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Advances in Genetic Manipulation of Lignocellulose to Reduce Biomass Recalcitrance and Enhance Biofuel Production in Bioenergy Crops

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Abstract

Lignocellulose biomass derived from plant cell walls is a rich source of biopolymers for the production of biofuels. Biomass recalcitrance is the noticeable and main features of lignocellulose which can reduces by genetic modification of plant cell wall. The aim of the present review is to provide the reader a new insight for enhancing biomass yield and biofuels production. This can be issued by focusing on major perennial grasses, cereal crops and woody feedstock which have high biomass yield or large biomass residues and also the effects of distinctive cell wall polymers (cellulose, hemicellulose, lignin, and pectin) on the enzymatic saccharification of biomass under different pretreatments. Moreover the present review paper will also major gene candidates which are involved plant cell wall biosynthesis, degradation and modification for improving biomass yield and digestibility in transgenic plants and genetic mutants.

Keywords: Bioenergy crops; Plant cell walls; Genetic manipulation; Biomass pretreatment

Introduction

Recent economic developments in many countries all around the world have elevated the requirement for alternative energy resources because of well-recorded weaknesses of fossil fuels:

- their limited supply
- global warming and greenhouse gasses emission
- increasing price and unanticipated fluctuations.

All these disadvantages have fortified the interest in alternatives, renewable, sustainable, and economically viable fuel such as bioethanol [1]. In the first generation biofuels, starch and sugar derived from sugar cane and maize are employed as feedstock, but contribution to the global energy supply is small. In the second generation bioethanol production, lignocellulose has the most important role and used, because lignocellulosic materials are cheap, abundant (1.5×10^{10} tons/year of biomass), and renewable [2,3]. Besides, lignocellulosic ethanol, has the potential to fill most global transportation fuel needs and does not present a conflict between energy demand and food supply [4,5].

On the earth, plant cell wall has shown as a plentiful renewable biomass resource for biofuels. A cell wall is a structural layer surrounding some types of cells, situated outside the cell membrane and extends to the protoplast. It can be tough, flexible, and sometimes rigid. The composition of cell walls varies between species and may depend on cell type and developmental stage, but mainly divided into primary (PCW) and secondary cell wall (SCW) based on their biosynthetic composition and cellular location (Figure 1) [6-10]. The transformation of lignocellulose to ethanol associated with three main steps: pretreatments, enzymatic hydrolysis and yeast fermentation [11,12]. The production of ethanol from lignocellulose because of lignocellulose recalcitrance is unacceptably expensive. Mainly, biomass recalcitrance affected by cell wall compositions and wall polymer features [13,14].

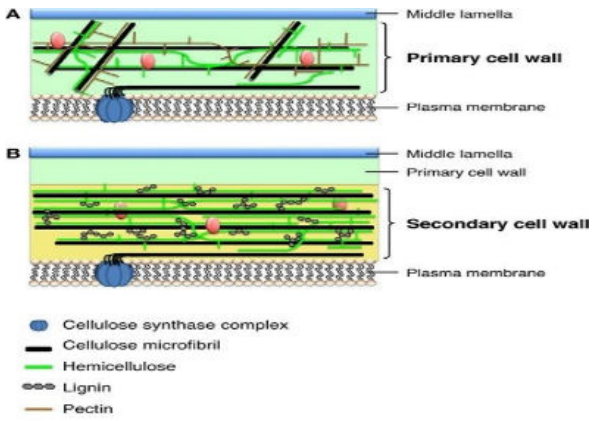

Figure 1: Plant cell walls (A) Primary cell wall; (B) Secondary cell wall, which is deposited between the primary cell wall and the plasma membrane.

The PCW of plants is composed of the polysaccharides cellulose, hemicellulose (mainly xyloglucan) and often rich in pectin (Figures 1 and 2A), Cellulose microfibrils in the PCW are relatively short and thin, compared with those in the SCW. The SCW mainly contains relatively long and thick cellulose microfibrils, hemicellulose (mainly xylan), and lignin (Figures 1 and 2B) but they have specific compositions in different plant species. Genetic modification of plant cell walls is often correlated with deficiency in plant growth and development, it could be due to numerous cell types with highly

complicated wall constitutions and various biological purposes [15-17]. Then, it becomes critical to realize an optimal genetic engineering approach that carry on normal plant growth, improve biomass yield and lignocellulose digestibility [10,11,15]. In this review, we describe the latest research advancement about cell wall polymer dominant influence on biomass enzymatic digestibility under different pretreatment methods (physical, chemical, and biological) in natural germplasm accessions, genetic mutants and transgenic plant in main bioenergy crops such as perennial grasses of high biomass yield (Miscanthus, switchgrass), cereal crops (sweet sorghum, rice, maize, wheat), commercial plants (rapeseed, cotton, sugarcane) with high biomass wastes, and woody feedstock trees rich in cellulose [7,13,17,18]. In addition, we discuss the key genes engaged in cellulose, hemicellulose, lignin and pectin synthesis and degradation which may improve biomass and biofuel yield [18].

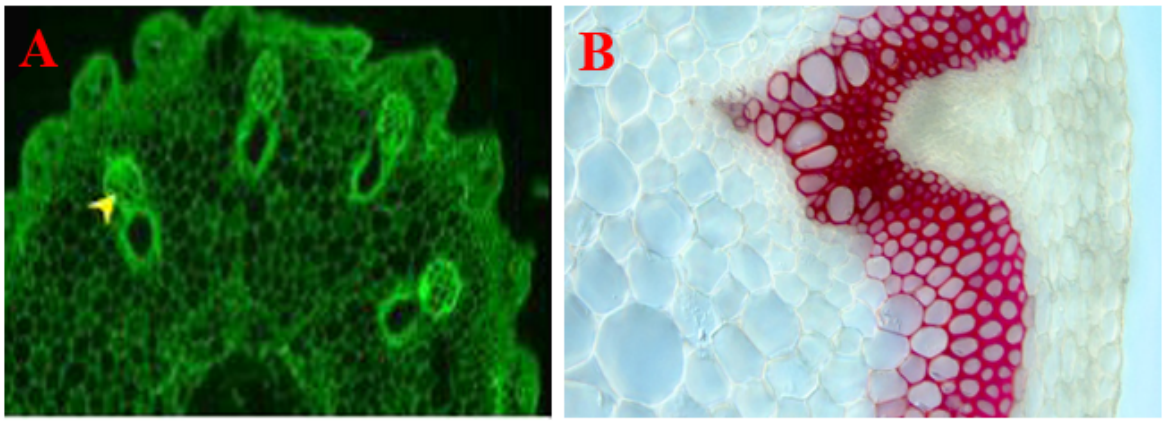

Figure 2: (A) pectin stained with anti-rhamnogalacturonan (arrow highlights pectin); (B) Lignin (stained red).

Assessment of Major Bioenergy Plants

Lignocellulosic biomass which are known as a second generation of renewable energy possibly assembled from perennial grasses, food crop wastes, and woody feedstock. For the improvement of lignocellulosic biofuels the main barriers remain for the highest biomass yield and also competition with food production [12]. In this section, some of the most extensively studied bioenergy crops for cellulose feedstock are described.

Perennial grasses

Switchgrass (*Panicum virgatum* L.), a C4 native warm-season perennial grass, demonstrated high productivity across many environments, is suitable for marginal and erosive lands, needs low water and nutrient requirements, and has positive environmental benefits [19,20]. Switchgrass among the 18 perennial grass species because of its variability for the high biomass yield has been classified on the top [21]. New four switchgrass cultivars with improved biomass yield and different lignin composition (in particular in the ratio of H, G, and S monomers and respectable amount s of p-coumaric acid and ferulic acid) have been exhibited [22].

Miscanthus (*Miscanthus* × *giganteus*), a cool hardy, vegetatively-propagated C4 grass native to Asia with more than 17 species, requires low amounts of water and fertilizers. Low-input, high-density mixtures of perennial grasses grown on degraded lands were advocated as better bioenergy sources [23,24]. Four main Miscanthus genotypes have thousands of natural germplasm accessions which present different wall polymer components and structures, and diverse biomass digestibility and biofuel. Moreover, in the transgenic Miscanthus accessions by expressing of the key genes that are involve in the wall polymer structures like lignocellulose crystallinity (CrI), cellulose degree of polymerization (DP) and hemicellulosic Xyl/Ara, could improve biomass yield and enzymatic digestibility [25-27].

Cereal crops

Sweet sorghum among the annual cereal crops has revealed as a superior bioenergy crop due to large amounts of soluble sugars at stalk and reducible lignocellulose at bagasse [28]. It's a fast-growing crop and has the considerable resistance to drought condition, salt stresses. In the north of China has reported that sweet sorghum in the alkaline soils can possibly produce 20 million tons of bioethanol per year [29]. In a study, has represented that both soluble sugar and dry bagasse level in 63 sweet sorghum accessions are not remarkable correlation with lignocellulose enzymatic digestibility. Suggesting that desirable sweet sorghum accessions should be collected as a bioenergy crops [30].

All over the world the main annual cereal crops are wheat, rice, barley, and maize with almost 75% of total agricultural lignocellulose residues. Despite just about 20% to 50% of total lignocellulose used for biofuel production, because for conservation of soil and maintainable grain production amounts of crop wastes need to remain in the field [31]. Dozens of rice mutants have selected, which two distinctive mutants present intensified plant lodging resistance, high biomass yield efficient lignocellulose enzymatic digestibility [16]. It indicates a theory for improving mechanic strength and reducing lignocellulose recalcitrance in the mutant genotypes by using silicon fertilizer to field [25]. Recently, a few varieties of maize and wheat cultivars from large populations with high biomass enzymatic digestibility have distinguished [32-34]. To enhance biomass yield and digestibility by selecting of transgenic crops and genetic mutants the breeding of bioenergy crops becomes noticeable.

Woody feedstock

Short rotation coppice (SRC) trees species are regarded as an ideal energy plants because of high lignocellulose, low-land occupation, high-resistance disease, and low-cost management [35,36]. The genus Populus has emerged as a model system for plant and tree biology and has established as the world's top biomass for excellent plants with interesting traits by using molecular breeding individual to its rather mature transgenic method [37]. Moreover, eucalyptus and willow are also considered as a lignocellulose resources, but the suitable genetic modification aims to improve biomass digestibility and biofuel alteration rates remain under progress [38,39].

Influence of plant cell wall components on biomass digestibility

Plant cell wall compositions is extremely variable among different plant cell types and tissues (Table 1). So, it remains technically challenging to recognize the effect of wall polymers on biomass enzymatic digestion. For instance, selection of one genetic mutant may result in multiple wall polymer modifications. In the biomass crops, have been distinguished three major wall polymers including cellulose, hemicellulose, and lignin. The chemical structure of the three components is represented in Figure 3.

Plant species	Cellulose	Hemicellulose	Lignin	Reference
Perennial Grasses				
Miscanthus				
M. sinessis	22-40	24-38	22-29	[26]
M. lutarioriparius	28-46	27-35	25-31	[43]
Switchgrass (*P. virgatum*)	32-39	25-33	17-22	[44]
Reed (*P. australis*)	34-36	26-27	21	[45]
Cereal crops				
Wheat (*T. aestivum*)	34-38	20-35	22-24	[33]
Rice (*O. sativa*)	14-30	Aug-18	Nov-19	[16,25]
Maize (*Z. may*)	20-38	21-32	13-21	[32]
Barley hull (*Hordeum vulgare* L.)	33	35	19	[48]
Barley straw (*Hordeum vulgare* L.)	34	22	15	[49]
Sweet sorghum (*S. bicolor*)	26-38	25-38	14-24	[30]
Commercial Crops				
Rapeseed				
B. napus	28-31	16-20	15-20	
B. rapa	20-35	15-22	16-20	[46]
B. carinata	27-32	19-20	21-23	
B. junjea	24-35	20	23	
Cotton				
G. hirsutum	32	14	15	[27]
G. barbadense	40	16	26	
Sugarcane (*S. officinarum*)	42-46	25-27	20	[47]
Fiber crops				
Poplar	43.8	15	28	[50]
Ramie (*B. nivea*)	48	26	26	
Jute (*C. capsularis*)	44	28	28	[51]
Kenaf (*H. cannabinus*)	42	29	29	

Table 1: The percentage of three main wall polymers in bioenergy crops (% w/w).

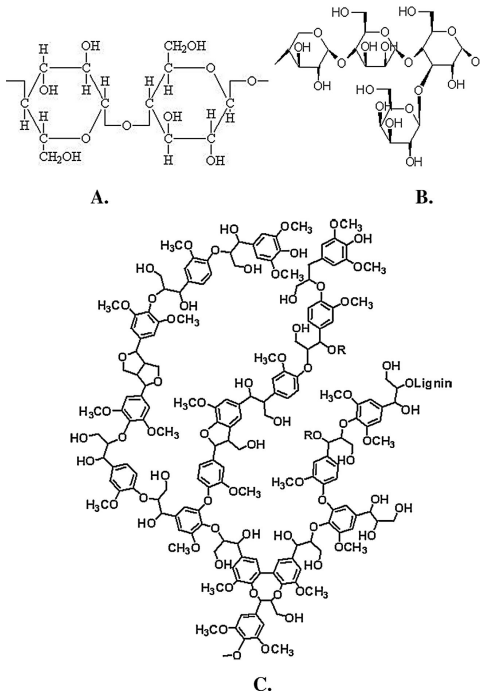

Figure 3: Chemical structure of: (A) Cellulose, (B) Hemicellulose, (C) Lignin.

Cellulose

Cellulose is the major abundant polysaccharide produced in nature and generally serves as the main scaffolding component for plant cell wall. Cellulose is composed of linear chain of D-glucose linked by β-(1,4)-glycosidic bonds to each other (Figure 4).

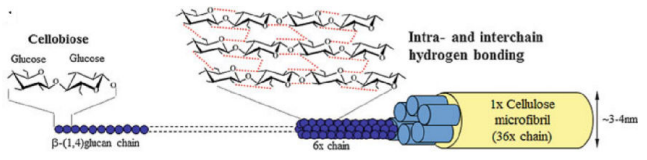

Figure 4: Molecular features of cellulose: Cellulose consists of paracrystalline microfibrils (yellow) containing as many as 36 individual β-(1,4)-linked glucan chains (dark blue) [40,41].

Individual glucan chains are synthesized at the plasma membrane by GTs, known as cellulose synthase catalytic subunits A (CesAs), which use UDP-glucose as activated sugar-donor substrates and Mg^{2+} cofactors [40,41]. The percentage of cellulose counting around 2-4% and 95% in cereal endosperm walls and secondary cell walls of cotton fibers, respectively [27,30,42]. The percentage of cellulose among perennial grasses in Miscanthus accessions display a large discrepancy from 20% to 46% [26,43], while this proportion in reed and switchgrass are around 32-36% and 32-39%, respectively [44,45]. Cellulose variation has been announced in agronomic plants such as wheat cultivars [33], rice [16,25], maize, rapeseeds cultivars [32,46], sweet sorghum, sugar cane, cotton cultivars [27,30,47] barley hull and straw [48,49]. Fiber crops like popular, ramie, jute and, kenaf are very rich in cellulose, with levels ranging from 42% to 48% [50,51]. A key features of cell wall is cellulose Crl which is account for amorphous and crystalline regions of native cellulose and also reflects mutual action with other wall polymers [52]. Cellulose Crl or cellulose index has been discovered in many biomass materials by using x-ray diffraction [53]. Under various physical and chemical pretreatments in almost all plant species cellulose CrI has been decided to be a primary negative factor on biomass enzymatic digestibility [16,54]. Additionally, the cellulose level is known to have a negative impact on biomass enzymatic saccharification in most plant species examined, probably due to its positive correlation with cellulose CrI.

Another important feature of cellulose which is favorably variable among different plant species is cellulose DP [27]. It has been reported that cellulose DP is positively correlated with cellulose Crl in 80 different Miscanthus accessions. Cellulose DP is the factor that considerably negatively affect biomass digestibility [54].

Hemicelluloses

Hemicelluloses $(C_5H_8O_4)_m$, located in secondary wall, are heterogeneous polysaccharides with diverse monosaccharide containing pentoses (β-D-xylose, α-L arabinose), hexoses (β-D-mannose, β-D-glucose, α-D galactose) and/or urgonic acids (α-D-glucuronic, α-D-4-O-methyl-galacturonic and a-D-galacturonic acids) (Figure 5) with separate composition in various plant species. In the mature tissues of grasses and woody plants the major hemicelluloses are found xylans and arabinogalactan, relatively.

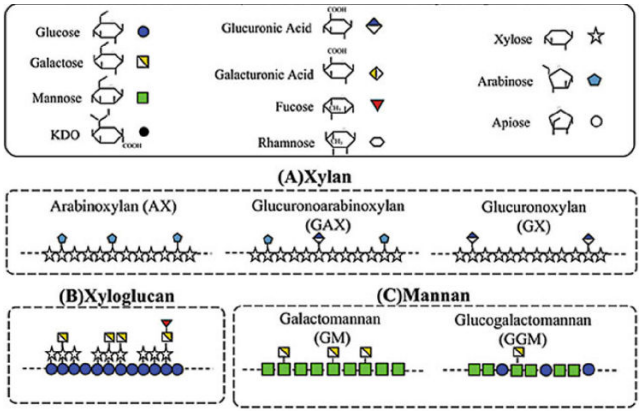

Figure 5: Structures of hemicelluloses. Top panel shows the presentation of the structures and symbols of monosaccharide building blocks (monomers). Panels A-C represent simplified structures of xylan, xyloglucan and, mannan, respectively [55,56].

Xyloglucan is discovered in both woody plants and grasses [55,56]. Furthermore, among different plant species hemicellulose component fluctuates greatly. For instance, in Miscanthus accessions, wheat cultivars, sweet sorghum different high-level hemicellulose are distinguished (around 35%-38%), while rice mutants have low-level hemicellulose contents about 3%-8%, (Table 1) [16,27,30,33,43]. Hemicelluloses has a cross-linkage with cellulose which is the major biological role of cellulose, these interactions embed crystalline cellulose elementary fibrils to intensify the cell wall and form a wall barrier against enzymes accessible to the cellulose surface, a major cause of lignocellulose recalcitrance [55]. According to recent studies, in Miscanthus and rice hemicelluloses positively affect biomass enzymatic digestibility under various physical and chemical pretreatments by reducing cellulose crystallinity. In all grass species, the replacement degree of xylan (Xly/Ara ratio) is a main positive factor on biomass saccharification. Substituted Ara may interact with the β-1,4-glucan chains in amorphous areas of cellulose micro fibrils via hydrogen bonding, especially on the non-KOH-extractable residues that consist of 10%-30% of total hemicelluloses. Therefore, cellulose crystallinity significantly affected by xly/ara ratio [57]. In addition, it has reported in rice mutants that the Ara level in non-KOH-extractable residues by reducing the crystallinity of cellulose positively affects plant lodging resistance [16].

Lignin

Lignin $[C_9H_{10}O_3(OCH_3)0.9\text{-}1.7]_n$ is an aromatic polymer synthesized from phenylpropanoid precursors. The major chemical phenylpropane units of lignin consisting of primarily three monomers: syringyl (S), guaiacyl (G) and, P-hydroxy phenol (H) (Figure 6) [58,59]. Lignin principally accumulation vary largely in SCWs in different plant species. Generally, grass and woody plants have lignin components by notable ranging from 15% to 30%, accounting for 30%-40% of the energy content of the biomass (Table 1) [60]. In Miscanthus accessions the level of lignin is high up to 28%-31%, but several rice mutants have low lignin contents ranging from 11% to 19% [27,43,54].

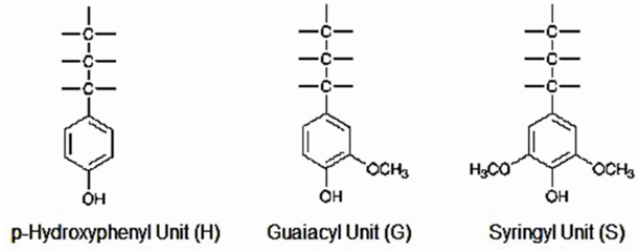

Figure 6: Chemical structures of Monomeric Units (H,G and S) of lignin.

Lignin play a critical role in the adaptation of plants to terrestrial environments, because it is firmly associated with hemicelluloses to maintain plant mechanical strength and biomass recalcitrance [16]. Lignin is regarded to apply dual influence on biomass enzymatic hydrolysis: decrease surface area access for cellulose enzymes by inhibiting cellulose microfibril enlargement, and preventing cellulose action on the cellulose surface [61]. Lignin under various pretreatment has a negative impact on biomass digestibility by indirect way of increasing cellulose crystallinity in Miscanthus accessions. Although, recently have reported in rice mutants that lignin not only could enhance biomass yield but also, increase lignocellulose enzymatic digestion [16,33]. Thus, positive effect of lignin can be explained in three manner:

- Lignin formed of high proportions of G and H monomers which is more extractable after alkaline pretreatment [62],
- After lignin is extracted by physical and chemical pretreatments, the remaining non-KOH-extractable lignin-hemicellulose compounds could maintain cellulose microfibrils in the native state that are accessible by enzymes in amorphous regions [34,62],
- The raised monolignol levels in genetic mutants and transgenic plants may not be interlinked to form a complete lignin-carbohydrate compound [62].

Pectin

In plant biology, pectin consists of a complex set of polysaccharides that are present in most PCWs (Figure 1) and found in smaller amounts in the SCWs and also abundant in the non-woody parts [63]. In primarily, pectin polysaccharides have been organized into domains that include Homogalacturonan (HG), xylogalacturonan (XGA), apiogalacturonan (AGA), rhamnogalacturonan-I (RGI) and rhamnogalacturonan- II (RGII) (Figure 7) [63]. Typical components of pectin is uronic acids, which are found in glucuronoarabinoxylans and galactosyluronic acid-rich pectin [64]. Pectin can form a macromolecular wall-network through molecular substitution with side chains associated with cellulose or hemicelluloses [65,66]. It implying that plays a role in preserving cell wall structure and biomass enzymatic digestibility. It is technically difficult to recognize the particular influence of pectin on lignocellulosic enzymatic digestibility after physical or chemical pretreatment, because of the low level and complicated structure of pectin in mature tissues. In a large population of Miscanthus accessions have been proved that AO-extractable uronic acids are predominately accounting for the positive effect of pectin on biomass enzymatic digestibility by reducing cellulose Crl. In addition, these research propose that uronic acid-rich pectin may interact with the β-1,4-glucan chains that reduce cellulose CrI for high biomass saccharification in Miscanthus accessions [65].

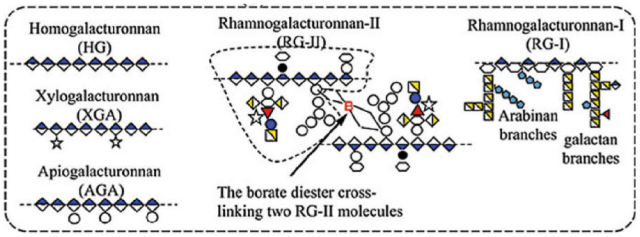

Figure 7: Structure of pectin domains [63].

Lignocellulosic Modification: Biosynthesis and Degradation

Genetic modification not only maintains normal plant growth but also enhances biomass yield and lignocellulose enzymatic digestibility. Although, to maintaining normal plant growth and high biomass yield is difficult, but by identification of appropriate genes, proper promoter and productive systems for gene transformation it can solve this challenge [67]. Up to now more than one thousand genes are engage in cell wall biosynthesis, degradation and modification, but a few number of them have been distinguished.

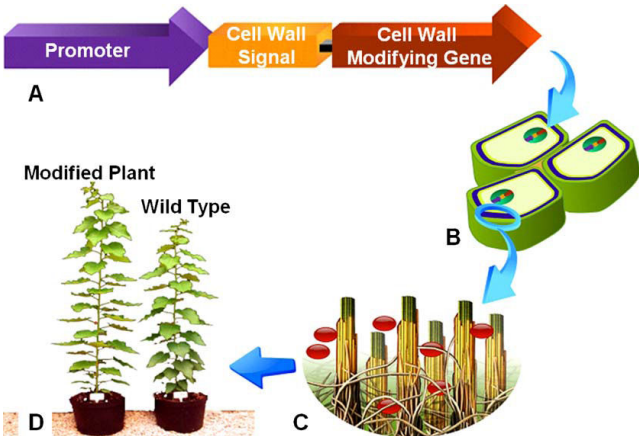

Figure 8: Modification of plant cell wall components to increase biomass and biofuel yields. The model describes the outline of recombinant expression of cell wall-targeted enzymes or proteins in transgenic plants. (A) Gene construct consisting of a gene for a cell wall modifying protein (red), a developmental specific promoter (purple) and a cell wall targeting signal sequence (yellow). (B) Integration of the gene into the plant genome via transformation. (C) The modifying protein (red oval) is then expressed and secreted to the cell wall (green strands-crystalline cellulose; yellow strands-amorphous cellulose; brown strands - hemicellulose). (D) Genetic modification of cell wall composition and its physical properties may result in boosting biomass and biofuel yields.

Cellulose biosynthesis and degradation

The main purpose of bioenergy engineering is improving biomass yield of bioenergy plants via intensification of wall polymer particularly on cellulose. Cellulose synthase (CesA) gene synthesize cellulose which is identified in 1998, [68,69]. For cellulose biosynthesis, first CesA compounds gathered into Golgi apparatus and then transmitted to the plasma membrane in three stage: initiation, elongation, and termination [70] In secondary cell walls, the presence of $CesA_4$, $CesA_7$, and $CesA_8$ is needed [71], while in PCWs the interaction of $CesA_1$, $CesA_3$, and $CesA_6$ (or $CesA_1$, $CesA_3$, and $CesA_6$-releated proteins) is required [68]. In numerous plant species, the CesA families have been distinguished, comprising Arabidopsis [72], rice [73,74], wheat [75], barley [76], maize [77], poplar [78], cotton [79]. Through various genetic approaches numerous specific CesA mutants have been distinguished, which most mutants present reduced cellulose levels and imperfect plant growth (Table 2). Because of this diminution in cellulose, many mutants have presented low cellulose Crl and high biomass enzymatic digestibility. Although, in poplar and barley have been reported that overexpression of CesA genes leading to reduce biomass yield and imperfect plant growth [80,81].

In plant cell wall different types of enzymes there are, which involving in degradations of wall polymer. Endo-β-1,4-glucanases (EGases) spilt the internal β-1,4-glycosidic bonds between two glucose at the center of polysaccharide chain. Plant EGase gens compose of three division classes which is belong to glycoside hydrolase family 9 (GH_9) [82]. KORRIGAN protein, a GH_9A family member, can play a role in cellulose biosynthesis by either cleaving a sterol-cellodextrin substrate or removing glucan chains incorrectly assembled in the growing microfibrils. KORRIGAN (kor) mutants show reduced cellulose levels and imperfect plant growth, while overexpression of $PtCel_9A_1$ (GH_9A) leads to reduced cellulose CrI and increased biomass yield [83]. In rice mutants, the expression levels of $OsGH_9B$ family genes are meaningfully associated with cellulase activity and cellulose CrI, recommending that GH9B family should play a role in cellulose degradation. It have reported that the overexpression of $PtGH_9B_5/C_2$ genes redound to low plant growth and biomass yield, but RNAi silencing of the $AtGH_9C_2$ gene could reduce cellulose CrI and improve biomass yield [83].

Hemicellulose biosynthesis and degradation

The biosynthesis of hemicellulose takes place in the Golgi apparatus and involves the action of several glycosyltransferases enzymes (GTs). Almost seven GT gene families typically involves to hemicellulose biosynthesis [2,55,84]. Traditionally, biotechnological processes of lignocellulosic biomass have made use of mainly C5 sugars such as Xyl and Ara, which are more difficult to ferment. Moreover, as xylan by reducing cellulose CrI has a positive influence on biomass enzymatic digestibility, especially on Ara substitution degree in non-KOH-extractable hemicelluloses [16]. Improving biomass yield and lignocellulose enzymatic digestibility in bioenergy plants by increasing hemicellulose providing another source of hope. Lately, in many genetic mutants and transgenic plants (rice, poplar, maize, and wheat) involved to hemicellulose biosynthesis have presented low biomass yield and high biomass digestibility [85-88]. Among the recognized mutants, GT43 and GT47 synthesize the backbone [89,90], while GT8 catalyze the addition of glucuronic acid residues and GT61 family have been recommended as candidates performing arabino furanose residue addition [91,92]. Currently, Xylan bioengineering is an important subject of research, because its presence in plant lignocellulosic biomass forcefully impacts the overall efficiency of enzymatic hydrolysis. In transgenic crops by using of tissue-specific promoters, plan to enhancing biomass yield and lignocellulose enzymatic saccharification [85,86].

In degradation of hemicellulose two enzymes GH10 and GH11 are engaged. For example in transgenic maize have been reported that overexpression of GH11 (xynB) gene lead to enhances biomass enzymatic digestibility [93], while in poplar have showed that GH10 (xyn10A) gene by RANi silencing increasing biomass yield [94].

Lignin biosynthesis and degradation

Monolignols with different types of genes are synthesized in the cytoplasm and then transported by ABC transporters to the apoplast [95]. For the biosynthesis of monolignols there are two main steps, in the first stage more than ten genes are engaged which are including: cinnamate 4-hydroxylase (C4H) [96], 4-coumarate-CoA ligase (4CL) [58], coumarate 3-hydroxylase (C3H) [97], cinnamoyl-CoA reductase (CCR) [98], cinnamyl alcohol dehydrogenase (CAD) [99], ferulate 5-hydroxylase (F5H) [100], and 5-hydroxyferulic acid O-methyltransferase (caffeic acid/COMT) [101], caffeoyl-CoA 3-O-methyltransferase (CCoAOMT) [79], phenylalanine ammonia lyase (PAL) [102], shikimate hydroxycinnamoyl transferase (HCT) [103]. In the second steps, catalyze hydroxylation and methylation reactions then synthesize lignin monomers [104]. Until now, lignin biosynthesis have been recognized in various plant species in particular in transgenic and genetic mutants plants (Table 2). For instance, in Arabidopsis overexpression of CCoAOMT results in enhanced plant height with concomitant increase in lignin compared to control plants [105], In addition, in sorghum four site mutations of COMT, have shown lower levels of lignin and improved biomass digestibility [106], while RNAi silencing of the Pv4CL1 gene in transgenic switchgrass leads to reduced lignin content and improved fermentable sugar yields [107]. Moreover, in sugarcane RNAi suppression of SbCOMT gene reduces lignin content and recalcitrance [108]. Although, in almost all samples the down-regulation of these genes in genetic mutants and transgenic plants may enhance biomass enzymatic digestibility, but it affects normal plant growth and stress tolerance with an important reduced biomass yield in these plants (Table 2). Therefore, it has mentioned that the low of lignin is not a proper aim to cell wall modification in bioenergy crops.

Plant species	Wall polymer	Gene	Theory	Affect	References
Arabidopsis	Cellulose synthesis	AtCesA2, 5	pAtCesA6: Prc1-1 (OE)	Increase cellulose	[71]
Arabidopsis	Cellulose synthesis	AtCesA1,3	Aegeus (A903V), ixr1-2 (T942I)	Reduce cellulose, Crystallinity	[146]
Arabidopsis	Cellulose synthesis	AtCOBL2	cobl2-1, cobl2-2 (T-DNA)	Reduce CrI	[147]

Barley	Cellulose synthesis	HvCesA4, 8	CesA4, 8 (OE)	Reduce cellulose; defective plant growth	[81]
Poplar	Cellulose synthesis	PtdCesA8	CesA8 (OE)	Reduce cellulose, defective plant growth	[80]
Rice	Cellulose synthesis	OsCesA4	bc11 (G858R), NE1031, ND5658 (Tos17)	Reduce cellulose, defective plant growth	[148]
Brassica distachyon	Cellulose synthesis	BdCesA4, 7	pUBI:CESA4, 7 (amiR)	Reduce cellulose, CrI; defective plant growth	[149]
Arabidopsis	Cellulose degradation	AtKORRIGAN1	irx2-2(P553L), kor1-1 (T-DNA)	Reduce primary cellulose; increase CrI; defective plant growth	[145]
Arabidopsis	Cellulose degradation	PtGH9B5, C2	pAtCesA8:GH9B5, C2 (OE)	Increase CrI; defective plant growth	[83]
Arabidopsis	Cellulose degradation	AtGH9C2	GH9C2 (RNAi)	Reduce CrI	[83]
Arabidopsis	Hemicelluloses synthesis	AtIRX10, 10L (GT47)	irx10, irx10l (T-DNA)	Reduce GX; defective plant growth	[90]
Arabidopsis	Hemicelluloses synthesis	AtIRX14,14L (GT43)	irx14, irx14L (T-DNA)	Reduce Xyl, GX; defective plant growth	[89]
Arabidopsis	Hemicelluloses synthesis	AtIRX15, 15L (DUF579)	irx15, 15l (T-DNA)	Reduce xylan, Xyl	[146]
Arabidopsis	Hemicelluloses synthesis	AtESK1 (DUF231)	esk1 (T-DNA)	Reduction in xylan acetylation	[147]
Arabidopsis	Hemicelluloses synthesis	AtMUR3/ AtMURUS3 (GT47)	mur3 (T-DNA)	Reduce xyloglucan, defective plant growth	[153]
Arabidopsis	Hemicelluloses synthesis	AnAXE1 (GT43)	AXE1-eGFP	Reduction in xylan acetylation, increase ethanol yields	[154]
Wheat	Hemicelluloses synthesis	TaXAT1, 2 (GT61)	XAT1,2 (RNAi)	Increase Xyl /Ara	[155]
Poplar	Hemicelluloses synthesis	PtGAUT12.1,12.2 (GT8)	GAUT12.1, 12.2 (RNAi)	Reduce xylan	[85]
Rice	Hemicelluloses synthesis	OsIRX10 (GT47)	Osirx10 (RGT6229D)	Reduce Xyl/Ara	[156]
Rice	Hemicelluloses synthesis	OsXAX1(GT61)	axa1 (T-DNA)	Reduce Xylan, ferulic and coumaric acid	[86]
Poplar	Hemicelluloses degradation	PtxtXyn10A (GT10)	xtXyn10A (RNAi)	Not affected	[94]
Maize	Hemicelluloses degradation	XynB, ThiXynB (GT11)	XynB, iXynB (OE)	Not affected	[93]
Rice	Lignin synthesis	Os4CL3	4CL3 (RNAi)	Lignin reduction	[157]
Sorghum	Lignin synthesis	SbCOMT	comt (A71V, P150L, G225D, G325S)	comt (A71V, P150L, G225D, G325S)	[106]
Switchgrass	Lignin synthesis	Pv4CL1	4CL1 (RNAi)	Reduce lignin, G and increase H, S/G	[107]
Switchgrass	Lignin synthesis	PvCOMT	COMT (RNAi)	Lignin reduction	[158]
Maize	Lignin synthesis	ZmCOMT	pZmAdh1::COMT (RNAi)	Reduce lignin and S	[159]
Poplar	Lignin synthesis	PtCCR	CCR (RNAi)	Lignin reduction, increase G and hemicellulose	[98]
Arabidopsis	Lignin synthesis	AtMOMT	momt3 (T133L-E165I-F175I)	Reduce lignin, G, S	[160]
Arabidopsis	Lignin synthesis	AtCSE-1	cse-1 (T-DNA)	Reduce lignin and G, increase H	[161]

Alfalfa	Lignin synthesis	MsHCT	HCT (RNAi)	Lignin reduction, increase in H	[103]
Poplar	Pectin synthesis	PtGAUT12	GAUT12 (RNAi)	Reduce Xyl, GalA, HG, RG; Increase Man and Gal	[85]
Arabidopsis	Pectin synthesis	AtQUA2-1	qua2-1 (R2389stop)	Reduce GalA and de-methyl-esterified HG, increase Gal and Xyl	[115]
Arabidopsis	Pectin synthesis	AtPMEI	PMEI (OE)	Reduce de-methyl-esterified HG	[114]
Arabidopsis	Pectin synthesis	AtPME3	pme3 (T-DNA)	Reduce de-methyl-esterified HG, increase DM	[115]
Arabidopsis	Pectin degradation	PcPL1	pMDC7_SpPcPL1-HA (OE)	Increase Glc	[116]
Arabidopsis	Pectin degradation	AnPG	PG (OE)	Reduce GalA and de-methyl-esterified HG	[116]
Poplar	Pectin degradation	PtxtPL1-27	PL1-27 (OE)	Increase pectin and xylan's solubility	[162]

Table 2: Dominant genes nominate and genetic engineering theory feasible for plant cell wall manipulation.

Lignin degradation is a very complicated phenomenon requiring the concerted action of many hydrolytic and oxidative enzymes [109]. The lignin degradation process is further involved by the cooperative action of several supplementary enzymes such as glyoxal oxidase, aryl-alcohol oxidase, pyranose 2-oxidase, cellobiose dehydrogenase, or cellobiose/quinone oxidoreductase [110]. Recent research presented that in transgenic Arabidopsis, overexpression of microRNA (miRNAs) reduced lignin deposition with a concomitant decrease in the thickness of the secondary walls of vessels leading to the weakening of vascular tissues [110].

Pectin biosynthesis and degradation

Pectin biosynthesis because of complex organization in plant cell walls is extremely involved in plant growth and stress response [111]. There are many genes that are distinguished to play a role in pectin biosynthesis, but their influence on enzymatic saccharification are not clear and needs more research [112]. For instance, in transgenic Arabidopsis recent research has shown that expression of a fungal polygalacturonase or pectin methylesterase inhibitor could lead to a reduced de-methyl-esterified homogalacturonan (HG) and increased biomass digestibility, In addition, down regulation of PME3, QUA2-1 and GAUT12 could drastically increase biomass digestibility and influence biomass yield in Arabidopsis mutants and poplar transgenic plants [85,113].

Pectin degradation, in transgenic Arabidopsis and poplar have indicated that overexpression of PL and PG genes result in low biomass yield and high digestibility [114]. Hence, a new theory is necessitated to improve both biomass yield and digestibility by genetic manipulation of GH9, GH10, GH11 genes which are connected in cellulose and hemicelluloses modification but not in pectin degradation.

Effects of Pretreatments on Biomass Digestibility

Biomass pretreatment mainly is one of the major steps in the production of biofuel [115]. Degradation of lignocellulosic biomass because of natural recalcitrance is very hard. The rate of biomass digestibility is affected by these main factors:

- Crl of cellulose,
- breaking down cross-linked matrix of hemicelluloses and lignin,
- Accessible porosity,
- Lignin protection [116].

In the past few decades, different pretreatment processes have been developed to enhance the biomass digestibility, including physical (hot water, microwave irradiation and steam explosion), chemical (alkali, acid, and ionic liquid), and biological methods [117]. The main effect of different pretreatment methods on the compositions of lignocellulosic biomass summarized in Table 3. As shown in Table 3, it can be obvious that different pretreatments play specific roles by removing wall polymers or increasing the accessibility of biomass particles [34]. Moreover Table 4 shows the percentage of biomass digestibility by different pretreatments in various plant species.

Pretreatment method	Lignin removal	Hemicellulose removal	Cellulose de-crystanilization	Increase accessible surface
Alkaline	H[a]	H	ND[a]	H
Acid	M[a]	H	ND	H
Ionic liquid	M	L[a]	H	H
Steam explosion	L	H	L	H

Microwave irradiation	L	M	H	H
Hot water	H	H	ND	M
Biological	H	M	ND	H

Table 3: Effect of different pretreatment methods on the compositions lignocellulosic biomass. H[a]: high effect; M: medium effect; L: low effect; ND: not determined.

Chemical pretreatment

For chemical pretreatment using alkaline (NaOH, CaO, NH_3, H_2O) or acid (H_2SO_4, H_3PO_4, HCl), lignin and hemicellulose removal is influenced by pH. Alkaline pretreatment using NaOH usually extracts more lignin than acid pretreatment using HCl and H_2SO_4 by disassociating hydrogen and other covalent bonds with cellulose microfibrils, while acid pretreatment often gives higher wall polymers by splitting strong chemical bonds under high temperatures [116,118,119]. Besides, alkali-based pretreatment at high temperatures had minor impact on biomass digestibility, but at the low temperatures could lead to much higher biomass digestibility, compared to acid pretreatment executed in the biomass samples [120-122]. Additionally, both acid and alkaline pretreatments removed almost all carboxylic acid substitutions such as acetyl groups and uronic acids [120].

Lately, ionic liquid (IL) is also known as one of the most favorable pretreatment which can solubilize and separate cellulose from other plant cell wall efficiently at mild temperature [121-125]. Furthermore, it have reported the effect of anion component on the efficacy of pretreatment between two ILs ([Bmim][OAc] and [Bmim] [$MeSO_4$]), their result suggested that acetate anion removed >32% of lignin from maple wood flour and considerably reduced cellulose Crl, but pretreatment in [Bmim][$MeSO_4$] only removed 19% of lignin without decreasing the Crl [126]. Moreover, IL pretreatment could improve lignocellulose enzymatic saccharification in biomass samples with low cellulose CrI and low lignin levels [127-130], by comparison mild alkali pretreatment in Miscanthus efficiently extracts G-rich lignin for high biomass digestibility [125]. Recently, in Miscanthus stem have presented that two-step pretreatments with 2% NaOH and 1% H_2SO_4 are optimal for improving biomass digestion in hemicelluloses-rich samples via the efficient co-extraction of hemicelluloses and lignin [131-135].

Pretreatment method	Plant species	Pretreatment	Biomass digestion (%)	References
	Miscanthus stem	NaOH, H_2SO_4	100	[131]
	Miscanthus stem	NaOH	93-100	[130]
	Miscanthus stem	NaOH, H_2SO_4	99	[124]
	Wheat and rice straw	NaOH	60-93	[34]
	Maize straw	NaOH, H_2SO_4	98	[32]
	Sweet sorghum bagasse	NaOH, H_2SO_4	40-100	[30]
Chemical and Physic-chemical pretreatments	Rice straw	$(NH_4)CO_3$	72	[97]
	Miscanthus stem	NaOH, H_2SO_4	26-86	[54]
	Switchgrass stem	Ionic liquid	80	[163]
	Sugarcane bagasse	Ionic liquid	98	[164]
	Poplar wood	Ionic liquid	97	[165]
	Rice straw	Microwave, alkali	70	[166]
	Sugarcane bagasse	Hot water, NaOH, HCl	72-77	[167]
	Cotton stalk	Steam explosion, NaOH	78	[27]
	Mustard stalk	Steam explosion, alkali, dilute acid	81	[168]
	Poplar wood	Hot water	91	[137]
Physical Pretreatments	Oilseed rape straw	Steam explosion	86	[136]
	Wheat bran	Hydrothermal microwave	91	[139]
	Rice straw	*Trichoderma viride*	56	[143]
	Poplar wood	White rot fungus	85	[144]
Biological Pretreatments	Wheat straw	white rot fungi (*Pleurotus ostreatus*)	35	[145]

Table 4: The percentage of biomass digestibility by different pretreatments in various plant species.

Physical pretreatment

The purpose of physical pretreatments are to increase the accessible specific surface area of lignocellulosic materials to enzymes via diminishing of biomass particle size or disrupting their structural regularity [136-139]. Size reduction not only increases the specific surface area of biomass but also reduces cellulose DP and Crl, but it depends on biomass compositions [140-152]. Liu et al. [132]

investigated the effect of steam explosion pretreatment on corn stalk particle size for enhancing enzyme digestibility and the result shown that the amount of secondary product was higher and sugar recovery was lower for larger biomass particle size; although, during enzymatic hydrolysis sugar conversion and yield were higher. With the increase of particle size, individual surface area and Crl reduction. It have reported that stem explosions are powerful for improving biomass digestibility in oilseed rape straw and cotton stalks by giving higher wall polymers and reducing cellulose DP [153-155], Whereas reported in Populus wood that hot water is effective for high bioethanol production in rich in lignin level [156].

Another method of physical pretreatment of lignocellulosic biomass is microwave irradiation. Over many years this pretreatment method has been advanced, and is distinguished for its high heating efficiency and easy operation. In addition, it was reported that association of microwave with chemical pretreatments are more effective than the formal heating chemical pretreatments [157]. Wheat bran pretreatment by using hydrothermal microwave and their results showed that hydrothermal microwave could increase biomass hydrolysis by 91% with high arabinoxylans [158].

Biological pretreatment

The most expensive pretreatment method due to the high cost of specific microorganisms is biological pretreatment. There are three main groups of fungus: white rot, brown rot and soft rot fungi which have been used for lignin and hemicelluloses degradation [159]. The most greatly used microorganisms among these fungi are white-rot fungi [160] which displayed obvious impact on delignification, cellulose DP reduction, and partial hydrolysis of hemicellulose [161]. For instance, white rot fungi (*Trichoderma viride*) in rice straw can be used for the digestion of lignin (56%) [162] and also white rot fungus in poplar wood can efficiently deconstruct lignocellulose construction, resulting in biomass enzymatic saccharification enhancement [163]. After wheat straw was pretreated with white rot fungi (*Pleurotus ostreatus*) for five weeks, about 35% of the original wheat straw was changed into reducing sugars in the following enzymatic hydrolysis by comparison with 12% of the un-pretreated samples [164].

Conclusion

Collectively, the recent researches described in this review clearly suggest that:

(1) Based on the cell wall structures, cellulose Crl and DP are the key factor that negatively effects on biomass digestibility under various physical and chemical pretreatment in almost all plant species investigated.

(2) Hemicellulose Ara level or reverse Xyl/Ara has a positive influence on biomass enzymatic hydrolysis, in most plant species investigated by reducing cellulose Crl, likely though the interlinking of Ara with β-1,4-glucan of the native cellulose by hydrogen bonds.

(3) Pectin and uronic acids by reducing cellulose Crl (Miscanthus accessions) have a positive effect on biomass scarification.

(4) The influence of G-monomer on biomass digestion is dual, but enhances biomass yield. The negative impact because of varied interrelation of G-monomer with hemicelluloses indirectly affect Ara mutual action with amorphous regions or lead to an effective extraction in vitro of lignin-hemicellulose complex for more cellulose access after different pretreatment.

(5) The major enzymes on lignocellulosic engineering (Biosynthesis and degradation) in bioenergy crops are GH9, GH10, GH61 and GT43. GH9 genes may has specific action on producing amorphous regions on the cellulose surface, while GH10, GT43, and GT61 genes could catalyze Ara and uronic acids production to have more connection with the amorphous regions which support normal plant growth and high biomass yield.

(6) Increased amorphous areas of cellulose (low Crl and DP) may result in optimal cell wall modification.

(7) An appropriate mild pre-treatment especially dilute acid and physicochemical methods could be applied for biofuel production subjective to cell wall modification in amorphous regions of cellulose microfibrils in bioenergy plants.

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