materials during pyrolysis process, whereas cellulose and hemicellulose tend to breakdown quickly for generating micropores (Deng et al., 2016; Han et al., 2017). In addition, the fermentable sugars and soluble lignin obtained from the optimal pretreatments could be further utilized for biofuels and biochemicals as a value-added process.

5. A full-chain lignocellulose utilization of major bioenergy crops and woody plants

Based on recent advances for cost-effective biofuels and highvaluable bioproducts under green-like biomass processes as described above, this study proposed three major routes for a full lignocellulose utilization in bioenergy grassy crops and woody plants (Fig. 3). (1) Green-like pretreatments are considerable for woody plants or highlylignified grassy crop such as bamboo to effectively extract lignin in situ by using DES and organosolv chemicals. The extracted lignin is applicable for production of nanomaterials by consequentially performing selectable green-like pretreatments, whereas the bulk wood and bamboo could be modified for functional materials after appropriate chemical modification and physical treatment. (2) Green-like pretreatments under mild conditions are sufficient for near-complete biomass enzymatic saccharification to maximize bioethanol production using the recalcitrance-reduced lignocellulose substrates of genetic-improved bioenergy grassy crops and engineered yeast strain. Meanwhile, the remaining lignin residues could be fully used for production of nanomaterials as described just. (3) Integrated green-like pretreatments are selectable for effective enzymatic saccharification of the most lignocellulose substrates towards high bioethanol production in desirable grassy crops. The remaining lignocellulose residues are further treated with green-like chemical to extract lignin, and all extracted lignin liquors are thus combined for production of nanomaterials. Finally, the remaining cellulose is applicable for valuable bioproduct.

6. Conclusions

Based on recent progress achieved about biomass process technology under cost-effective and green-like manner, this study classifies major

Table 4

Selectable pretreatments with undigested and desirable lignocelluloses to produce high-yield and high-quality carbon quantum dots and graphitic nanocarbon.

Biomass type	Pretreatment	Nanocarbon	Performance	Reference
Pristine wood	DES: Choline chloride and oxalic acid, 8 h, 110 $^\circ\text{C}$	CQDs	High crystallinity CQDs & PVA film with transmittance of 88	Tao et al.,
Corncob	Hydrothermal, 3 h, 200 °C	CQDs	$Fe_3O_4/BiOBr/CQDs photocatalyst remove rate of carbamazepine at 99.52 % within 120 min irradiation$	2022 Xie et al., 2021
Cotton stalk	Hydrothermal oxidative: mixed with water and H_2O_2 , 160–260 °C	Porous/graphitic carbon	Energy density increases by 30.31 % from 17.78 GJ \cdot m ⁻³ to 23.17 GJ \cdot m ⁻³ at 200 °C	Xu et al., 2022
Cotton stalk	Collect torrefaction liquid & wash, 30 min, 250 °C	Porous/graphitic carbon	S_{BET} increases by 40.58 % from 134.63 $m^2 \cdot g^{-1}$ to 189.27 $m^2 \cdot g^{-1}$	Chen et al., 2017
Waste cotton textile	Hydrothermal, 30–90 min, 300–340 $^\circ\mathrm{C}$	Porous/graphitic carbon	$I_{\rm D}/I_{\rm G}$ value was 0.58 for 320 °C, 90 min	Zhao et al., 2022
Corn stover	-52.1 °C, vacuum condition, 2 kw; 50 % ultrasonic, 50 psi, 60 s, 20 kHz	Porous/graphitic carbon	Porosity of drying- and VFD-pretreated increased from 1.28 m^2 , g^{-1} to 1.61 m^2 , g^{-1} and 1.53 m^2 , g^{-1}	Meng et al., 2021
Eupatorium adenophorum	A. tubingensis, 28 °C, 7–21 d	Porous/graphitic carbon	Pb(II) adsorption performance of 122.7 mg g^{-1}	Liu et al., 2022a
Raw oil palm; mesocarp fiber	0.1–4.0 M HCl, room temperature, 24 h; 0.1–4.0 M NaOH, 95 $^{\circ}$ C, 8 h	Porous/graphitic carbon	Peak power density of 11.8 mW \cdot cm $^{-2}$	Jafri et al., 2021
Corn cob	1 M formic acid, acetic acid, oxalic acid, and propionic acid, room temperature, 2 h	Porous/graphitic carbon	Specific surface area increases from 3.26 $m^2 \cdot g^{-1}$ to 14.65 $m^2 \cdot g^{-1}$	Liu et al., 2022b
Walnut shell	0.1 M acetic acid, 0.1 M hydrochloric acid, room temperature, 12 h	Porous/graphitic carbon	$^{\circ}_{I_{D}/I_{G}}$ value less than 1, thermostability reached 448.78 $^{\circ}\text{C}$	Diao et al., 2021
Yard waste	1 M H_2SO_4 , room temperature, 24 h	Porous/graphitic	Pretreated sample specific surface area of 316.7 $\mbox{m}^2\mbox{g}^{-1}$	He et al., 2021
Larch and oak	70 mM H ₂ SO ₄ , 170 °C, 10 min	Porous/graphitic	Pretreated oak specific surface area of 543.59 $\text{m}^2 \cdot \text{g}^{-1}$	Ban et al., 2022
Corn stover	DES: ChCl and oxalic acid anhydride, formic acid,	Porous/graphitic	3D porous structure and high crystallinity	Zhang et al.,
Sugarcane bagasse	2.4 % H ₂ SO ₄ , 170 °C, 15 min; enzymatic hydrolysis	Porous/graphitic	Specific surface area of 1436.7 m^2/g and specific capacitance of 185 SF g^{-1}	Wang et al.,
Chestnut shell	2.5 M NaOH/0.4 M Na ₂ SO ₃ ,70 °C, 120 min	Porous/graphitic	Specific surface area of 2621 m ² /g and appealing capacitance of 393 H σ^{-1}	Li et al., 2019c
Corncob and cottonseed husk	Fungi etching	Porous/graphitic carbon	Specific surface area of 3463 m ² /g, effective sorption of Cl-VOCs of 716.9 mg g ⁻¹	Chen et al., 2020b



Fig. 3. Flowchart of full lignocellulose utilization of bioenergy crops and woods.

types of biomass pretreatments that have been recently explored for distinctively enhanced enzymatic saccharification in typical grassy crops and woody plants. By sorting out the most important parameters and factors that are accountable for lignocellulose recalcitrant properties, this work has further highlighted distinct mechanisms of major pretreatments enabled for biomass conversion into low-cost biofuels and high-value nanomaterials, thereby providing a novel strategy for a full utilization of lignocellulose residues with zero-biomass-waste release into environment in bioenergy crops and woody plants.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

Data availability

No data was used for the research described in the article.

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