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REVIEW

A mini review of xylanolytic enzymes with regards to their synergistic interactions during hetero-xylan degradation

Samkelo Malgas[1] · Mpho S. Mafa[1,2] · Lithalethu Mkabayi[1] · Brett I. Pletschke[1]

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Abstract

This review examines the recent models describing the mode of action of various xylanolytic enzymes and how these enzymes can be applied (sequentially or simultaneously) with their distinctive roles in mind to achieve efficient xylan degradation. With respect to homeosynergy, synergism appears to be as a result of β-xylanase and/or oligosaccharide reducing-end β-xylanase liberating xylo-oligomers (XOS) that are preferred substrates of the processive β-xylosidase. With regards to hetero-synergism, two cross relationships appear to exist and seem to be the reason for synergism between the enzymes during xylan degradation. These cross relations are the debranching enzymes such as α-glucuronidase or side-chain cleaving enzymes such as carbohydrate esterases (CE) removing decorations that would have hindered back-bone-cleaving enzymes, while backbone-cleaving-enzymes liberate XOS that are preferred substrates of the debranching and side-chain-cleaving enzymes. This interaction is demonstrated by high yields in co-production of xylan substituents such as arabinose, glucuronic acid and ferulic acid, and XOS. Finally, lytic polysaccharide monooxygenases (LPMO) have also been implicated in boosting whole lignocellulosic biomass or insoluble xylan degradation by glycoside hydrolases (GH) by possibly disrupting entangled xylan residues. Since it has been observed that the same enzyme (same Enzyme Commission, EC, classification) from different GH or CE and/or AA families can display different synergistic interactions with other enzymes due to different substrate specificities and properties, in this review, we propose an approach of enzyme selection (and mode of application thereof) during xylan degradation, as this can improve the economic viability of the degradation of xylan for producing precursors of value added products.

Keywords Carbohydrate esterases · Degradation · Glycoside hydrolases · Lytic polysaccharide monooxygenase · Synergy · Xylan

Abbreviations

AA	Auxiliary activity
Abf	α-Arabinofuranosidase
Agu	α-Glucuronidase
AGX	Arabinoglucuronoxylan
AX	Arabinoxylan
AXE	Acetyl xylan esterase
AXH-d	Doubly substituted L-Araf specific α-arabinofuranosidase
AXH-m	Mono-substituted L-Araf specific α-arabinofuranosidase
CAZy	Carbohydrate active enzyme database
CAZyme	Carbohydrate-active enzyme
CE	Carbohydrate esterase
DS	Degree of synergy
EC	Enzyme commission number
FA	Ferulic acid
FAE	Feruloyl esterase
GE	Glucuronoyl esterase
GH	Glycoside hydrolase
GX	Glucuronoxylan
LPMO	Lytic polysaccharide mono-oxygenase
Rex	Oligosaccharide reducing-end xylanase
RS	Reducing sugar(s)
XOS	Xylo-oligosaccharide(s)
Xyn	β-Xylanase
Xyl	β-Xylosidase

✉ Brett I. Pletschke
b.pletschke@ru.ac.za

[1] Enzyme Science Programme (ESP), Department of Biochemistry and Microbiology, Rhodes University, Grahamstown, Eastern Cape 6140, South Africa

[2] Protein Structure-Function Research Unit (PSFRU), School of Molecular and Cell Biology, Wits University, Johannesburg, Gauteng 2000, South Africa

Introduction

Lignocellulosic biomass is made up of three major components, namely, cellulose (40–60%), hemicellulose (20–40%) and lignin (10–25%) (Kang et al. 2014). Hemicelluloses are the second most abundant terrestrial polysaccharide in nature, after cellulose, and represent about 20–40% of the dry weight of the lignocellulosic biomass. Hemicellulose is a hetero-polysaccharide composed of pentoses (xylose and arabinose), hexoses (mannose, glucose and galactose) and sugar acids (methyl-glucuronic acid) (Saha 2003). Hemicelluloses are usually grouped into classes based on the main sugar residues present in the backbone, and these include xyloglucans, xylans, mannans and glucomannans, and β-glucans (Scheller and Ulvskov 2010).

Over the past few decades, xylan has attracted much attention for its industrial importance in the bioconversion of lignocellulosic biomass to biofuels, pulp and paper, food, improvement of animal feedstock digestibility, production of pre-biotic oligosaccharides and organic synthesis of value added products (VAPs) such as xylitol (Guo et al. 2013; Kamat et al. 2013; Samanta et al. 2015; Charoensiddhi et al. 2017). Enzymatic hydrolysis of plant carbohydrates such as xylan using xylanolytic enzymes has emerged as the most prominent technology for the conversion of biomass into VAPs (Van Dyk and Pletschke 2012).

Xylanolytic enzymes are produced by a variety of micro-organisms including bacteria, fungi and yeast, which are naturally found in diverse niches such as insect guts, manure, waste water, hot environmental samples and chicken cecum to name a few (Kumar et al. 2016; Chadha et al. 2019). In addition to the production of a variety of xylanolytic enzymes, many micro-organisms produce multiple isoforms of the same class of xylanolytic enzyme with different properties (Collins et al. 2005; Malgas et al. 2017; Chadha et al. 2019). It is noteworthy to mention that not all micro-organisms produce all the enzymes required in a xylanolytic arsenal for efficient xylan degradation. For instance, *Thermomyces lanuginosus* only produces a single GH11 xylanase, while *Thermomyces stellatus* produces ten xylanases from GH families 10, 11 and 30 (Chadha et al. 2019). With a huge reservoir of xylanolytic enzymes available, it is important to know which enzymes would be required (i.e. enzymes with high stability and activity, cooperability with other enzymes and tolerance to inhibitors) for efficient xylan degradation in industry for high yields of VAP production.

Recent studies have demonstrated synergistic interactions between various xylanolytic enzymes that occur and improve xylan and xylan-containing biomass bioconversion into the precursor sugars required for VAP synthesis. Here, we summarize recent studies and hypotheses on how the glycoside hydrolase (GH) families, auxiliary activity enzymes (LPMOs and carbohydrate esterases) and mode of application of the xylanolytic enzymes affect their synergistic associations during xylan degradation for industrial applications.

Xylan structure

The structure of xylan is quite variable, ranging from linear backbones constituted of β-1,4-linked poly-xylose residues denoted as homo-xylans to branched hetero-xylans, whereby the prefix 'hetero' denotes the presence of branching sugar residues other than D-xylose. The branching sugars in hetero-xylans consist of either L-arabinofuranose linked to the C-3 positions of D-xylose residues, these hetero-xylans are denoted as arabinoxylans (AX) (Schendel et al. 2015), or of D-glucuronic acid or its methyl derivative, 4-O-methyl-D-glucuronic acid, linked to the C-2 positions of D-xylose residues, these hetero-xylans are denoted as glucuronoxylans (GX) (Togashi et al. 2009), and/or a mixture of both sugars, these hetero-xylans denoted as arabinoglucuronoxylans (AGX) (Ebringerová 2006). The α-L-arabinofuranosyl units in hetero-xylans may further be substituted by hydroxycinnamates (i.e. ferulic acid and *p*-coumaric acid) at the C-5 position (Schendel et al. 2015). The degree and type of branching sugar residues in hetero-xylans vary depending on the plant source of the xylan in question. Xylans of several hardwoods are acetylated at either the C-2 or C-3 position and/or at both of these positions of D-xylose residues (Pinto et al. 2005). Xylan and lignin are generally considered to be linked through covalent bonds to form lignin–carbohydrate complexes (LCCs). In the case of GX, cross linkages are formed between 4-O-methyl-D-glucuronic acid residues and aliphatic chains of lignin (Li and Helm 1995).

Xylan degradation

A consortium of xylanolytic Carbohydrate-Active enzymes (CAZymes), including glycoside hydrolases (GH) and auxiliary activity enzymes [i.e. carbohydrate esterases (CE) and lytic polysaccharide monooxygenases (LPMOs)], are required for complete hetero-xylan degradation in lignocellulosic biomasses. In this section, we provide a summary of the biochemical properties of the enzymes required for hetero-xylan degradation.

Xylanases (EC 3.2.1.8) are key enzymes for xylan degradation, they act on the xylan backbone, cleaving randomly at internal sites on β-1,4-glycosidic linkages between xylopyranosyl residues. Since xylanases randomly cleave the xylan backbone, their action products

are diverse and may include xylobiose, xylotriose, xylotetraose, longer and/or branched xylo-oligomers (XOS). Xylanases belong to several GH families i.e. family 5, 8, 9, 10, 11, 16, 30, 43, 51 and 98 in the CAZy database (www.cazy.org). Some GH5 subfamily 34 arabinoxylanases have been reported to possess a decoration requirement which shows catalytic specificity for arabinose-substituted xylans, generating XOS branched at the reducing end (Karlsson et al. 2018). GH8 xylanases are mechanistically distinct from other xylanase GH families (retaining mechanism) as they are the only family which executes catalysis via a net inversion mechanism. GH10 xylanases are highly active on short XOS, soluble and branched xylans (Biely et al. 2016; Karlsson et al. 2018). GH11 xylanases, on the other hand, are highly active on unsubstituted regions of xylan and insoluble xylan, with diminished activity on decorated xylans (Mendis and Simsek 2015). GH30 subfamily 8 xylanases have been shown to be dependent on methyl-glucuronic acid substitutions for activity, and as a result, are called glucuronoxylanases (Biely et al. 2014, 2015).

Recently discovered oligosaccharide reducing-end xylanases, also called Rexs (EC. 3.2.1.156), are strictly found in family GH8 (Valenzuela et al. 2016). Rexs hydrolyse the xylan backbone or XOS from the reducing ends producing short XOS and xylose (Lagaert et al. 2007; Juturu and Wu 2012; Malgas and Pletschke 2019). The xylosidases (E.C 3.2.1.37), on the other hand, hydrolyse the xylanase and Rex-produced XOS by continuously removing D-xylose residues from the non-reducing termini, but do not hydrolyse xylan (Yan et al. 2008; Knob et al. 2010; Huy et al. 2015). Xylosidases are presently found in families GH 1, 2, 3, 5 (Subfamily 22), 30, 39, 43, 51, 52, 54, 116 and 120.

Alpha-arabinofuranosidases, also called Abfs (EC 3.2.1.55), hydrolyse substituents of α-L-arabinofuranoside (L-Araf) residues in AXs and arabinosyl substituted XOS (Lagaert et al. 2014). Abfs belong to GH families 2, 3, 10, 43, 51, 54 and 62. Abfs that release L-Araf units from mono-substituted main-chain D-xylopyranosyl (D-Xylp) motifs are termed AXH-m, while those that release single L-Araf residues from double-substituted main-chain D-Xylp motifs are termed AXH-d. Only GH43 and 51 Abfs have been demonstrated to readily de-branch L-Araf on both mono- and di-substituted D-Xylp motifs (Lagaert et al. 2014). Alpha-glucuronidases (EC 3.2.1.139), on the other hand, hydrolyse α-(1,2)-D-(4-O-methyl)-glucuronosyl side chains in the main chains of GXs and AGXs. Generally, GH67 glucuronidases prefer short glucuronic acid substituted XOS and are generally intracellular or membrane associated (Nagy et al. 2002; Nurizzo et al. 2002; Golan et al. 2004), while GH115 glucuronidases are more active on polymeric glucuronic acid-containing xylans, these being consequently extracellularly produced enzymes (Tenkanen and Siika-Aho 2000; McKee et al. 2016).

LCCs pose a barrier to xylan hydrolysis by glycosyl hydrolases and lead to a major limitation on the utilisation of plant biomass as a renewable source (Jeffries 1990). Therefore, efficient enzymatic hydrolysis of xylan also requires the carbohydrate esterases (CEs) such as feruloyl esterases (FAEs), glucuronoyl esterases (GEs) and acetyl xylan esterases (AXEs). Acetyl xylan esterases (EC 3.1.1.72) are mainly found in CE families 1–7 and 16 in the CAZy database and are primarily involved in the hydrolysis of ester bonds to liberate acetic acid from acetylated polysaccharides, making the main chain accessible to glycoside hydrolase enzymes (Zhang et al. 2011). Feruloyl esterases (E.C. 3.1.1.73), on the other hand, are classified into CE family 1 (Lei et al. 2016). FAEs catalyse the cleavage of ester bonds between a hydroxycinnamate and AX, releasing a phenolic acid such ferulic acid or *p*-coumaric acid (Wong et al. 2013). Finally, glucuronoyl esterases (EC3.1.1.-) belong to CE family 15; GEs cleave ester bonds between lignin aliphatic alcohols and the 4-O-methyl-D-glucuronic acid substituents of GX (Baath et al. 2016).

Recently, lytic polysaccharide monooxygenases (LPMOs) or Auxiliary activity proteins (AAs, EC 1.14.99.53-54/56) have been discovered and hold major potential for future biomass degradation applications (Horn et al. 2012; Arfi et al. 2014). These enzymes enhance glycoside hydrolase activity by cleaving glycosidic bonds of polysaccharides in the crystalline and insoluble portion via an oxidative mechanism, consequently resulting in complete polysaccharide degradation (Cragg et al. 2015; Müller et al. 2015). LPMOs are currently sequence-classified into four families in the CAZy database. Members of the AA9 family are mainly active on cellulose with a few reported to be active on hemicellulose. On the other hand, members from family AA10 exhibit activity on cellulose or chitin. Members from AA11 and AA13 families are active on chitin and starch, respectively.

A number of comprehensive reviews on the biochemical characteristics of xylanolytic enzymes (Knob et al. 2010; Juturu and Wu 2012; Lagaert et al. 2014) and non-GH activity CAZymes (Hemsworth et al. 2015; Oliveira et al. 2019) have been published over the past decade, this review will focus on recent advances in understanding the synergism which occurs between xylanolytic enzymes during the degradation of xylans in lignocellulosic biomass.

Synergistic actions of xylanolytic enzymes during xylan hydrolysis

As mentioned before, a consortium of xylan specific CAZymes synergistically act on xylans, leading to their complete hydrolysis into monomeric sugars, acids and monophenols. Synergism between hemicellulolytic enzymes is

characterised into two modes, namely homeosynergy (that between two backbone-cleaving enzymes or two side-chain-cleaving xylanolytic enzymes) and heterosynergy (that between a side-chain-cleaving and a main-chain-cleaving enzyme) (Moreira and Filho 2008). Based on the complexity of xylan, which includes the presence of substituents on its backbone, xylanolytic enzymes are expected to exhibit these two types of synergisms during its hydrolysis.

Homeosynergy studies between glycoside hydrolases during xylan hydrolysis

Synergism between xylanolytic enzymes such as xylanases, exo-xylanases and xylosidases is vital for efficient xylan backbone degradation and the production of xylose (see Table 1). Synergistic combinations of (1) xylanase with xylanase and (2) exo-xylanase (Rex) with xylanase(s) have been investigated and generally lead to higher production of XOS. As mentioned previously, xylanases of different GH families show varied substrate specificities (Christakopoulos et al. 2003; Beaugrand et al. 2004; Broeker et al. 2018), therefore, combining different GH family xylanases generally leads to a diversity and higher production of XOS (Goncalves et al. 2015; Malgas and Pletschke 2019). On the other hand, the Rex with xylanase synergism is as a result of the Rex showing a different specificity compared to xylanases; (1) acting from the reducing end of xylans and (2) on the xylanase generated XOS to produce smaller XOS and xylose (Liu et al. 2019a; Malgas and Pletschke 2019). The xylosidases then further hydrolyse the XOS that are produced by both Rex and xylanases into xylose (see Table 1). Interestingly, xylan backbone degradation is not a linear process, but a relational loop between the enzymes involved as Liu and co-workers showed higher synergism between xylanase and xylosidase when the enzymes are applied *simultaneously* compared to when applied *sequentially* (Liu et al. 2019b). We now know that XOS inhibit glycoside hydrolases and hamper biomass degradation (Kumar and Wyman 2009; Qing et al. 2010). Therefore, hydrolysis of XOS by xylosidases, which are their preferred substrates compared to xylans, should reduce product inhibition of xylanases—leading to a complementary relationship between the two enzyme classes whereby xylosidases further hydrolyse the XOS that are produced by both exo- and endo-xylanases (after product inhibition alleviation) into xylose.

Heterosynergy studies between glycoside hydrolases during xylan hydrolysis

Generally, with regards to heterosynergistic interactions between backbone- and side-chain-cleaving enzymes, two cross relationships appear to lead to synergism between these enzymes during hetero-xylan degradation (see Table 2). Firstly, synergism appears to result when a side-chain-cleaving enzyme (i.e. GH115 glucuronidase) removes decorations on hetero-xylans that would have hindered the action of a backbone cleaving enzyme (i.e. xylanases) from liberating XOS (Yang et al. 2015). It is noteworthy to mention that, to date, there is no Abf reported to display activity on intact xylan polymers, therefore, the above-mentioned cross relationship may be only applicable to xylanases and GH115 glucuronidases. This type of synergism leads to a higher production of XOS when these enzymes are applied, and has been reported to work both *simultaneously* and *sequentially* (see Table 2). Secondly, synergism also occurs when a main-chain-cleaving enzyme liberates decorated XOS from hetero-xylans (which are preferred substrates compared to polymeric xylan) for side-chain-cleaving enzymes (Rosa et al. 2013). This type of synergism leads to a higher production of the hetero-xylan decorating sugars such as L-Araf and 4-O-methyl-glucuronic acid. Interestingly, combining GH67 glucuronidases with GH10 xylanases always yields synergism, however, combining them with GH11 xylanases doesn't lead to synergism (Rosa et al. 2013; Rhee et al. 2017) (see Table 2). It is likely that the GH10 xylanase produces 4-O-methyl-glucuronic acid terminal substituted XOS that are a more preferred substrate for GH67 glucuronidase than the internally substituted XOS produced by GH11 xylanases (Karlsson et al. 2018). However, the GH115 derived glucuronidases appear to tolerate the GH11 xylanase-produced 4-O-methyl-glucuronic acid substituted XOS, as synergism is observed between these enzymes (Rhee et al. 2017).

Synergy studies on xylan hydrolysis by GHs and axillary activity CAZymes

A few studies have been reported in literature where glycoside hydrolases have been used in conjunction with axillary activity CAZymes (i.e. CEs or LPMOs) for improved hetero-xylan degradation. Here we give a summary of the findings from these studies.

CEs exhibit a strong synergistic relationship with xylanases for degradation of various lignocellulosic substrates (see Table 2). It appears that the removal of side groups by CEs from the xylan main chain and on branching sugars on the xylans increases accessibility of xylanases to the substrate and improves the production of XOS. Hydrolysis of xylan by xylanases is often restricted in the presence of acetyl substituents. AXEs are known for their ability to remove acetyl substituents from the xylan main chain and thereby increase accessibility of xylanases to xylan. A number of studies have reported on synergism between AXEs and xylanases for hydrolysis of different substrates (Yang and Liu 2008; Zheng et al. 2013). Secondly, CEs (mainly FAEs) seem to prefer short substituted XOS generated by xylanase as substrates for cleaving ester bonds releasing FA.

Table 1 Homeosynergy studies during xylan degradation

Biomass	Enzyme combination	Order of enzyme addition	Degree of synergy/synergy	References
Xylanase to xylanase synergism				
Wheat bran	XYL10 and XYL11	Simultaneous	No synergy	Beaugrand et al. (2004)
Sugarcane bagasse	XynZ-C and Xyn11A	Simultaneous	Synergy; 2.8-fold RS	Goncalves et al. (2015)
	XynZ-C and XlnB		Synergy; 3.5-fold RS	
	XynZ-C and XlnC		Synergy; 3.3-fold RS	
	Xyn10B and Xyn11A		Synergy; 3.3-fold RS	
	Xyn10B and XlnB		Synergy; 1.3-fold RS	
	Xyn10B and XlnC		Synergy; 3.3-fold RS	
Beechwood xylan	Xyn2A and XT6	Simultaneous	Synergy; 1.15-fold RS	Malgas and Pletschke (2019)
Wheat flour arabinoxylan		Simultaneous	Synergy; 1.15-fold RS	
Beechwood xylan	XynA and XynB	Simultaneous	Synergy; + xylobiose	Ghio et al. (2018)
Extruded wheat straw	XynA and XynB	Simultaneous	Synergy; + xylose	
Xylanase to oligosaccharide reducing-end xylanase (Rex) synergism				
Beechwood xylan	XynA and XynB	Simultaneous	Synergy; 1.6-fold xylose	Santos et al. (2014)
Beechwood xylan	Exo-xylanase and xylanase	Simultaneous	Synergy; 1.2-fold xylose	Juturu et al. (2014)
Oil palm empty fruit bunch		Simultaneous	No synergy	
Beechwood xylan	Xyn10A and Rex8A	Simultaneous	Synergy; + XOS	Valenzuela et al. (2016)
Corncobs	PbRex8A and PbXyn10A	Simultaneous	Synergy, 1.4-fold xylose	Liu et al. (2019a)
Beechwood xylan	Xylanases and BaRex8A	Simultaneous	No synergy	Malgas and Pletschke (2019)
	Xylanases and BhRexA	Simultaneous	Synergy; 1.1-fold xylose	
Wheat flour arabinoxylan	Xylanases and BaRex8A	Simultaneous	No synergy	
	Xylanases and BhRexA	Simultaneous	Synergy; 1.5-fold xylose	
Xylanase (and Rex) to xylosidase synergism				
Beechwood xylan	XynA and GH3 xylosidase	Simultaneous	Synergy; 1.1-fold xylose	Choengpanya et al. (2015)
Barley straw	PcXynC and PcXyl5	Simultaneous	Synergy; ± RS	Huy et al. (2015)
		Sequential	Synergy; + RS	
Beechwood xylan	XynA and XynB	Simultaneous	Synergy; 1.9-fold xylose	Banka et al. (2014)
Finger millet straw	CtXyn11A and BoGH43A	Simultaneous	Synergy; + XOS	Jamaldheen et al. (2019)
Beechwood xylan	Bxcg and Excg1	Simultaneous	Synergy; threefold xylose	Romano de Carvalho et al. (2018)
Beechwood xylan	XynC and Xyl2	Simultaneous	Synergy; 1.5-fold xylose	Faundez et al. (2019)
	XynA and Xyl2	Simultaneous	Synergy; twofold xylose	
Birchwood xylan	XynC and Xyl2	Simultaneous	Synergy; twofold xylose	
	XynA and Xyl2	Simultaneous	No synergy	
Beechwood xylan	XynG 1–1 and rXYL	Simultaneous	Synergy; 16-fold xylose	Liu et al. (2019b)
		sequential	Synergy; 11-fold xylose	
Beechwood xylan	XynA and β-xylosidase	Simultaneous	Synergy; threefold XOS	Martins et al. (2018)
Oat spelt xylan	Xyn455 and Xyl455	Simultaneous	Synergy; + xylose	Sheng et al. (2014)
Beech- and birch-wood xylan	Xylanase and bifunctional xylosidase/arabinofuranosidase	Simultaneous	Synergy; + RS	Kambourova et al. (2007)
Oat spelt xylan			Synergy; + RS	
Beech- and birch-wood xylan, and oat spelt and water-soluble wheat xylan	Xyn11A and Xyl43A	Simultaneous	No synergy	Yang et al. (2014a)
	Xyn11A and Xyl43B			
	Xyn11A and Xyl43A	Sequential	Synergy; 1.2-fold RS	
	Xyn11A and Xyl43B			
Oat spelt xylan	rXyn162 and rXylCD2	Simultaneous	Synergy; + RS	Zhuo et al. (2018)
Cornstalk	rXyn162 and rXylCD2	Simultaneous	Synergy; + RS	
Corncobs	Rex8A, Xyn10A and Xyl43	Simultaneous	Synergy; 98% xylose yield	Liu et al. (2019a)

Where ± represents a moderate synergy and + represents a high DS, RS represents reducing sugars and XOS represents xylo-oligomers

Table 2 Heterosynergy studies during xylan degradation

Biomass	Enzyme combination	Order of enzyme addition	Degree of synergy/synergy	References
Xylanase to arabinofuranosidase synergism				
Wheat xylan	Xylanase and arabinofuranosidase	Simultaneous	Synergy; + RS and XOS	Guerfali et al. (2011)
	Xylanase and arabinofuranosidase	Sequential	Synergy; + RS and XOS	
	Arabinofuranosidase and xylanase	Sequential	No synergy	
Beech- and birch-wood xylan, and oat spelt and water-soluble wheat xylan	XynBE18 and Abf43A	Simultaneous	Synergy; + RS	Shi et al. (2013)
	XynBE18 and Abf43B			
	Abf43A and XynBE18	Sequential	Synergy; RS	
	Abf43B and XynBE18			
Beechwood xylan	HiAbf43 and Xyn11A	Sequential	Synergy; 1.2-fold xylose	Yang et al. (2014b)
Birchwood xylan	HiAbf43 and Xyn11A	Sequential	Synergy; 1.2-fold xylose	
Wheat xylan	HiAbf43 and Xyn11A	Sequential	No synergy	
Xylanase to glucuronidase synergism				
Birchwood xylan	XylA and AguA	Simultaneous	Synergy; + glucuronic acid	Rosa et al. (2013)
	XylB and AguA	Simultaneous	No synergy	
Beechwood xylan	Xyn10A and Agu67A	Simultaneous	No synergy	Jia et al. (2014)
Methyl-glucuronoxylan	Xyn10A and TtAguA	Simultaneous	Synergy; 1.1-fold RS	Wang et al. (2016)
Beechwood xylan	GH10-XA and GH67-GC	Simultaneous	Synergy; + RS	Cobucci-Ponzano et al. (2015)
Methyl-glucuronoxylan	GH10-XA and GH67-GC	Simultaneous	Synergy; + RS	
Sorgum methyl-glucuronic acid	Xyn10 and Agu67	Simultaneous	Synergy; + XOS	Rhee et al. (2017)
	Xyn10 and Agu115	Simultaneous	Synergy; ± XOS	
	Xyn11 and Agu67	Simultaneous	No synergy	
	Xyn11 and Agu115	Simultaneous	Synergy; + XOS	
Beechwood xylan	BoGH30 and BoAgu115A	Sequential	Synergy; + glucuronic acid	Rogowski et al. (2014)
Birchwood xylan	BoGH30 and BoAgu115A	Sequential	Synergy; + glucuronic acid	
Xylanolytic glycoside hydrolase enzyme(s) to carbohydrate esterase (CE) synergism				
Birchwood xylan	Endo I or Endo III, xylosidase and AE	Simultaneous	Synergy, + RS	Kormelink and Voragen (1993)
Birchwood xylan	GLUR + AXE + XYL + βX	Simultaneous	Synergy, + glucuronic acid	Tenkanen and Siika-Aho (2000)
Spruce wood xylan	GLUR + AXE + XYL + βX	Simultaneous	Synergy, + glucuronic acid	
Oat-spelt xylan	AFASE + AE + Xyl + XII	Sequential	Synergy, 1.25-fold RS	Raweesri et al. (2008)
Corn cob	AFASE + AE + Xyl + XII	Sequential	Synergy, 1.32-fold RS	
Corn husk	AFASE + AE + Xyl + XII	Sequential	Synergy, 1.21-fold RS	
Corn bran, wheat bran and switchgrass	RuFae and GH10 xylanase	Simultaneous	Synergy; + FA	Wong et al. (2013)
	RuFae and GH11 xylanase	Simultaneous	Synergy; ± FA	
Insoluble wheat xylan	BiFa1A and BACINT_00569	Simultaneous	Synergy; + RS	Wefers et al. (2017)
	BiFa1B and BACINT_00569	Simultaneous	Synergy; + RS	
Wheat bran	AnFaeA4 and xylanase	Simultaneous	Synergy; 5.5% FA boost	Long et al. (2018)
	AnFaeB5 and xylanase	Simultaneous	Synergy; 6.9% FA boost	
Insoluble wheat xylan	AtFaeD and xylanase	Simultaneous	Synergy; ± FA	Makela et al. (2018)
	AtFaeD and xylanase	Sequential	Synergy; + FA	
Lignin-birchwood xylan	CuGE and GH10 xylanase	Simultaneous	Synergy; + xylose	Mosbech et al. (2018)
Beechwood xylan	rAXE and xylanase	Simultaneous	Synergy; + RS	Hettiarachchi et al. (2019)

Where ± represents a moderate synergy and + represents a high synergy, RS represents reducing sugars, XOS represents xylo-oligomers and FA represents ferulic acid

Currently, there is still very limited information on the synergistic action of GEs and xylanases during degradation of plant biomass as only one study has been reported to date (Mosbech et al. 2018).

Recent studies have broadened the known substrate specificity of LPMOs to include isolated xylan and XOS—such findings have been reported for AA9-family LPMOs from *Lentinus similis* (LsAA9A) and *Collariella virescens* (CvAA9A) (Simmons et al. 2017), and *Myceliophthora thermophila* C1 (MtLPMO9A) (Frommhagen et al. 2015). The implications of these findings are the potential application of LPMOs synergistically with glycoside hydrolases for the degradation of xylans and xylan containing lignocellulosic biomass. Indeed, LPMOs have been shown to synergise with xylanases during the degradation of isolated xylans (Kim et al. 2016; Sanhueza et al. 2018) and xylan-containing lignocellulosic biomass (Jung et al. 2015; Kim et al. 2016). Recently, for the first time, an actinomycete, *Kitasatospora papulose*, AA10-family LPMO has been shown to boost xylose release by a xylanase in beechwood xylan and by Celluclast (a xylanase containing enzyme preparation) on sugarcane bagasse (Corrêa et al. 2019). The synergism between these two enzyme classes is suggested to be due to the mode of action of LPMOs which leads to loosening of the rigid xylan–cellulose polysaccharide matrix in plant biomass and a reduction in inter-microfibril bonding, enabling increased accessibility to the matrix for glycoside hydrolases (Frommhagen et al. 2015; Hu et al. 2018).

A proposed up-to-date model of xylan degradation

A proposed up-to-date general scheme showing how xylanolytic enzymes mechanistically degrade hetero-xylans (i.e. AGXs) in a synergistic fashion is presented below (Fig. 1). Firstly, GH11 xylanases preferably cleave unsubstituted regions of the xylan backbone or insoluble xylans (Kumar et al. 2016). GH11 xylanases may be sterically hindered by the presence of acetyl groups on the xylopyranosides constituting the xylan backbone; this then necessitates the action of CE1 acetyl xylan esterases to remove these groups on the xylan backbone to allow xylanase action to proceed (Adesioye et al. 2016). Secondly, GH10 xylanases (Xyn) cleave highly decorated AGX backbones or the soluble XOS produced by GH11 Xyn and release XOS which contain arabinose or glucuronic side chains at the non-reducing end (Karlsson et al. 2018). On the other hand, GH115 glucuronidases (Agu) are efficient at removing the methyl-glucuronic acid residues from non-terminal positions of both XOS and polymeric xylans (Rhee et al. 2017). The GH115 Agu action removes substituents which otherwise would have sterically hindered GH10/11 Xyn activity during xylan degradation. The GH8 Rex can then hydrolyse xylan from the reducing ends and on the GH10/11 Xyn-produced XOS, leading to the production of shorter XOS and xylose (Malgas and Pletschke 2019). However, arabinofuranosidases and XOS specific glucuronidases may be required for debranching the GH10-produced XOS before Rex can act on them. The arabinofuranosidases (AXH-d) release single L-Araf residues from double-substituted XOS while AXH-m release single L-Araf residues from single-substituted XOS, on the other hand, GH67 glucuronidases (Agu67A) prefer short methyl-glucuronic acid substituted XOS (Lagaert et al. 2014). Regions rich with arabinose and/or glucuronic acid substituents may require the action of both GH5 arabinoxylanase and GH30 glucuronoxylanase, respectively, to cleave these xylans into highly substituted XOS (Biely et al. 2016; Karlsson et al. 2018). These branched XOS can then be acted upon by the debranching enzymes, AXH and Agu67A, respectively. Finally, GH43 xylosidases (Xyl) release xylose from the non-reducing ends of XOS, and as a result, alleviate product inhibition to xylanases by their products (XOS).

A recent review by Biely and co-workers postulated that the addition of side-chain-cleaving enzymes such as α-glucuronidase to a mixture of xylanase and xylosidase (and even Rex) would bring about only small changes in the saccharification yield of xylan (Biely et al. 2016). The reason for this is that some xylan fragments remain esterified with acetic acid. The authors, therefore, postulated that, on de-glucuronylated oligosaccharides, the action of xylosidase would stop at the first acetylated Xylp residue from the non-reducing end as a result, enzymatic saccharification cannot proceed to completion without deacetylation of XOS by acetyl xylan esterases (AXEs) (Biely et al. 2016). CE4/7/16 AXEs have been reported to specifically de-acetylate XOS (Adesioye et al. 2016, 2018). The role of CE16 may be particularly critical for the efficient degradation of the mono-acetylated aldotetraouronic acid ($3''$-Ac^{3}MeGlcA^{3}Xyl$_3$), generated from acetyl-GX degradation by GH10 Xyn, as it is one of the most enzyme resistant acetyl-GX fragments to Agu and Xyl action (Puchart et al. 2016). More CEs, specifically targeting esterified compounds (i.e. hydroxycinnamate groups or lignin) on side chain sugars found on xylan such as arabinose and glucuronic acid, may also be required as debranching enzymes are restricted by these esterified compounds.

In addition to CEs, it has recently been shown that LPMOs are critical in boosting xylan degradation into monosaccharides by GHs (Jung et al. 2015; Kim et al. 2015; Corrêa et al. 2019). Several studies have reported that in a given xylan, the linear and unsubstituted fractions tend to self-associate so as to become aggregated into insoluble aggregates that can interact with crystalline cellulose (Linder et al. 2003; Hu et al. 2018). Interestingly, a recent study has shown that xylans are susceptible to AA14 oxidative cleavage only when they are adsorbed onto crystalline cellulose, and not when they are in solution (Couturier et al.

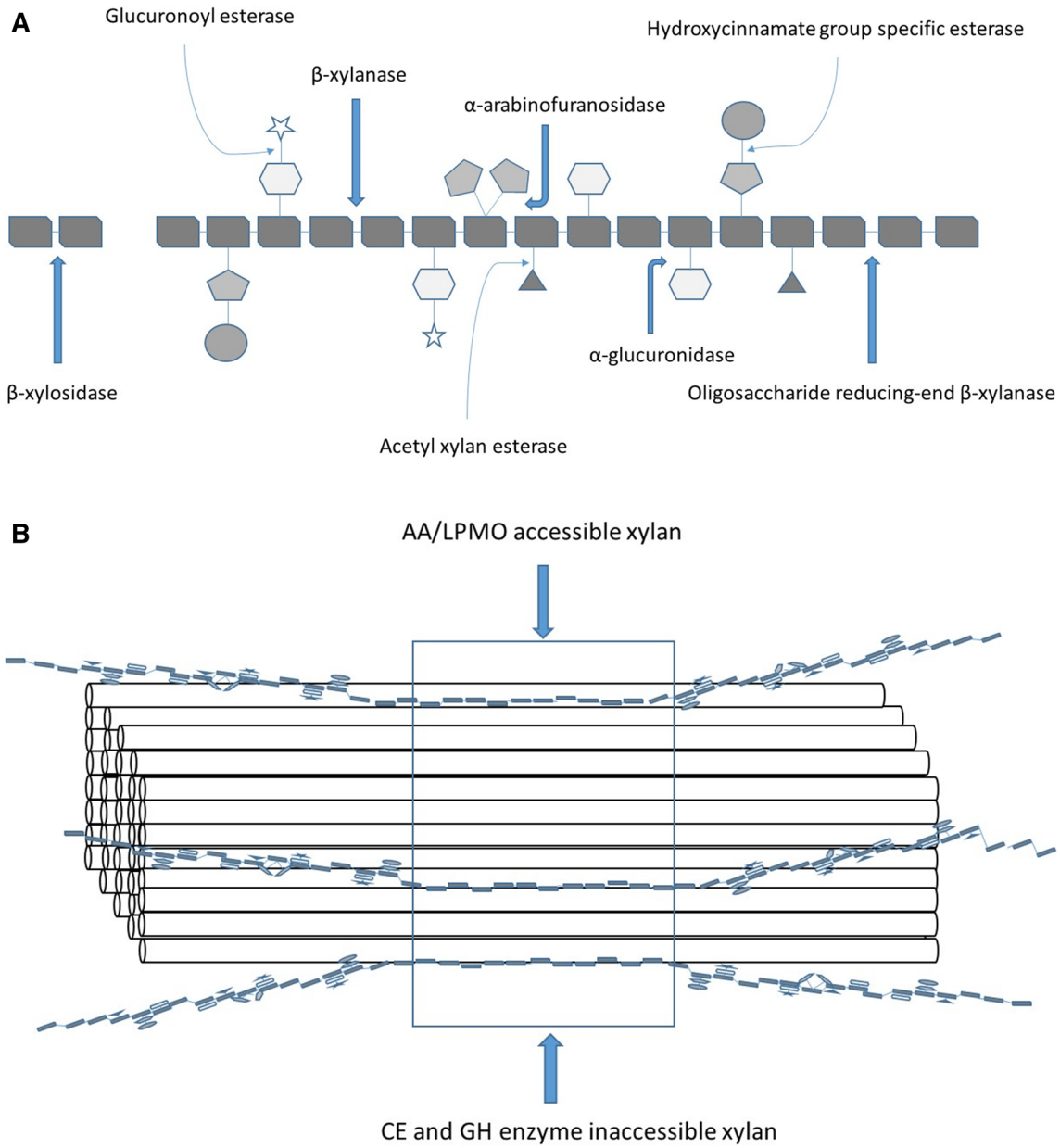

Fig. 1 An illustration of the enzyme sites of the enzymes required to completely degrade **a** hetero-xylans and **b** hetero-xylans associated to cellulose fibers. *Snip diagonal corner rectangles* represent xylose, *pentagons* represent arabinose, *hexagons* represent (methyl)-glucuronic acid residues, *triangles* represent acetyl groups, *circles* represent hydroxycinnamate groups (i.e. ferulic acid or *p*-coumaric acid), *stars* represent aliphatic alcohol groups and *cylinders* represent cellulose chains. The *arrows* represent glycosidic (thick arrows) or ester bonds (thin arrows) recognized by the respective enzymes and the rectangle represents regions of xylan which are flat and in a twofold helical screw ribbon bound to cellulose microfibrils

2018). This has been attributed to recalcitrant xylans bound to cellulose microfibrils displaying a two-fold screw axis conformation aligned parallel to the cellulose chain direction, which seems to be compatible with the proper orientation of the carbohydrate H1 and H4 atoms with respect to the LPMO catalytic center (Linder et al. 2003; Couturier et al. 2018). These xylan-xylan and xylan-cellulose entanglement junctions are believed to be inaccessible to glycoside hydrolases, therefore, the action of LPMOs is crucial in reducing these inter-microfibril bonding sites to allow accessibility of xylanolytic glycoside hydrolases to act on the xylan polysaccharides found in these regions. As it is known that LPMOs are copper dependent enzymes requiring an electron donor, recently, the mechanism and origin of the electron supply for these enzymes in biological systems such as plant biomass has been shown to be from

Table 3 A list of all the enzymes required for efficient degradation of AGX

Enzyme name (EC number)	CAZyme family (Sub-family)	Substrate specificity
Abf (EC 3.2.1.55)	GH43, 51 (AXH-d)	Active on XOS with doubly substituted L-Araf residues
	GH43, 51, 54, 62 (AXH-m)	Active on XOS with single substituted L-Araf residues
LPMO (EC 1.14.99.53,54,5)	AA9-10, 14	Disruption of carbohydrates and oxidative cleavage of carbohydrates
Agu (EC 3.2.1.72)	GH115	Active on glucuronic acid substituted on polymeric AG/AGX
	GH67	Active on glucuronic acid substituted on short XOS
AXE (EC 3.1.1.72)	CE1, 5, 6	Liberates acetic acid from acetylated xylan
	CE4	Liberates acetic acid from long acetylated XOS
	CE7	Liberates acetic acid from acetylated XOS
	CE16	Liberates acetic acid from then non-reducing ends of acetylated XOS
FAE (EC 3.1.1.73)	CE1	Liberates phenolic acids from XOS and xylan
GE (EC 3.1.1.-)	CE15	Releases lignin aliphatic alcohols from LCC composed of lignin and GX
Rex (EC 3.2.1.156)	GH8	Reducing end specific exo-xylanase
Xyn (EC 3.2.1.8)	GH5(34)	L-Araf substitution requiring xylanase (only active on AX/AGX)
	GH10	XOS and soluble (branched) xylan active xylanase
	GH11	Insoluble xylan active xylanase
	GH30(8)	Glucuronic acid substitution requiring xylanase (only active on AG/AGX)
Xyl (EC 3.2.1.37)	GH1-3, 5(22), 30, 39, 43, 51, 52, 54, 116, 120	Releases xylose from non-reducing ends of XOS

long-range electron transfer involving soluble low molecular weight lignins produced by ligninases (i.e. laccases and peroxidases) from high molecular weight lignins (Westereng et al. 2015). The implication of these findings is that xylan degradation may, to some degree, be linked to lignin modification, particularly with respect to electron donation for LPMO activity efficiency.

It is clear that with the entire consortium of xylanolytic enzymes, including accessory/non-GH enzymes such as esterases and LPMOs, hetero-xylan hydrolysis with monomeric sugar yields as high as 100% can be attained. We have compiled a list of all the enzymes which, to date, have been shown to be essential for the efficient degradation of AGX (see Table 3).The aforementioned model of xylan hydrolysis by xylanolytic enzymes will hopefully shed insights into the selection of not only the necessary enzyme classes required, but also the specific families as described in the CAZy database and the sequence (*sequential* versus *simultaneous*) of application of these enzymes in an industrial setting in order to achieve high yields of VAP production from xylans and xylan-containing biomass. This will hopefully lead to a significant improvement in the economic viability of the bioconversion of xylan—containing lignocellulosic biomass into various VAPs. It is noteworthy to mention that industrial application of these xylanolytic enzyme cocktails demands that the enzymes must be able to withstand harsh processing conditions such as acidic/alkaline conditions, elevated temperatures, and the presence of biomass pre-treatment by-products and enzyme reaction products which could be inhibitory to these enzymes in the catalysis process (Malgas et al. 2017; Chadha et al. 2019). Therefore, caution regarding the aforementioned conditions should be taken during the selection of xylanolytic enzymes to constitute an enzyme cocktail for lignocellulosic biomass degradation.

Conclusion and future perspectives

In this review, it was demonstrated that the complex structure of xylans presents a great challenge to degradation. A model consisting of multiple xylanolytic enzyme activities which are required to fully hydrolyse xylans was then proposed. It was clearly shown that hydrolysis of xylans to completion is most likely obtained through the synergistic interactions of complementary endo-, exo- and side-chain-acting-xylanolytic activities complemented by auxiliary activity enzymes (CEs and LPMOs). We are hopeful that the proposed model of xylan degradation by xylanolytic enzymes will inform industry of a suitable approach for the application of these enzymes in an industrial setting in order to achieve high yields of VAP production from xylans and xylan-containing biomass. However, limitations and knowledge gaps in the field of xylan degradation by enzymatic means are also highlighted in this review. Listed below are but a few:

1. Metagenomic mining for novel CAZymes with unique properties regarding xylan degradation is still not fully explored.

2. The characterisation of xylanolytic enzymes—both biochemically and according to families in the CAZy database—requires more work on enzymes such GH5 arabinoxylanases, GH8 Rex or exo-xylanases, GH30 glucuronoxylanases, CE15 GEs and LPMOs (AA9-10, 14), as their catalytic properties and mechanisms are still unclear.
3. It may be of interest to probe into the implications of lignin modifying enzymes (i.e. laccases and peroxidases) for their influence on xylan degradation.
4. Some of the remaining challenges in the field of biomass degradation include the use of protein engineering to produce new enzyme functionalities such as broad substrate specificity, tolerance to products and pre-treatment by-product inhibition, and thermal stability.
5. Finally, the design of chimeric multi-functional enzymes and enzyme complexes (i.e. artificial xylanosomes) has not been well explored compared to that of the design of cellulosomes for cellulose degradation. Such work could greatly advance xylan degradation.

Exploration of such research avenues can lead to an improvement in the efficiency of xylan degradation and this would subsequently lead to an improvement in the economic viability of the bioconversion of high xylan-containing lignocellulosic biomass into fermentable sugars for bioethanol and the production of other fine chemicals.

Compliance with ethical standards

Conflict of interest The authors report no further conflicts of interest. The authors are responsible for the content and writing of this article and are grateful for financial support from the National Research Foundation (NRF) and Council for Scientific and Industrial Research (CSIR) in South Africa. Any opinion, findings and conclusions or recommendations expressed in this material are those of the author(s) and therefore the NRF does not accept any liability in regard thereto.

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