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Review

Fungal xylanolytic enzymes: Diversity and applications

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HIGHLIGHTS

- Fungal genome sequencing aids functionality prediction of carbohydrate-active enzymes.
- Genome comparison revealed significant differences in the enzyme sets of fungi.
- An expansion of CAZyme-encoding genes was observed in specific fungi.
- Xylanolytic enzymes have high potential in sustainable bioprocesses.

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ABSTRACT

As important polysaccharide degraders in nature, fungi can diversify their extensive set of carbohydrate-active enzymes to survive in ecological habitats of various composition. Among these enzymes, xylanolytic ones can efficiently and sustainably degrade xylans into (fermentable) monosaccharides to produce valuable chemicals or fuels from, for example relevant for upgrading agro-food industrial side streams. Moreover, xylanolytic enzymes are being used in various industrial applications beyond biomass saccharification, e.g. food, animal feed, biofuel, pulp and paper. As a reference for researchers working in related areas, this review summarized the current knowledge on substrate specificity of xylanolytic enzymes from different families of the Carbohydrate-Active enZyme database. Additionally, the diversity of enzyme sets in fungi were discussed by comparing the number of genes encoding xylanolytic enzymes in selected fungal genomes. Finally, to support bio-economy, the current applications of fungal xylanolytic enzymes in industry were reviewed.

1. Introduction

Lignocellulosic biomass is one of the most abundant renewable resource on earth, and its dry matter is majorly composed of cellulose, hemicellulose, and lignin (Usmani et al., 2020). Xylan represents the most common hemicellulose and is also considered to be the second most abundant biopolymer in the plant kingdom (Ebringerová and Heinze, 2000). Xylan generally consists of a β-(1 → 4)-linked D-xylosyl backbone, which is further decorated by different residues, i.e., α-L-arabinose, α-D-glucuronic acid, 4-*O*-methyl-glucuronic acid (MeGlcA), acetic acid (Ebringerová and Heinze, 2000). In addition, linear β-(1 → 4)-homoxylan without decorations has been isolated successively from esparto grass (Chanda et al., 1950), guar seed husk (Montgomery et al., 1956), and tobacco stalks (Eda et al., 1976). Furthermore, xylan with mixed β-(1 → 3)(1 → 4)-linked D-xylosyl units as backbone has also been found in *Plantago* species (Deniaud et al., 2003). Since β-(1 → 4)-homoxylan and β-(1 → 3)(1 → 4)-linked xylan are rarely found in plants, we mainly focus on β-(1 → 4) linked xylan with different decorations. Although xylan content, type and degree of xylan substituents vary amongst different botanical species and tissue types (Gírio et al., 2010), generally two main types are recognized: glucuronoxylan (GX, *O*-acetyl-4-*O*-methylglucuroxylan), and glucuronoarabinoxylan (GAX, (*O*-acetyl-)*arabino*-4-*O*-methylglucuronoxylan) (Gírio et al., 2010; Vuong and Master, 2022) (Fig. 1).

GX is mainly found in hardwoods, accounting for 10–35% of the total dry mass (Gírio et al., 2010; Vuong and Master, 2022). Around 10% of the xylosyl residues are *O*-2 substituted with MeGlcA residues, and about 35–70% are *O*-2 and/or *O*-3 linked with acetic acid (Gírio et al., 2010). Acetylation has been found to occur more frequent at the *O*-3 than at the *O*-2 positions of the xylosyl resides (Beg et al., 2001). GAX is the

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representative xylan in softwoods (5–10% of dry weight) and grasses (or cereals) (20–35% of dry mass) (Gírio et al., 2010; Hatfield et al., 2017; Vuong and Master, 2022). GAX of softwoods has generally no acetylation (de Carvalho et al., 2019), around 20% of the xylosyl residues are *O*-2 substituted with (Me)GlcA residues, and about 13% are *O*-3 substituted with arabinosyl residues (Smith et al., 2017). Whereas, GAX of grasses and cereals are lightly acetylated (Gao et al., 2020), the amount of arabinosyl residues is relatively high, and for example for corn pericarp GAX the arabinose can be further substituted via *O*-2 to one or more carbohydrate residues (Smith et al., 2017). GAX in cereals usually contain less or no (Me)GlcA residues, and mainly found in cereal grain endosperm (Gírio et al., 2010). Up to a ratio of arabinosyl substitutions to xylosyl of 0.4 to 1.0 has been found for endospermic xylans from different cereal species (Izydorczyk and Biliaderis, 1993). Arabinosyl units in GAX can be further esterified at their *O*-5 position by ferulic acid and, although to a lower extent, by *p*-coumaric acid (Gírio et al., 2010; Vuong and Master, 2022).

To degrade xylan, an array of carbohydrate-active enzymes (CAZymes) is required, named xylanolytic enzymes (Biely et al., 2016). Xylanolytic enzymes can be produced by various microorganisms, e.g. fungi, bacteria, and actinomycetes, of which fungi, especially filamentous fungi, are most popular from an industrial point of view (Madhavan et al., 2017; Nevalainen et al., 2005). Apart from biomass degradation, xylanolytic enzymes are of particular interested as they can be used in other applications in the food, animal feed, biofuel, pulp and paper, medical and pharmacological industries (Cho et al., 2020; Orozco Colonia et al., 2019; Lian et al., 2020). With the advent of fungal genome sequencing, an increasing number of genes encoding CAZymes has been identified. Still, regardless the vast number of already characterized xylanolytic enzymes, the function of many of these genes remains uncertain (de Vries et al., 2018; de Vries and Mäkelä, 2020). Detailed characterization of more-and-more of such uncharacterized proteins will potentially help us to discover new xylanolytic enzymes with potential industrial applications.

In this review, we first discuss the difference in substrate specificity of xylanolytic enzymes from different families of the Carbohydrate-Active enZyme (CAZy) database. Considering the popularity of fungal enzymes in industry, the number of CAZymes-encoding genes related to xylan degradation in selected fungal genomes was compared, revealing a clear expansion of genes encoding CAZymes in specific families of fungi. This suggested diversification within families in terms of substrate specificity and/or biochemical properties might help the discovery of novel enzymes for industry. Finally, we reviewed the current industrial applications of xylanolytic enzymes.

2. Distinct substrate specificity of xylanolytic enzymes

Enzymatic hydrolysis of xylan involves a multi-enzyme system (Table 1), including main- and side- chain degrading enzymes (Biely et al., 2016). These enzymes are all included in the CAZy database, in which they are classified into different classes and further divided into different families based on their amino acid sequences, structures and molecular mechanisms (Lombard et al., 2014). Moreover, some families have been subdivided into different subfamilies (SFs).

Table 1
Overview of fungal xylanolytic enzymes for xylan degradation.

CAZy	Activity	EC number	Abbreviation	Main CAZy family[b]
GH	Endoxylanase	3.2.1.8	XLN	GH10, GH11
	Xylosidase	3.2.1.37	BXL	GH3, GH43
	Xylobiohydrolase	3.2.1.-	XBH	GH30_7
	Arabinofuranosidase	3.2.1.55	ABF	GH43, GH51, GH54, GH62
	Arabinoxylan arabinofuranohydrolase	3.2.1.55	AXH	GH62
	Glucuronidase	3.2.1.131	AGU	GH67, GH115
CE	Acetyl xylan esterase	3.1.1.72	AXE	CE1
	Feruloyl esterase	3.1.1.73	FAE	CE1
	Glucuronoyl esterase	3.1.1.B11	GE	CE15
AA	Lytic polysaccharide monooxygenase	N.A.[a]	LPMO	AA9, AA14[c]

[a] N.A., not categorized by the International Union of Biochemistry and Molecular Biology (IUBMB).

[b] Only main families of characterized enzymes from fungi based on the current CAZy annotation are shown, for detail see Section 2.

[c] To date, only two AA9 LPMO has been shown to cleave isolated xylan oxidatively (e.g., *Ls*AA9A (Simmons et al., 2017) and PMO9A_MALCI (Basotra et al., 2019)). For various AA9 and AA14 LPMOs, oxidative xylan cleavage has been observed, but only when xylan was bound to cellulose, resulting in a simultaneous oxidative cellulose cleavage (reviewed in (Ipsen et al., 2021)).

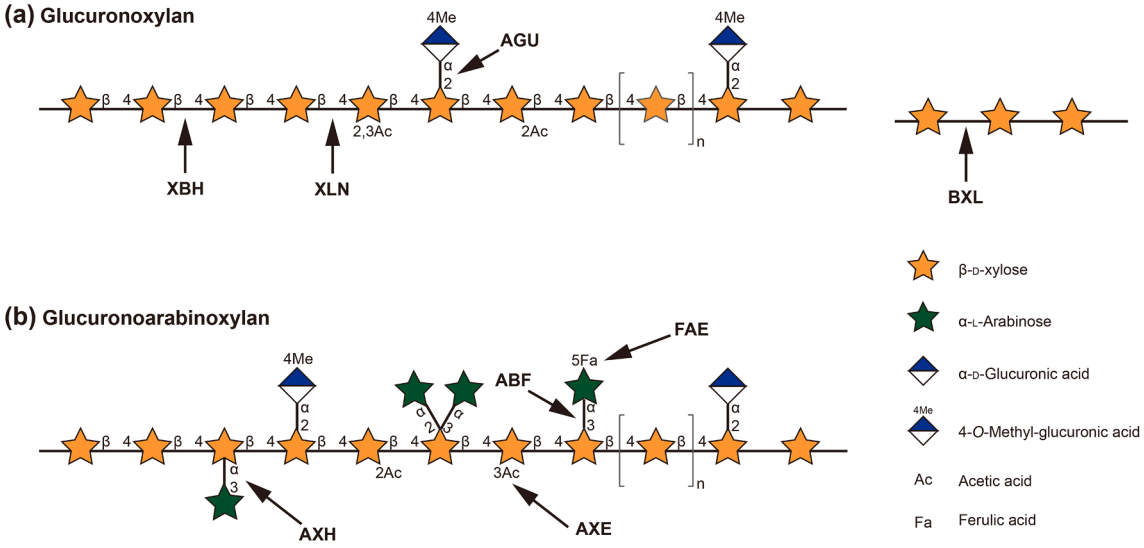

Fig. 1. Schematic representation of xylans and corresponding xylanolytic enzymes. (a), glucuronoxylan; (b), glucuronoarabinoxylan. Enzyme abbreviations are presented in Table 1. Polysaccharide structures were drawn by using data reported previously by Vuong and Master (2022) and de Carvalho et al. (2019).

2.1. Xylan main chain degrading enzymes

β-D-Xylanase (XLN) and β-D-xylobiohydrolase (XBH) are glycoside hydrolases (GHs) able to cleave the xylan backbone, likewise, β-D-xylosidase (BXL) degrade the β-(1 → 4)-xylosyl backbone, but preferably of oligosaccharides. XLN is typical *endo*-active, hence, releasing mainly xylooligosaccharides, while XBH and BXL have been recognized as *exo*-active, releasing solely xylobiose and xylose, respectively (Agrawal et al., 2021; Lian et al., 2020; Šuchová et al., 2020). Fungal XLNs are mainly classified in GH10 and GH11, XBHs in GH30_SF7, and BXLs in GH3 and GH43. XLNs and BXLs have been described in detail in several reviews (Bhardwaj et al., 2019; Bosetto et al., 2016; Knob et al., 2010; Paës et al., 2012; Pollet et al., 2010), whereas XBH as a novel activity has only recently been discovered and reported (Li et al, unpublished data) (Katsimpouras et al., 2019; Nakamichi et al., 2019; Ravanal et al., 2010; Šuchová et al., 2020).

GH10 XLNs generally have a broader substrate specificity than GH11 XLNs, as GH10 XLNs tolerate the presence of decorations on the xylan backbone more than GH11 XLNs do (Chadha et al., 2019). As a result, GH10 XLNs can cleave the glycosidic linkage next to a xylosyl residue decorated with one or two residues (e.g., at the non-reducing side), whereas GH11 XLNs only cleave the xylan backbone that has at least three consecutive undecorated xylosyl residues, and cannot cleave at the glycosidic linkage next to a branch (Kolenová et al., 2006; Paës et al., 2012). BXL is characterized generally using an artificial substrate, i.e. *p*-nitrophenyl-β-D-xylopyranoside (*p*NPXyl). So far, almost all reported GH3 and GH43 BXLs are active against this substrate. Some BXLs were reported to exhibit multiple activities, shown by the hydrolysis of different substrates in addition to *p*NPXyl, e.g. *p*-nitrophenyl-α-L-arabinofuranoside (*p*NPAra) (Bauer et al., 2006; Kitamoto et al., 1999; Wakiyama et al., 2008; Yang et al., 2014) and *p*-nitrophenyl-β-D-glucopyranoside (*p*NPGlc) (Wakiyama et al., 2008). GH43 BXLs generally do not have the ability to transglycosylate at high substrate concentrations (Jordan et al., 2007; Knob et al., 2010), whereas transglycosylation activity has been reported for several GH3 BXLs (Herrmann et al., 1997; Kurakake et al., 2005; Wakiyama et al., 2008). This suggests that candidates for typical BXL hydrolase-activity can better be selected from GH43 (Knob et al., 2010).

XBH, as novel enzyme, has only attracted the attention of researchers in recent years. The earliest XBH activity was suggested for *Penicillium purpurogenum* 'arabinofuranosidase ABF3′ of GH43, since it released more xylobiose than xylose when X3 up to X5 were used as substrates. However ABF3 released several xylooligosaccharides when incubated with arabinoxylan (AX) (Ravanal et al., 2010). However, the subsequently reported XBHs were all from SF7 of GH30, and almost all of them showed a preference for less decorated GX, compared to highly substituted GAX (Katsimpouras et al., 2019; Nakamichi et al., 2019; Šuchová et al., 2020). As an exception, *Acremonium alcalophilum* XBH (*Aa*Xyn30A) exhibited the highest activity towards rhodymenan, which is a linear β-(1 → 3)(1 → 4)-xylan, followed by GX (Šuchová et al., 2020). To date, only a limited number of fungal XBHs have been characterized, which to some extent hinders to understand the diversity of XBH in terms of substrate specificity.

2.2. Xylan side chain degrading enzymes

Xylan side chain degrading enzymes are able to remove side branches and decoration groups in the different types of xylan, mainly including α-L-arabinofuranosidase (ABF), α-glucuronidase (AGU), acetyl xylan esterase (AXE), feruloyl esterase (FAE), and glucuronoyl esterase (GE). They belong to different classes, i.e. GH and carbohydrate esterase (CE).

ABF is an *exo*-acting enzyme of the GH class, which hydrolyzes the linkages between arabinosyl residues and xylosyl units of the xylan backbone to release arabinose. Some ABFs also degrade pectin side chains and other L-arabinosyl-containing oligosaccharides (Bauer et al., 2006; Kaur et al., 2015; Sakamoto and Kawasaki, 2003). In the CAZy database, the fungal ABFs mainly belong to GH43, GH51, GH54 and GH62 (Lombard et al., 2014). According to their mode of action towards substrates, ABFs are divided into two groups. ABFs in group A are able to remove arabinosyl residues decorated at *O*-2 or *O*-3 position of mono-substituted xylosyl residues, e.g., *Myceliophthora thermophila* C1 Abf3 in GH51 (Pouvreau et al., 2011). In contrast, ABFs in group B can selectively release *O*-3 arabinosyl from doubly arabinosylated xylosyl residues (*O*-2 and *O*-3), e.g., *M. thermophila* C1 Abn7 in GH43 (Pouvreau et al., 2011). In addition, based on substrate preference, ABFs have been classified into four types (1, 2, 3, 4) (Beldman et al., 1997): type 1, not active towards polymers; type 2, active towards polymers; type 3, specific for arabinoxylan; type 4, not active on the synthetic substrate *p*NPAra. Previously, type 1 and 2 were assigned to GH51 and GH54 ABFs, respectively, and type 3 corresponded to GH43 and GH62 ABFs (Maehara et al., 2014). However, as additional enzymes were characterized, the drawbacks of this classification based on substrate specificity became evident, because multiple types of ABF were present in the same family. For example, in GH51 corresponding to type 1, some ABFs, like *Aureobasidium melanogenum* ATCC 20,524 AbfB (Ohta et al., 2013) and *P. chrysogenum* 31B AFQ1 (Sakamoto and Kawasaki, 2003), were also active on AX. ABFs have proven to degrade different substrates, e.g. *p*NPAra, sugar beet arabinan and/or AX (Bauer et al., 2006; Contesini et al., 2017; Gielkens et al., 1997; Kaur et al., 2015; Siguier et al., 2014). Enzymes that specifically hydrolyze linkages between arabinosyl and xylosyl residues in AX are also named arabinoxylan arabinofuranohydrolases (AXHs) and are mainly from GH62 (Gielkens et al., 1997; Kormelink et al., 1991; Sakamoto et al., 2011).

AGU is another key xylan side chain degrading enzyme in the GH class, which catalyzes the breakdown of α-(1 → 2)-glycosidic linkages between (Me)GlcA and xylosyl residues in glucuronoxylooligosaccharides or GX. Fungal AGUs are classified into GH67 and GH115. Fungal GH115 AGUs release MeGlcA by the hydrolysis of α-(1 → 2)-glycosidic bond between MeGlcA and mono-substituted internal- and end-xylosyl units, of polymeric GX and/or xylan oligomers (Chong et al., 2011; Martínez et al., 2016; Ryabova et al., 2009; Tenkanen and Siika-aho, 2000). However, fungal AGUs from GH67 reported cannot operate on polymeric substrates, and exclusively hydrolyze the α-(1 → 2)-glycosidic bond between MeGlcA and terminal, non-reducing end, xylosyl residues of xylooligosaccharides (Biely et al., 2000; de Vries et al., 1998; Martínez et al., 2016; Siika-aho et al., 1994). As an exception, *A. nidulans* AguA was also active on larch wood xylan (Bauer et al., 2006). So far, only a limited number of fungal AGU has been characterized.

AXE belongs to the CE class, which catalyzes the hydrolysis of ester linkages between the acetyl groups and the xylan backbone to release acetic acid. Common model substrates used for detection of AXE activity are including *p*NP-acetate, 4-methylumbelliferyl acetate (MUB-acetate), α-naphthyl acetate, and 2,3,4,5-tetra-*O*-acetyl-D-xylose, of which the first former three are commercially available. Apart from that, AXE is also active on natural substrates, e.g. acetylated xylan and xylooligosaccharides. The characterized AXEs from fungi are classified into CE1, CE2, CE3, CE4, CE5, CE6 and CE16. CE1 is the largest family which contains most characterized fungal AXEs, while CE4 and CE5 mainly contained chitin deacetylases and cutinases, respectively. Currently, there are only few characterized fungal enzymes from CE2, CE3 and CE16. The specificity of AXEs from different families varies significantly towards natural substrates. CE1 AXEs regioselectively cleave the substituents in the *O*-2 and *O*-3 position, and deacetylate the *O*-2 position faster than the *O*-3 position (Altaner et al., 2003). CE4 AXEs prefer to deacetylate oligosaccharides with longer chain, which cannot attack di-acetylated xylosyl residues (Biely et al., 2016; Karnaouri et al., 2019). Altaner et al. (2003) reported that CE4 AXEs seem to interact only with acetyl groups at the *O*-3 position of xylosyl units, whereas CE5 AXEs attack solely the *O*-2 position. CE6 AXEs have a broad specificity, which are able to target *O*-2 mono-acetylated xylosyl residues as well as *O*-2

and *O*-3 di-acetylated xylosyls (Uhliariková et al., 2013). AXEs from CE16 showed various specificity of deacetylation. For example *Myceliophthora thermophila Mt*AcE of CE16 preferred to release the acetyl group at the *O*-2 position, similar to CE1 AXEs (Mai-Gisondi et al., 2017), whereas *Trichoderma reesei Tr*CE16 had a preference for removing the acetyl group of xylosyl units at the *O*-3 and *O*-4 positions in oligosaccharides of acetyl-glucuronoxylan (Biely et al., 2014). *A. niger An*CE16A tended to rapidly attack *O*-2 and *O*-3 di-acetylated xylosyls in polymeric xylans, followed by *O*-2 and *O*-3 mono-acetylated xylosyls, whereas, it poorly hydrolyzed acetyl groups of the *O*-2 xylosyl position in methyl β-D-xylopyranoside diacetates and triacetates (Puchart et al., 2016). The mode of action of CE2 and CE3 AXEs still needs to be studied.

FAE hydrolyzes the ester bonds between hydroxycinnamic acids (e.g., mostly (di-) ferulic acid and, to a minor extent, coumaric acid) and arabinosyl residues in xylan. Methyl ferulate (MFA), methyl sinapate (MSA), methyl caffeate (MCA), and methyl *p*-coumarate (MpCA) are most often used as model substrates to determine FAE activity. Based on activity towards these model substrates, FAEs were classified into four types (A, B, C and D) (Crepin et al., 2004). Type A and B are inactive towards MCA containing methyl 3,4-dihydroxycinnamate and MSA containing methyl 3,5-dimethoxy-4-hydroxycinnamate, respectively, while type C and D can hydrolyze all four model substrates. Unlike type C FAEs, type D FAEs are also capable of releasing 5-5′-diferulic acid from natural substrate. However, the characterization of additional FAEs revealed that this classification system cannot classify all the known FAE consistently. Recently, Dilokpimol et al. (2016) introduced a refined FAE classification based on phylogenetic analysis of available fungal genome. This refined classification separated FAEs into 13 subfamilies, which not only classifies different types of FAE, but also reflects the evolutionary relationship among different FAEs (Dilokpimol et al., 2016). Only two SFs (SF5 and SF6) are classified as CE1 in the CAZy database, which are related to AXE. Other SFs are not in the CAZy database (Lombard et al., 2014). These FAEs are related to tannases (SF1-4 and SF9-11), lipases (SF7), and lipases and choline esterases (SF12 and SF13). This demonstrates that FAEs are evolved from highly diverse esterase families (Benoit et al., 2008; Dilokpimol et al., 2016).

GE belongs to CE15, which catalyzes the hydrolysis of ester bonds between aliphatic alcohols in lignin and the MeGlcA side chains of glucuronoxylan (Špániková and Biely, 2006). Benzyl D-glucuronate is the commercially available substrate for screening of GE activity, while others, e.g. benzyl methyl α-D-glucopyranosiduronate, benzyl methyl 4-*O*-methyl-α-D-glucopyranosiduronate and lignin–carbohydrate complexes (LCCs) are prepared by specific methods. GEs not only synergistically act with xylanases, but also potentially with other lignocellulolytic enzymes (Bååth et al., 2018; Mosbech et al., 2018).

2.3. Lytic polysaccharide monooxygenases

In recent years, it has been reported that lytic polysaccharide monooxygenase (LPMO) in the class of auxiliary activity (AA) also contribute to xylan degradation (i.e., from AA9 and AA14) (Basotra et al., 2019; Couturier et al., 2018; Frommhagen et al., 2015; Hüttner et al., 2019; Simmons et al., 2017). AA9 is the largest (fungal) LPMO family, and these LPMOs have been shown to oxidatively degrade cellulose. A selection of AA9 LPMOs has been shown to also oxidatively cleave xyloglucan, while so far only limited LPMOs are described to be active towards xylan (Quinlan et al., 2011). *Lentinus similis Ls*AA9A (Simmons et al., 2017) and *Malbranchea cinnamomea* rPMO9A_MALCI (Basotra et al., 2019) were reported to oxidatively cleave isolated xylan substrates. Other xylan-active LPMOs in AA9, such as *Malbranchea cinnamomea Mc*AA9s (*Mc*AA9A, *Mc*AA9B, *Mc*AA9F, *Mc*AA9H) (Hüttner et al., 2019) and *Myceliophthora thermophila* C1 *Mt*LPMO9A (Frommhagen et al., 2015), oxidatively cleaved only cellulose-associated xylan. For AA14 LPMOs, Couturier et al. (2018) characterized the first two xylan active LPMOs, i.e. *Pc*AA14A and *Pc*AA14B from *Pycnoporus coccineus*, which acted on xylan coated crystalline cellulose, whereas they were inactive towards pure xylan. Remarkably, the combination of LPMOs and GHs showed a strong synergistic effect on xylan degradation (Malgas et al., 2019; Zerva et al., 2020). Similar synergistic effects were also found between xylan main- and side chain degrading enzymes, and even between different side chain degrading enzymes (de Vries et al., 2000; Karnaouri et al., 2019; Malgas et al., 2019). Therefore, complete hydrolysis of xylan is achievable only through a rational combination of multiple enzyme activities.

3. Diverse enzyme sets in fungal genome

Fungi are of interest because they are able to secrete a complete enzyme system required for their growth habitat (Bennett, 1998; Nevalainen et al., 2005; Polizeli et al., 2005). Recently, the global fungal diversity is estimated to range between 2.2 and 3.8 million species (Hawksworth et al., 2017), indicating a rich resource of enzymes to be exploited. In particular, the advent of genome sequencing, more than 1000 complete fungal genomes have been publicly released (Grigoriev et al., 2014). These available genomes have greatly enhanced our understanding of the diversity of fungi in terms of plant cell wall degradation.

As an illustration, Table 2 shows a comparison of CAZymes involved in plant polysaccharides degradation of 28 fungal genomes from MycoCosm (Grigoriev et al., 2014), focusing on the gene number encoding xylanolytic enzymes. This table shows that fungi from different phyla, i.e. Ascomycota and Basidiomycota, differ significantly in the number of genes encoding xylanolytic enzymes. On average, Ascomycota has higher gene copies in GH3, GH11, GH43, GH54, GH62 and GH67 enzymes than Basidiomycota, while the number of AA14 genes in Ascomycota is less than in Basidiomycota. In addition, some genes encoding specific family present phyla specificity. For example, GH54 ABF and GH67 AGU encoded genes are only present in Ascomycota, which might indicate that these enzymes play an essential role in Ascomycota (Chong et al., 2011). However, gene numbers are even variable within the same fungal genus. A comparison of gene numbers in *Penicillium* shows that *P. subrubescens* contains significantly more genes than *P. chrysogenum* in most of the CAZy families related to xylan degradation (Peng et al., 2017). A similar phenomenon also occurs in some CAZy families (e.g. GH10, GH11 and GH115) of *Aspergillus* (de Vries et al., 2017).

Genes encoding GH10 and GH11 enzymes, which mainly show XLN activity, are present in variable copies from 0 to 8 in the genomes of these selected fungi. The genomes of *Podospora anserina*, *M. thermophila* and *Coprinopsis cinerea* contain more copies of XLN than the other fungi, with especially high gene numbers of GH10 XLN in *P. anserina* (eight genes) and GH11 XLN in *M. thermophila* (eight genes). This shows strong expansion of specific families in fungi, probably pointing to diversification within the family in terms of substrate specificity and/or biochemical properties. In addition, genes encoding GH10 XLN are widely present in almost all selected fungi, while genes encoding GH11 XLN are absent in some fungi, e.g. *C. lunatus, N. crassa*.

Most of fungi harbor high copies of GH3 and GH43 coding genes, which might be due to the fact that GH3 and GH43 contain various catalytic activities in addition to BXL. e.g. BGL in GH3, ABF / ABN / 1,3GAL (β-(1 → 3) galactanase) in GH43 (Lombard et al., 2014). In addition, species like *P. subrubescens* that have more copies of genes coding xylan side chain degrading enzymes, such as ABF, AXH and AGU than other fungi, showing strong expansions of CAZymes in specific CAZy families (e.g. GH43, GH51) (de Vries and Mäkelä, 2020). This feature confirms that *P. subrubescens* is a promising new fungal cell factory for enzyme production, as has been reported previously (Dilokpimol et al., 2020; Mäkelä et al., 2016).

For the LPMOs that oxidatively degrade plant biomass, the selected fungal genomes contain highly variable gene numbers (0–34), most of which are from AA9 rather than AA14. AA9 harbors a considerable amount of lytic cellulose monooxygenase (Rani Singhania et al., 2021).

Table 2
Comparison of the number of genes from selected fungal in the related xylan degrading enzyme families in the CAZy database. The data was based on the CAZy annotation from published genomes (until September 2021) in MycoCosm (Grigoriev et al., 2014). Values in bold represent the highest number of genes per fungal strain found per CAZy family.

Phylum	Xylanolytic enzyme	XLN		XBH	ABF					AGU		AXE/FAE	GE	LPMO	
					BXL				AXH						
	Species Main Family	GH10	GH11	GH30_7	GH3	GH43	GH51	GH54	GH62	GH67	GH115	CE1	CE15	AA9	AA14
Ascomycota	*Aspergillus niger*	2	3	0	19	11	4	1	1	1	0	3	0	7	0
	Aspergillus oryzae	4	4	0	23	20	3	1	2	1	**4**	3	0	8	0
	Aspergillus nidulans	3	2	0	21	19	2	1	2	1	1	3	0	10	0
	Aspergillus japonicus	2	3	0	20	13	4	1	1	1	0	1	0	5	1
	Aspergillus fumigatus	4	3	0	19	18	2	1	2	1	1	2	1	7	1
	Aspergillus luchuensis	2	4	0	16	11	4	1	1	1	0	1	0	6	0
	Trichoderma reesei	1	3	**2**	13	2	0	2	1	1	1	0	1	3	1
	Penicillium chrysogenum	3	1	0	18	14	3	1	1	1	0	1	1	4	0
	Penicillium subrubescens	3	7	0	**25**	**30**	**6**	**4**	**4**	**4**	3	3	0	8	1
	Podospora anserina	**8**	6	2	11	12	1	0	2	1	3	**13**	3	**32**	1
	Neurospora crassa	4	2	0	11	7	1	1	0	1	1	6	1	14	0
	Cochliobolus lunatus	1	0	0	2	2	1	0	1	0	1	0	0	4	0
	Mycosphaerella graminicola	2	1	0	16	1	3	1	1	0	1	3	0	1	0
	Zymoseptoria pseudotritici	2	1	0	16	11	3	1	1	0	1	1	0	2	0
	Botrytis cinerea	2	2	0	16	6	3	1	1	0	1	1	0	10	0
	Myceliophthora thermophila	4	**8**	2	13	13	2	0	2	1	1	6	2	23	0
	Tuber borchii Tbo3840	2	0	0	6	1	0	0	0	0	0	0	0	6	1
Basidiomycota	*Puccinia graminis f. sp. tritici*	5	0	0	2	2	0	0	0	0	0	0	0	1	0
	Ustilago maydis	2	1	1	3	4	2	0	1	0	1	1	0	0	0
	Agaricus bisporus var bisporus	2	2	1	8	4	1	0	0	0	2	1	1	11	2
	Coprinopsis cinerea	6	6	1	7	4	1	0	3	0	1	4	**17**	**34**	**5**
	Dichomitus squalens	5	0	0	8	7	2	0	0	0	2	1	2	16	4
	Laccaria bicolor	0	0	0	0	0	0	0	0	0	0	0	0	0	4
	Phanerochaete chrysosporium	6	1	1	10	4	2	0	0	0	1	4	2	16	2
	Pleurotus ostreatus	3	2	2	13	8	3	0	1	0	1	2	1	29	2
	Postia placenta	3	0	0	6	1	1	0	0	0	1	0	1	2	2
	Pycnoporus cinnabarinus	6	0	0	8	3	2	0	0	0	2	3	2	17	4
	Trametes versicolor	6	0	1	13	3	2	0	0	0	2	3	2	18	4

As an exception, the *L. bicolor* genome contains four putative AA14-encoding genes, but no AA9-encoding gene, while no LPMO-encoding genes are present in the genome of *Ustilago maydis*. Furthermore, Basidiomycota genomes generally contain more AA14 genes than Ascomycota genomes, which may be related to the habitat of Basidiomycota. Basidiomycota is reported to live in higher organic-matter forest habitats (Lundell et al., 2014), which are rich in xylan as the main hemicellulose.

Considering that current genome sequencing has already uncovered a large number of genes with unknown functions (de Vries et al., 2018), further characterization of these unknown sequences is expected to lead to the discovery of novel enzymes. Genome mining combined with amino acid sequence-based phylogenetic analysis can greatly improve the efficiency of discovering novel enzymes from fungal genomes (de Vries and Mäkelä, 2020). Some studies have confirmed the feasibility of the genome mining approach to discovery of new enzymes. For example, Dilokpimol et al. (2018b) successfully identified 20 out of 27 putative FAE candidates based on mentioned approaches, by testing their activity towards *p*NP-ferulate and/or methyl hydroxycinnamate substrates. Similarly, this author also confirmed the ability of the above approaches to identify fungal glucuronoyl esterase (GE) encoding genes, by successfully obtaining 18 GEs from 21 selected candidates, which were active against benzyl D-glucuronate (Dilokpimol et al., 2018a).

4. Current applications of xylanolytic enzymes

Apart from their ability to efficiently degrade xylan in lignocellulosic biomass, xylanolytic enzymes have been reported to play considerable roles in biotechnological processes for various industrial applications (Cho et al., 2020; Orozco Colonia et al., 2019; Lian et al., 2020). Here, we provide an overview of their application in the following fields: 1) food industry, 2) animal feed, 3) biofuel production, 4) pulp and paper industry, 5) medical and pharmacological industry.

4.1. Food industry

Enzymatic processing of food has distinct advantages over traditional chemical-based technology, in that there is less waste and by-products, less energy consumption, and decreased environmental impact. Fungal enzymes are utilized in food industry for modification of products, rather than their full degradation. The most widely used xylanolytic enzymes is XLNs, which have been employed as additive in different baking products, e.g. bread and biscuits. XLNs, as dough strengtheners, are alternatives to chemical dough conditioners, because of their excellent tolerance to the dough with respect to variations in processing parameters and in flour quality (Shahi et al., 2016). They can make the doughs soft and slack in rye baking, and improve the quality of whole wheat bread, by increasing the specific bread volume (Shah et al., 2006). In biscuits, addition of XLNs can improve the texture and taste

(Raveendran et al., 2018). In addition, the product of enzymatic lignocellulose degradation can also be used as additives in food industry. Ferulic acid is a released product from AX by FAEs, which has been regarded as precursor for the synthesis of flavor compounds, such as vanillin and guaiacol. These are aroma compounds used in foods, beverages and fragrance industries (Di Gioia et al., 2011; Gallage et al., 2014; Priefert et al., 2001). Similarly, xylose is the hydrolysis product of xylans by BXLs, which can be further used for xylitol production (Baptista et al., 2018; Romaní et al., 2020). Xylitol is a polyalcohol, which can be employed as a natural food sweetener, dental caries reducer and a sugar substitute for diabetics (Baptista et al., 2020; Baptista et al., 2018).

4.2. Animal feed

Feed ingredients used in monogastric diets (i.e., pigs and poultry) usually contain cellulose and hemicellulose, which are indigestible as these components or fractions have no match with the animals' endogenous enzymes (Vieira et al., 2014). Some fractions, such as β-glucans, pentosans, and phytates are even considered antinutritive (Ravindran, 2013). To ensure maximum uptake efficiency, the supplementation of exogenous enzymes in animal diets has been widely accepted (Bedford and Schulze, 1998). Xylanolytic enzymes are commonly added to diets containing cereals such as wheat, barley, and rye. These diets contain large amount of water-insoluble AX, which is considered to be the major limiting factor for use of cereals in animal feed (Bengtsson and Aman, 1990; Jürgens et al., 2012). XLNs can hydrolyze water-insoluble AX to its soluble form by breaking down the backbone of the polysaccharide, thereby reducing viscosity in the diet and improving digestibility by the animal (Mireles-Arriaga et al., 2015). The *arabino*-xylooligosaccharides as (by-)product from the hydrolysis of AX by XLNs, have been reported to exert positive effects and may act as prebiotics (Courtin et al., 2008). Apart from monogastric diets, xylanolytic enzymes are also commonly used in ruminant diets, to potentially improve fiber degradability and subsequently increase the intake of digestible energy (Beauchemin et al., 2003). For example, FAEs can hydrolyze the linkages between lignin and the cell wall polysaccharides of forages, and therefore increase the accessibility for other enzymes (i.e., cellulases, XLNs) to degrade and improve the nutritive value (Addah et al., 2012; Krueger et al., 2008; Scalbert et al., 1985). Recently, related FAE products for feed have become commercially available (Muck, 2010).

4.3. Biofuel production

Fossil fuels are the most widely used energy sources worldwide, which are also the principal carbon dioxide emission source (Höök and Tang, 2013). Given fossil-derived fuels are nonrenewable, their depletion has been identified as a future challenge. Thus, biofuels derived from plant biomass, as a sustainable and clean alternative to fossil fuels, are attracting growing attention (Demirbas, 2008). Biofuels can be converted and produced from lignocellulosic biomass, while one of the major limitations for efficient conversion is the recalcitrant nature of the plant cell wall (Bhatia et al., 2020). Plant cell wall mainly consists of cellulose, hemicellulose and lignin, of which cellulose and hemicellulose are expected to be significant substrates in the future for bioconversion to biomethanol, bioethanol, or other higher molecular weight alcohols (Somerville, 2007). Xylan represents the most abundant hemicellulose. Xylanolytic enzymes can hydrolyze xylan into its constituent sugars, mainly xylose and arabinose, for subsequently fermented by microorganisms to produce biofuels. Based on xylan structure, to efficiently depolymerize xylan to the component monosaccharides, a mixture of different enzymatic functionalities is required, including XLNs, BXLs, ABFs, AGUs, FAEs, and AXEs (de Vries et al., 2020; Dodd and Cann, 2009). Additionally, xylanolytic enzymes (especially XLNs) in combination with cellulases/laccases/amylases have been reported to be greatly benefit bioethanol production, which significantly increase the ethanol yield (Althuri and Mohan, 2019; Choudhary et al., 2014).

4.4. Pulp and paper industry

Traditionally, the bleaching process used within the pulp and paper industry is divided into three stages, which involves the utilization of different chemicals in each step, such as chlorine dioxide in the first stage, sodium hydroxide and hydrogen peroxide in the second stage, and chlorine peroxides of the final stage. The obvious drawbacks associated with traditional process are the high chemical loads, harmful gas emission rates and the high economic costs. Xylanolytic enzymes as environmentally friendly alternatives have been employed in pulp and paper to minimize these problems (Walia et al., 2017). For example, XLNs can partially interrupt the bonds of lignin-carbohydrate complexes by hydrolysis of xylan, and thereby increase the accessibility of the subsequent bleaching chemicals to the pulps, as well as facilitate the removal of lignin. This action reduces the consumption of chlorine and chlorine dioxide, and significantly improves the final brightness value of pulp (Buchert et al., 1994; Kumar et al., 2019; Walia et al., 2017; Zhao et al., 2017). Additionally, other xylanolytic enzymes, like AGUs and FAEs, are also reported to be used for pulp and paper industry. Paper and pulp sectors are the traditional applications of softwood, which contain around 5–10% GAX. AGU can remove (Me)GlcA residues of xylan, allowing XLNs to access the xylan backbone, thereby improving the efficiency of xylan degradation (Willför et al., 2005). Annual plant fibers are also a cheap alternative source of raw materials for pulp and paper production, which contain up to 35% GAX. The combination of FAEs with other enzymes can promote xylan degradation, thus further improving pulp bleaching processes (Record et al., 2003).

4.5. Medical and pharmacological industry

Some by-products of xylanolytic enzymes show pharmaceutical and health beneficial functions, such as ferulic acid and other hydroxycinnamic acids from the hydrolysis of xylan by FAEs. They show antimicrobial, anti-inflammatory, anti-diabetic, anti-thrombosis, anti-cancer, and cholesterol-lowering agents, which are of interest for a wide range of applications in medical and pharmaceutical industries (Dilokpimol et al., 2016; Kumar and Pruthi, 2014; Ou and Kwok, 2004). (Arabino) *xylo*-oligosaccharides are products of xylan degradation, released during XLN treatment, which possess prebiotic effects. They can stimulate the growth of beneficial bacteria in the human gut, such as *Bifidobacteria*, while restricting harmful bacteria (Aachary and Prapulla, 2011).

4.6. Other applications

Apart from the above-mentioned applications, xylanolytic enzymes can also be used in other applications. For example, in detergents, an FAE-containing multi-enzyme system is used to improve the performance of liquid laundry detergents particularly at low temperature (Brooker et al., 2011), while XLN-containing detergents can effectively remove plant stains (Md Moid et al., 2021). In the beverage industry, adding XLNs and ABFs in juice clarification and extraction can result in improved yield, stabilization of fruit pulp, reduction of viscosity, and clearing of the juice (Polizeli et al., 2005; Whitaker, 1984). The addition of ABFs also can prevent haze formation in fruit juice (Whitaker, 1984). In seasonings and alcoholic beverages, FAEs have been used for both removing off-flavors/odors as well as enhancing the aroma (Dilokpimol et al., 2016). Ferulic acid produced by FAEs is also used as additive in beer as it is one of the major antioxidant constituents (Maillard and Berset, 1995).

5. Conclusion

Xylanolytic enzymes as alternatives to chemicals show great potential in industry. This review summarizes the difference in substrate

specificity of xylanolytic enzymes to facilitate their rational application. Fungal genome sequencing uncovered a large number of genes with unknown function, and a further comparison revealed a strong expansion of CAZymes-encoding genes in specific families. Future characterization of these unknown genes will not only reveal CAZymes with possibly extraordinary functions, but also further expand the toolbox of enzymes for bioprocessing in general.

CRediT authorship contribution statement

Xinxin Li: Formal analysis, Visualization, Writing – original draft. **Adiphol Dilokpimol:** Writing – review & editing. **Mirjam A. Kabel:** Writing – review & editing. **Ronald P. de Vries:** Conceptualization, Formal analysis, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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