BIOLOGICAL PRETREATMENT OF LIGNOCELLULOSES WITH WHITE-ROT FUNGI AND ITS APPLICATIONS: A REVIEW

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Lignocellulosic carbohydrates, i.e. cellulose and hemicellulose, have abundant potential as feedstock for production of biofuels and chemicals. However, these carbohydrates are generally infiltrated by lignin. Breakdown of the lignin barrier will alter lignocelluloses structures and make the carbohydrates accessible for more efficient bioconversion. White-rot fungi produce ligninolytic enzymes (lignin peroxidase, manganese peroxidase, and laccase) and efficiently mineralise lignin into CO_2 and H_2O. Biological pretreatment of lignocelluloses using white-rot fungi has been used for decades for ruminant feed, enzymatic hydrolysis, and biopulping. Application of white-rot fungi capabilities can offer environmentally friendly processes for utilising lignocelluloses over physical or chemical pretreatment. This paper reviews white-rot fungi, ligninolytic enzymes, the effect of biological pretreatment on biomass characteristics, and factors affecting biological pretreatment. Application of biological pretreatment for enzymatic hydrolysis, biofuels (bioethanol, biogas and pyrolysis), biopulping, biobleaching, animal feed, and enzymes production are also discussed.

Keywords: Biological pretreatment; White-rot fungi; Lignocellulose; Solid-state fermentation; Lignin peroxidase; Manganese peroxidase; Laccase; Bioethanol; Biopulping; Biobleaching; Ruminant feed

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INTRODUCTION

Lignocellulosic biomass from agricultural residues is produced in large quantities, approximately 73.9 Tg/year in the world (Kim and Dale 2004). These wastes are mostly left in the field, causing a disposal problem for the local producing agro-industries. However, lignocellulosic biomass actually has a great potential as feedstock for production of more value-added products such as low price chemicals, e.g. xylitol, xylose, glucose, furfural (Rahman et al. 2006; Sánchez 2009), fuels (Kim and Dale 2004), biofibres (Reddy and Yang 2005), ruminant feed (Okano et al. 2009), biopulp (Chen et al. 2002; Scott et al. 2002; Yaghoubi et al. 2008), or even for enzyme production (Hölker et al. 2004).

Lignocelluloses are composed of cellulose, hemicelluloses, lignin, extractives, and in general minor amounts of inorganic materials (Sjöström 1993). Cellulose and hemicelluloses are polysaccharides that can be hydrolysed to produce simple sugars. However, many factors such as lignin (content and composition), cellulose crystallinity, degree of polymerization, pore volume, acetyl groups bound to hemicellulose, surface area, and biomass particle size limit the digestibility of the hemicellulose and cellulose (Rivers and Emert 1988; Anderson and Akin 2008; Zhu et al. 2008; Alvira et al. 2010).

The aromatic barriers in lignocelluloses, including lignins (consisting of phenyl-propanoid units of various types) and low molecular weight phenolic acids, limit the fibres degradation. Cell walls with syringyl lignin, e.g. leaf sclerenchyma, are often less recalcitrant. However, coniferyl lignin appears to be the most effective limitation to biodegradation (Anderson and Akin 2008). Therefore, pretreatment methods targeted for removing or breaking down the lignin will generally increase the digestibility of cellulose fractions of lignocellulosic biomass. It has been pointed out that delignification causes biomass swelling, and disruption of the lignin structure, and consequently leads to an increase in internal surface area and median pore volume (Zhu et al. 2008). These changes could reduce irreversible adsorption of enzyme on lignin (Converse et al. 1990) and increase enzyme accessibility to cellulose (Mooney et al. 1998).

Pretreatment of lignocellulosic biomass can be performed by physical, mechanical, chemical, and biological methods (reviewed by e.g. Mosier 2005; Taherzadeh and Karimi 2008; Hu et al. 2008; Hendriks and Zeeman 2009; Alvira et al. 2010). Physical/mechanical pretreatments are based on milling, irradiation, and hydrothermal treatments. Examples of chemical pretreatments are ammonium fiber explosion (AFEX), alkali, acid, and organosolv treatments. Physical/mechanical and chemical pretreatments are most studied; they effectively reduce biomass recalcitrance in short time and are thus attractive for industrial application. These pretreatments increase accessible surface area, and decrease lignin contents and cellulose crystallinity and its degree of polymerization, and sometimes, partially or completely hydrolyze hemicelluloses. However, typical physical/mechanical and chemical pretreatments such as dilute-acid hydrolysis, require high-energy (steam or electricity) and/or corrosion-resistant high-pressure reactors, and extensive washing, which increase the cost of pretreatment. Furthermore, chemical pretreatments may produce toxic substances, interfering with the microbial fermentation, in addition to producing wastewater that needs treatment prior to its release to the environment (Keller et al. 2003; Shi et al. 2008). In view of these facts, biological pretreatment has attracted interest because of its potential advantages over physical/chemical pretreatments such as: (a) greater substrate and reaction specificity, (b) lower energy requirements, (c) lower pollution generation, and (d) higher yields of desired products (Kirk and Chang 1981). Compared to physical and chemical pretreatment methods, biological methods have been less investigated. One possible reason for this fact could be slow rates of the pretreatments, which makes the biological method industrially unattractive. Another drawback of biological pretreatment is the potential carbohydrate loss because of cellulose and hemicelluloses degradation. However, biomass pretreatment is a global issue that demands an environmentally friendly process. Thus, interest has been directed towards a biological method, and recent studies show increasing interest in this subject (Lee et al. 2007; Shi et al. 2008; Yu et al. 2009b;

Bak et al. 2010; Dias et al. 2010; Ma et al. 2010; Taniguchi et al. 2010).

Biological pretreatment employs microorganisms and their enzymatic machineries to break down lignin and alter lignocellulose structures. Some of the most promising microorganisms for biological pretreatment are white-rot fungi that can mineralise lignin to CO_2 and water in pure culture (Lundquist et al. 1977; Hatakka 1983). Several white-rot fungi such as *Phanerochaete chrysosporium*, *Ceriporiopsis subvermispora*, *Phlebia subserialis*, and *Pleurotus ostreatus* are capable of efficiently metabolising lignin in a variety of lignocellulosic materials (Kirk and Chang 1981; Hatakka 1983; Keller et al. 2003). The fungi have been studied in connection with several ligninolytic enzymes, such as lignin peroxidases (LiP), manganese peroxidases (MnP), laccase (Lac), and versatile peroxidases (VP) (Higuchi 2004; Wong 2009). Having these enzymes, white-rot fungi can have many applications in biopulping, biobleaching, ruminant feeds, xylose, ethanol, biogas, and enzymes productions (Kirk and Chang 1981; Reid 1989). Brown-rot fungi are also interesting class of fungi. However, these fungi do not degrade by modify lignin via demethylation (Hatakka 2001), and therefore, we do not cover brown-rot fungi in this review.

Biological pretreatments using white-rot fungi have mostly been carried out by solid-state fermentation (SSF). In SSF, production of ligninolytic enzymes has been shown to be higher than in submerged fermentation (SF) (Xu et al. 2001). The enzyme activity and lignin degradation are influenced by a number of factors such as fungal strain, nutrient composition (nitrogen, Mn^{2+}, and Cu^{2+}), moisture content, aeration, pH, and temperature (Kaal et al. 1995; Zhao et al. 1996; Fu et al. 1997; Dorado et al. 2001; Šnajdr and Baldrian 2007; Patel et al. 2009b). Controlling these factors leads to an optimum condition in the pretreatment process, which results in good performance of white-rot fungi. The present study reviews the biological pretreatment using white-rot fungi, as well as its biotechnical applications. In addition, some factors affecting pretreatment will also be briefly discussed in this paper.

WHITE-ROT FUNGI

Fungi that are active in the biodegradation of wood can be classified into three main groups according to their methods of degrading biomass, specifically white-rot, brown-rot, and soft-rot fungi. White-rot and brown-rot fungi belong to Basidiomycetes, whereas soft-rot fungi belong to Ascomycetes (Hatakka 2001). White-rot fungi are able to decompose all wood fractions, including lignin, and leave the wood with a white, fibrous appearance. Mostly, white-rot fungi grow on hardwoods e.g. birch and aspen. However, certain species such as *Heterobasidion annosum*, *Phellinus pini*, and *Phlebia radiata* grow on softwoods such as spruce and pine (Blanchette 1995).

White-rot fungi degrade lignin with two modes of action, namely selective and non-selective decays (Blanchette 1995). Selectivity of white-rot fungi regarding lignin degradation depends on the lignocellulose species (Hakala et al. 2004), cultivation time, and other factors (Hatakka and Hammel 2010). Examples of white-rot fungi that possess selective decay at least under certain condition are *C. subvermispora*, *Dichomitus squalens*, *P. chrysosporium*, and *Phlebia radiata.* Examples of white-rot fungi that

possess non-selective decay are *Trametes versicolor* and *Fomes fomentarius.* In selective decay, lignin and hemicellulose fractions are selectively degraded while the cellulose fraction is essentially unaffected. In non-selective degradation, approximately equal amounts of all fractions of lignocellulose are degraded (Blanchette 1995; Hatakka 2001).

Related to lignin degradation, white-rot fungi face three major challenges associated with lignin structure, i.e. (1) the lignin polymer is large; therefore ligninolytic systems must be extracellular, (2) lignin structure is comprised of inter-unit carbon-carbon and ether bonds, therefore the degradation mechanism must be oxidative rather than hydrolytic, and (3) lignin polymer is stereo-irregular, therefore the ligninolytic agents must be much less specific than degradative enzymes (Kirk and Cullen 1998). Enzymes involved in lignin degradation are lignin peroxidase (LiP, EC 1.11.1.14), laccase (Lac, EC 1.10.3.2, benzenediol:oxygen oxidoreductase), manganese peroxidase (MnP, EC 1.11.1.13), versatile peroxidase (VP, EC 1.11.1.16), and H_2O_2-forming enzymes such as glyoxal oxidase (GLOX) and aryl alcohol oxidase (AAO, EC 1.1.3.7) (Hatakka 2001; Wong 2009). White-rot fungi produce various enzymes involved in lignin degradation, but also produce cellulases, xylanases and other hemicellulases. Almost all white-rot fungi produce manganese peroxidase (MnP) and laccase (Lac), but only some of them produce lignin peroxidase (LiP) (Hatakka 2001).

Lignin Peroxidase

Lignin peroxidase (LiP, EC 1.11.1.14) was first discovered in the extracellular medium of *P. chrysosporium* grown under nitrogen limitation (Hammel and Cullen 2008). LiPs (lignin peroxidases) were reported to be produced by some white-rot fungi, e.g. *P. chrysosporium* (Ganesh Kumar et al. 2006), *T. Versicolor* (Hatakka 2001), *Bjerkandera* sp. (Kaal et al. 1993), and *T. cervina* (Miki et al. 2011), but are not observed in the culture of other fungi such as *D. squalens*, *C. subvermispora*, and *Pleorotus ostreatus* (Cohen 2002; Périé and Gold 1991). LiPs are monomeric homo-proteins with molecular masses around 40 kDa, and resemble classical peroxidase, in that their Fe^{3+} is pentacoordinated to the four heme tetrapyrrole nitrogens and to a histidine residue (Hammel and Cullen 2008). LiPs are oxidised by H_2O_2 to give a two-electron-oxidised intermediate (LiP-I) in which the iron is present as Fe^{4+} and a free radical resides on the tetrapyrrole ring (or on a nearby amino acid). LiP-I then oxidises a donor substrate by one electron, yielding a radical cation and LiP-II, in which the iron is still present as Fe^{4+}, but no radical is present on the tetrapyrrole. LiP-II then oxidises a second molecule of donor substrate, giving another radical cation and the resting state of the peroxidase. LiP oxidises non-phenolic units of lignin by removing one electron and creating cation radicals, which then decomposes chemically. LiP cleaves preferentially the Cα-Cβ bond in the lignin molecule, but is also capable of ring opening and other reactions (Hatakka 2001; Wong 2009). The general mechanism of LiP catalysed reaction is (Wong 2009):

$$LiP[Fe(III)] + H_2O_2 \rightarrow LiP\text{-}I\ [Fe(IV)=O^{\cdot+}] + H_2O \quad (1)$$

$$LiP\text{-}I + AH \rightarrow LiP\text{-}II\ [Fe(IV)] + A^{\cdot+}$$

$$Lip\text{-}II + AH \rightarrow LiP + A^{\cdot+}$$

Lignin peroxidases are known as strong oxidants because the iron in the porphyrin ring is more electron-deficient than in classical peroxidases (Millis et al. 1989). Another reason could be due to the fact that an invariant tryptophan residue – *trp171* in the isozyme named *LiPA* – is present in an exposed region on the enzyme surface, and thought to participate in long range electron transfer from aromatic substrates that cannot make direct contact with the oxidised heme. This makes LiPs enable to oxidise bulky lignin-related substrates directly (Hammel and Cullen 2008). Recent work showed that the catalytic efficiency (kcat/Km) for oxidation of a lignin model trimer by LiP was only about 4% of the value found for oxidation of a monomeric model (Baciocchi et al. 2003).

Manganese Peroxidase

Manganese peroxidase (EC 1.11.1.13, Mn(II):hydrogen-peroxide oxidoreductase, MnP) catalyses the Mn-dependent reaction $2Mn(II)+2H^{+}+H_2O_2=2Mn(III)+2H_2O$ (Wong 2009). MnP was purified from *P. chrysosporium* (Kuwahara et al. 1984). MnPs are more widespread than LiP (Hofrichter 2002). MnPs were reported to be produced by *P. chrysosporium*, *Pleurotus ostreatus*, *Trametes spp.*, and several species of the families of *Meruliaceae*, *Coriolaceae*, and *Polyporaceae* (Hofrichter 2002; Hatakka and Hammel 2010; Elisashvili and Kachlishvili 2009). Ultrahigh (0.93 Å) resolution structure of MnP from *P. Chrysosporium* was reported by Sundaramoorthy et al. (2010). MnP contains one molecule of heme as iron protoporhyrin IX and consists of 357 amino acid residues, three sugar residues (GlcNac, GlcNac at Asn 131, and a single mannose at Ser336), two structural calcium ions, a substrate Mn2+, and 478 solvent molecules. The catalytic cycles of MnP is described below (Wong 2009):

$$MnP + H_2O_2 \rightarrow MnP\text{-}I + H_2O \quad (2)$$
$$MnP\text{-}I + Mn^{2+} \rightarrow MnP\text{-}II + Mn^{3+}$$
$$MnP\text{-}II + Mn^{2+} \rightarrow MnP + Mn^{3+} + H_2O$$

Mn^{3+} in turn mediates the oxidation of organic substrates:

$$Mn^{3+} + RH \rightarrow Mn^{2+} + R^{\cdot} + H^{+} \quad (3)$$

Addition of H_2O_2 to native enzyme MnP yields MnP-I. The catalytic cycles thus involves the oxidation of Mn^{2+} by MnP-I and MnP-II to yield Mn^{3+}. The product, Mn^{3+}, is released from the active site if various bidentate chelators are available to stabilise it against disproportionation to Mn^{2+} and insoluble Mn^{4+} (MnO_2) (Glenn et al. 1986; Hatakka and Hammel 2010). In the reaction, the oxidising power of MnP is transferred to Mn^{3+} that can diffuse into the lignified cell wall and attack it from the inside (Hammel and Cullen 2008). However, MnPs naturally do not oxidise nonphenolic lignin-related structures directly as LiPs because they do not have the invariant tryptophan residue required for electron transfer to aromatic substrates (Hammel and Cullen 2008). Nevertheless, some reports (e.g. Hofrichter et al. 2001) say that non-phenolic compounds are oxidized under certain conditions.

A recent study (Hu et al. 2009) revealed a low-molecular weight compound that promotes Mn activities of *P. chrysosporium*. This compound, named *Pc-reducer*, was

reported to reduce the hydroxyl radical and the stable nitroxide radical under certain conditions. Pc-reducer could also weaken the repolymerisation of fragments from the oxidation of Na-lignosulfonate by lignin peroxidases and manganese peroxidases. It has the potential to improve the ligninolytic efficiency of peroxidases in *P. chrysosporium.*

Laccase

Laccases (Lac, EC 1.10.3.2, benzenediol:oxygen oxidoreductase) are blue copper-containing oxidases that catalyse one-electron oxidations of aromatic amines and phenolic compounds such as phenolic substructures of lignin. Most white-rot fungi produce laccase, with a large variation in the amounts (Wong 2009). The terminal electron acceptor in the catalytic reaction is molecular oxygen, which is reduced to water (Thurston 1994). The complete crystalline structure of laccase containing all four copper atoms in the active site has been published from *T. versicolor* and *Cerrena maxima* (Bertrand et al. 2002; Piontek et al. 2002). The structure of laccase consists of three cupredoxin-like domains, and resembles that of ascorbate oxidase (Bertrand et al. 2002). Laccases are glycoproteins and those of white-rot fungi generally have a molecular weight between 60-80 kDa and pI 3-6 (Hatakka 2001).

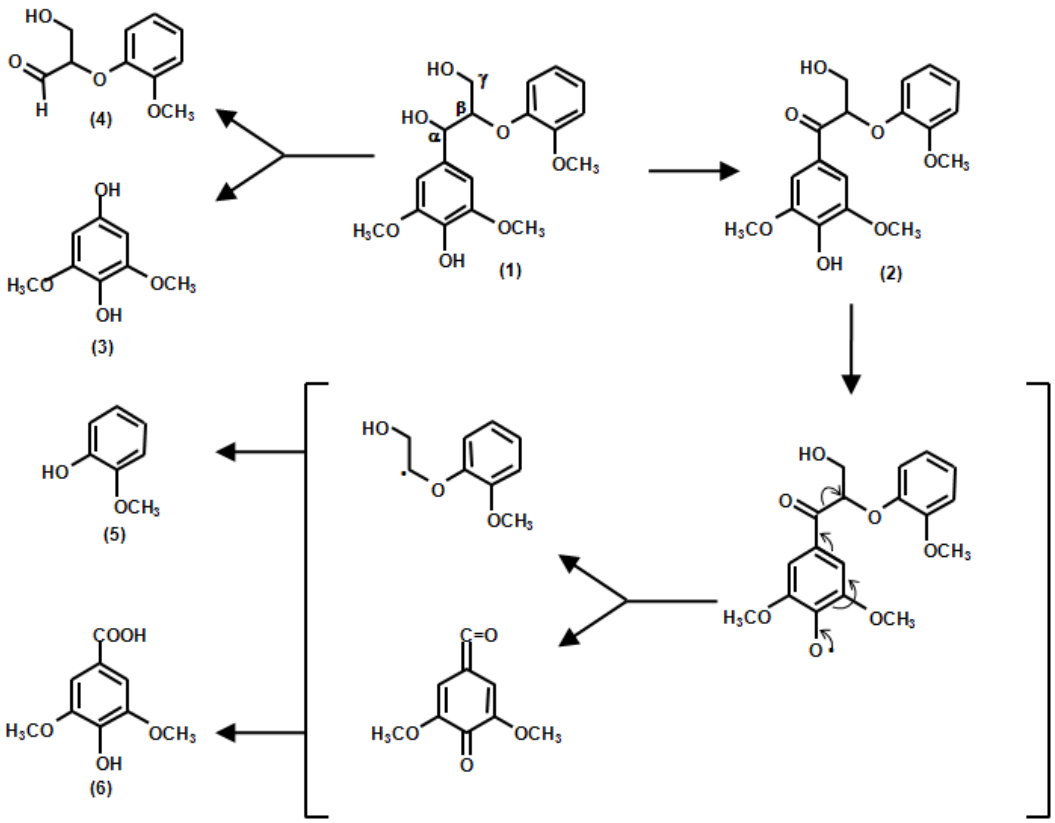

Fig 1. Mechanism of side chain cleavage of phenolic β-O-4 lignin substructure model by Lac of *C. versicolor*. (1), syringylglyceol-β-guaiacyl ether; (2),α-carbonyl dimer, (3), 2,6-dimethoxyhydro-quinone, (4) glyceraldehydes-2-guaiacyl ether; (5), guaiacol; (6), syringic acid (redrawn according to Higuchi, 2004)

The activity and function of laccase has been extensively studied for decades (Leonowicz et al. 2001). Laccase catalyse the formation of phenoxyl radicals and their unspecific reactions leading finally to Cα-hydroxyl oxidation to ketone, alkyl-aryl cleavage, demethoxylation and Cα-Cβ -cleavage in phenolic lignin substructures, as well as polymerization reactions (Fig. 1). Laccase is also able to oxidise non-phenolic substructures of lignin in the presence of a low molecular weight mediator like hydroxyl-benzotriazole (Call and Mücke 1997). In nature, the occurrence of laccase is widespread, and laccase has been found in fungi, bacteria, and plants. In the fungal kingdom, laccase has been found in phytopathogenic, soil, and fresh water inhabiting ascomycetes and in several basidiomycetes, including some mycorrhizal and brown-rot fungi. In lignin-degrading white-rot and litter-decomposing fungi, laccase has been found in almost every species studied (Baldrian and Šnajdr 2006).

White-rot fungi have usually several laccase encoding genes and secrete laccases as multiple isoforms (Hatakka 2001; Palmieri et al. 2000). An interesting exception in the occurrence of laccase is the widely studied white-rot fungus *P. chrysosporium*. In the sequenced genome of *P. chrysosporium*, no close match to known laccase encoding genes could be found (Kersten and Cullen 2007). There are few reports of laccase produced by *P. chrysosporium* (Srinivasan et al. 1995), but these results can be partly explained by the unspecific nature of 2,2′-azinobis (3-ethylbenzthiazoline-6-sulphonate) (ABTS) oxidation reaction and the possibility of variation in strains. However, it seems evident that most *P. chrysosporium* strains do not produce laccase.

As laccase is able to oxidise lignin and is produced by the most lignin-degrading fungi under ligninolytic conditions, it has been generally accepted to have a role in lignin degradation using white-rot fungi. Fungal laccase has been suggested to participate in morphogenesis, fungal plant pathogen interaction, stress defence, and detoxification of byproducts of lignin degradation (Thurston 1994). Laccase production using white-rot fungi can be induced by the addition of Cu^{2+} (Palmieri et al. 2000) or aromatic compounds such as veratryl alcohol (Couto et al. 2001) and 2,5– xylidine (Leonowicz et al., 2001; Eggert et al., 1996). In some fungi such as *C. subvermispora* (Fukushima and Kirk 1995) and *Ganoderma lucidum* (de Souza Silva et al. 2005), laccase production is increased in the presence of lignocellulosic material.

Versatile Peroxidase

Versatile peroxidase (VP) can oxidise phenolic and non-phenolic aromatic compounds as well as oxidise Mn^{2+}. Versatile peroxidases are found in various *Pleurotus* and *Bjerkandera* species and had been characterised (Cohen 2002; Chen et al. 2010), but VPs are not found in *P. Chrysosporium* (Hammel and Cullen 2008). *Phanerohaete chrysosporium* apparently lacks of VPs, although its genome encodes a putative extracellular peroxidase (GenBank accession AY727765) related to *Pleurotus* VPs. *P. chrysosporium* LiP had MnP activity when a Mn^{2+}-binding site was introduced into *P. chrysosporium* LiP genes by site-directed mutagenesis (Mester and Tien 2001). Conversely, *P. chrysosporium* MnP obtained LiP activity when a tryptophan residue analogous to the essential one in LiPs was introduced into *P. chrysosporium* MnP genes (Timofeevski et al. 1999). These results show that hybrid peroxidases with both activities could occur naturally (Hammel and Cullen 2008). The *P. eryngii* VP termed VPL has the

three acidic amino acid residues required for Mn^{2+} binding, and a catalytic efficiency (kcat/Km) for Mn^{2+} oxidation in the general range exhibited by typical MnPs. In addition, VPL has a tryptophan residue, *trp164*, analogous to the *LiPA trp171* that participates in electron transfer from aromatic donors and consequently enables the enzyme to oxidise nonphenolic lignin-related structures (Hammel and Cullen 2008).

The catalytic mechanism of VP is similar to LiP (Wong 2009). VP oxidise Mn^{2+} to Mn^{3+}, degrade the nonphenolic lignin model veratrylglycerol β-guaiacyl ether yielding veratraldehyde and oxidise veratryl alcohol and *p*-dimethoxybenzene to veratraldehyde and *p*-benzoquinone, respectively, as LiP does (Higuchi 2004).

Peroxide-Producing Enzymes

White-rot fungi require sources of extracellular H_2O_2 to support the oxidative turnover of the LiPs and MnPs responsible for ligninolysis. This H_2O_2 is supplied by extracellular oxidases that reduce molecular oxygen to H_2O_2 with the concomitant oxidation of a cosubstrate. One such enzyme, found in *P. chrysosporium* and many other white-rot fungi, is glyoxal oxidase (GLOX). GLOX accepts a variety of simple aldehydes as electron donors. Some GLOX substrates, e.g. glyoxal and methylglyoxal, are natural extracellular metabolites of *P. chysosporium* (Kersten 1990). Another substrate for the enzyme, glycolaldehyde, is released as a cleavage product when the major arylglycerol β-aryl ether structure of lignin is oxidised by LiP (Hammel et al. 1994).

Aryl alcohol oxidases (AAOs) provide another route for H_2O_2 production in some white-rot fungi. In certain LiP-producing species of *Bjerkandera*, chlorinated anisyl alcohols are secreted as extracellular metabolites and then reduced by a specific AAO to produce H_2O_2 (de Jong et al. 1994). It is noteworthy that, although many alkoxybenzyl alcohols are LiP substrates, chloroanisyl alcohols are not. The use of a chlorinated benzyl alcohol as an AAO substrate, thus, provides a strategy by which the fungus separates its ligninolytic and H_2O_2-generating pathways. A different approach is employed by some LiP-negative species of *Pleurotus*, which produce and oxidise a mixture of benzyl alcohols, including anisyl alcohol, to maintain a supply of H_2O_2 (Guillén et al. 1994). In yet other fungi, intracellular sugar oxidases might be involved in H_2O_2 generation (Kirk and Farrell 1987).

EFFECT OF BIOLOGICAL PRETREATMENT ON BIOMASS CHARACTERISTICS

Biological pretreatment of lignocellulosic biomass using white-rot fungi changes the biochemical and physical characteristic of the biomass (Fig. 2). Lignin degradation is the point of interest in many studies. For examples, lignin loss of corn straw was up to 54.6% after 30 days pretreatment with *T. versicolor* (Yu et al. 2010b); bamboo culm was > 20% after 4 weeks pretreatment with *Echinodontium taxodii* 2538 and *T. versicolor* G20 (Zhang et al. 2007b); and wheat straw was 39.7% decreased after pretreatment with *P. ostreatus* (Zadražil and Puniya 1994). The degradation of lignin by white-rot fungi is a non-specific oxidative process that finally results in complete degradation of the lignin.

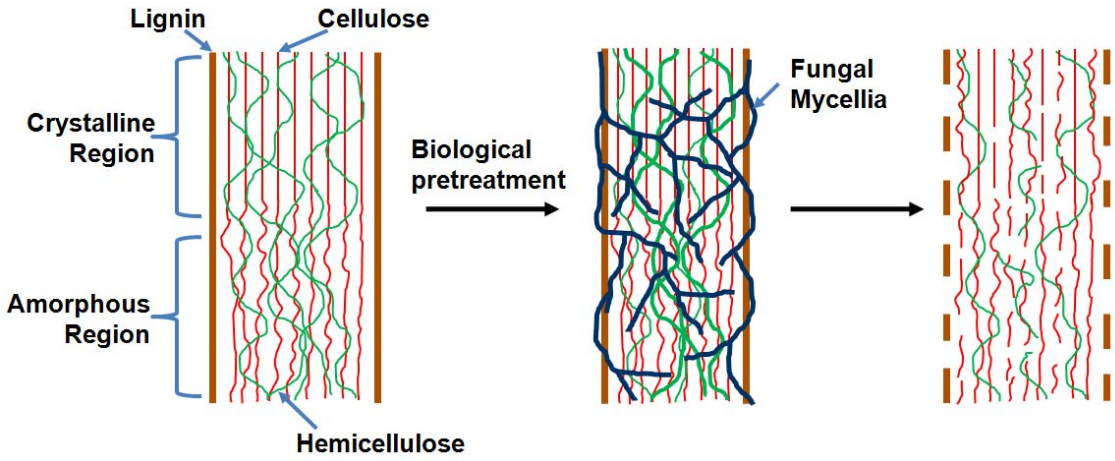

Fig. 2. Schematic diagram of biological pretreatment of lignocelluloses. White-rot fungi decrease lignin content and alter chemical and physical structures of lignocelluloses that make biodegradation of lignocelluloses more efficient.

White-rot fungi have unique capability to depolymerise, cleave carbon-carbon linkages, and mineralize lignin by ligninolytic enzymes. Studies with ^{14}C labeled lignin showed that white-rot fungi degraded them into $^{14}CO_2$ (Lundquist et al. 1977; Agosin, Daudin and Odier 1985; Pérez and Jeffries 1990; Hofrichter et al. 1999). *Pleurotus ostreatus* and *B. adusta* are highly specific lignin degraders based on ^{14}C-lignin-labeled degradation analysis (Agosin, Daudin and Odier 1985). Changes in the ratio between *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) lignin units were analysed using pyrolysis-gas chromatography-mass spectrometry. It was shown that 10 U of peroxidase per mg of straw decreased the proportion of phenolic H units from 31% in the control to 3% in the treated straw, the G units from 40 to 4%, and completely removed the small amount of phenolic S units present in wheat straw (Camarero et al. 2001). It is proposed that the susceptibility of the lignin units are in the following order: S>G>H. In general, biomass with S-rich lignins is more susceptible to fungal degradation than other lignin units (Valmaseda et al. 1991).

Hemicellulose is easier to degrade than other components in lignocellulosic biomass. White-rot fungus such as *P. chrysosporium* (Kirk and Cullen 1998), *Phlebia floridensis* (Sharma and Arora 2010), *C. subvermispora* (Mendonça et al. 2008), *Pleurotus ostreatus* (Baldrian et al. 2005), and *Pleurotus dryinus* (Kachlishvili et al. 2005) were shown to produce multiple endoxylanases. Compositional analyses of corn stover showed that during the 30 days biodegradation, white-rot fungi mainly degraded hemicellulose by 24.4 to 34.9% (Yang et al. 2010). Corn stover pretreated using *C. subvermispora* for 18 days lost up to 22.5% of hemicelluloses, and Chinese-willow pretreated using *Echinodontium taxodii* 2538 for 120 days lost 54.8% of its hemicellulose (Yu et al. 2009a). Degradation of hemicellulose combined with degradation of lignin may decrease recalcitration of lignocelluloses to enzymatic hydrolysis, but xylan loss increases the risk of lowering all sugar recovery in the bioconversion process (Yu et al. 2010a).

White-rot fungi also produce a battery of cellulases enzymes with different specificities and synergistic characteristics. Cellulases hydrolyse the β-1,4-glycosidic linkages of cellulose. Non-selective white-rot fungus degrades all lignocelluloses components in equal amounts, including cellulose. Otherwise, selective white-rot fungi degrade celluloses in negligible amounts (Blanchette 1995), and are suitable for biological pretreatment. Biological pretreatment causes microstructural changes of cellulose. XRD analyses revealed decreased crystallinity of cellulose after biological pretreatment. The crystallinity index of rice straw decreased from 44% in untreated ones to 15% in biological pretreated ones using *P. chrysosprorium* (Zeng et al. 2011). Contrarily, the crystallinity index of rice straw was slightly reduced after biological pretreatment using *D. squelens* (Bak et al. 2010). Biological pretreatment of Japanese red pine (*Pinus densiflora*) has been shown to reduce crystallinity of cellulose and increase the numbers of pores having size over 120 nm (Lee et al. 2007).

Surface morphology of lignocellulosic biomass has been examined by scanning electron microscopy (SEM). SEM images showed some of the physical changes in the surface of the biomass after biological pretreatments. Biological pretreatment of the biomass resulted in irregular holes on the surface of the corn straw (Yu et al. 2010b). This result indicates that biological pretreatment increases the porosity and surface area of the substrate. Biological pretreatment of corn stover with *Irpex lacteus* enhances pore volume and pore size remarkably (Xu et al. 2010). Wheat straw pretreated using *P. chrysosporium* has a more defined surface area, indicating aggressive removal or modification of lignin and making accessible the surfaces of hemicellulose and cellulose (Zeng et al. 2011). The surface of rice straw can have a rugged appearance and be partially broken after biological pretreatment using *D. squalens* (Bak et al. 2010).

FACTORS AFFECTING BIOLOGICAL PRETREATMENT WITH WHITE-ROT FUNGI

Activities of white-rot fungi and production of ligninolytic enzymes are influenced by several factors such as: fungal strain, concentration and source of nitrogen, addition of Mn^{2+} and Cu^{2+}, aeration, moisture content, acidity (pH), and temperature. Therefore, the activity of white-rot fungi could be regulated. Nutritional factors may control the mode of lignin degradation on lignocelluloses either selectively or simultaneously both in solid-state and submerged fermentation. In a previous work (Kirk et al. 1978), lignin degradation by *P. chrysosporium* was reported to be influenced by the concentration of nitrogen, agitation, O_2 concentration, pH, and vitamins. It is, therefore, important to take into consideration those factors on pretreatment of lignocellulose with white-rot fungi in order to obtain a high activity of the fungi and production of ligninolytic enzymes, and consequently high lignin degradation.

Fungal Strain

There are many species and strains of white-rot fungi, of which some produce all ligninolytic enzymes and others only partially produce ligninolytic enzymes (Elisashvili et al. 2008). For instance, *Pleurotus sajor-caju* strain Pl-27 and *Lentinus edodes* strain

LS4 produce MnP and Lac, but not LiP, when grown on a defined medium with glucose as the sole carbon source (Fu et al. 1997); *L. endodes* produces MnP and Lac, but not LiP (Buswell et al. 1995), while *P. chrysosporium* produces LiP, MnP, and Lac (Rodríguez et al. 1997; Rivela et al. 2000).

The first step in the utilisation of white-rot fungi is the screening of a large quantity of isolates in order to choose the right isolates with the highest ligninolytic enzymes production and activity, and high lignin degradation on the specific substrates. In such studies, 19 isolates of white-rot fungi were screened for enzymatic hydrolysis of straw (Hatakka 1983). After 5 weeks pretreatment with *Pleurotus ostreatus*, 35% of the original straw was converted to reducing sugars, 74% of which was glucose. On the other hand, only 12% of the untreated control straw was converted to reducing sugars, 42% of which was glucose. Preferential degradation also depends on the substrate. For example, *Pleurotus* sp. preferentially degrade lignin from straw, while they do not delignify the hardwood birch or the softwood pine (Hatakka 1983). In another study (Taniguchi et al. 2005), evaluation of four isolates of the white-rot fungi *Pleurotus ostreatus*, *P. chrysosporium*, *T. versicolor*, and *Ceriporioposis subvermispora* for pretreatment of rice straw followed by subsequent enzymatic hydrolysis was performed, and different results were reported. *P. ostreatus* preferred to degrade lignin more than polysaccharides in the rice straw, while *P. chrysosporium* and *C. subvermispora* degraded lignin and also polysaccharides of the straw.

Screening of the fungi for preferential lignin degradation may be carried out using scanning electron microscopy. In such studies (Blanchette 1984), 29 white-rot fungi were selectively removed, including lignin from various coniferous and hardwood tree species. In another study, 32 isolates of white-rot fungi for wheat straw were evaluated for enhancing biogas production (Muller and Trosch 1986). Straw pretreatment with *Pleurotus ostreatus* was found to have the highest rate in lignin degradation. Production of biogas from the fungal-pretreated straw was double compared to untreated straw.

Screening of white-rot fungi using ^{14}C-labelling was also proposed (Temp et al. 1998). For such screening, the fungal strains can be cultivated in tissue culture plates containing ^{14}C-ring-labelled dehydrogenation polymerizate (DHP). The method is especially useful for screening new and powerful lignin-degrading microorganisms. $^{14}CO_2$ is trapped in barium-saturated filter paper and is detected by exposing the paper to X-ray film to show autoradiograms corresponding to the positions of individual wells formed by evolved and trapped $^{14}CO_2$.

Nitrogen Source and Concentration

Nitrogen concentration in the culture medium either in solid-state and submerged fermentation plays an important role in the production and activity of ligninolytic enzymes. However, the effects of nitrogen vary among species and strains of white-rot fungi. An earlier study on the effect of medium composition on lignin degradation using white-rot fungi revealed that nitrogen concentration, regardless of its type and source, is critical for lignin degradation with *P. chrysosporium* (Kirk et al. 1978). Removed nitrogen content of hemp stem wood with protease could improve selective lignin degradation of *Bjerkandera* sp. strain BOS55 (Dorado et al. 2001). On the contrary, ligninolytic enzyme (Lac, MnP and peroxidase) activities of *Pleurotus ostreatus*

decreased when the medium was supplemented with inorganic nitrogen source. On the other hand, supplementing organic nitrogen (peptone and casein) at low concentrations showed positive effects on Lac, MnP, and LiP activities using *P. ostreatus* (Mikiashivili et al. 2006). Different responses of *Pleurotus* sp. caused by the supplementation of different kinds of nitrogen sources was also reported (Stajic et al. 2006a). *P. eryngii* and *P. ostreatus* produced Lac with the highest activity when $(NH_4)_2SO_4$ is used as the nitrogen source. Production of peroxidases using *P. ostreatus* was achieved when the nitrogen source in the medium was peptone.

Lac was produced when *L. edodes* was grown in the presence of high nitrogen content (Buswell et al. 1995). *Bjerkandera* sp. strain BOS55 produced LiP in nitrogen (N)-sufficient glucose-peptone medium, whereas no LiP was detectable in N-limited medium. The production of LiP was induced by the peptide-containing components of this medium and also by the soy bean proteins. Furthermore, the production of MnP was stimulated by organic N sources, although lower production was also evident in N-limited medium. Peptone induced LiP activity at all pH values was tested; however, the highest activity was observed at pH 7.3 (Kaal et al. 1993).

Different responses among species and strain of white-rot fungi on nitrogen source and concentrations are possibly due to different nitrogen metabolism. In a previous report (Li et al. 1994), LiP expression of *P. chrysosporium* was regulated at the level of gene transcription by nutrient nitrogen. Low nitrogen concentration and organic nitrogen are frequently used for ligninolytic enzyme production and activities, and improvement of lignin degradation using white-rot fungi. Another study (Kaal et al. 1993) showed that the induction of LiP depend on the combination of pH and the type of N source. An amino acid mixture and ammonium induced LiP only at pH 6.0 or 7.3.

Mn^{2+} and Cu^{2+} Addition

Inorganic nutrients such as+ Mn^{2+} and Cu^{2+} have been studied regarding their effects on lignin degradation using white-rot fungi (Jeffries et al. 1981; Tychanowicz et al. 2006). Expression and production of MnP are regulated by the presence of Mn^{2+} in the medium. Mn^{2+} controls the *mnp* gene transcription that is both growth and concentration-dependent (Brown et al. 1991; Gettemy et al. 1998). Mn^{2+} affects production of LiP and MnP enzymes (Bonnarme and Jeffries 1990). In the absence of Mn^{2+}, extracellular LiP isoenzymes predominated, whereas in the presence of Mn^{2+}, MnP isoenzymes were dominant. This regulatory effect of Mn^{2+} occurred in five strains of *P. chrysosporium*, two other species of *Phanerochaete*, and three species of *Phlebia*, *Lentinula edodes*, and *Phellinus pini*. LiP is formed exclusively when Mn^{2+} is low (1.6 to 0.3 ppm). Other results suggest (Kerem and Hadar 1995) that mineralisation of synthetic lignin is enhanced by the addition of Mn^{2+} (ranging from 30 to 620 mg) by *Pleurotus ostreatus*. Addition of Mn^{2+} (0.3 mM) into the culture increased lignin mineralisation by approximately 125% by *Pleurotus pulmonarius* (Camarero et al. 1996).

Coppers are included in crystal structure of Lac (Piontek et al. 2002; Polyakov et al. 2009). Addition of Cu^{2+} was reported to improve ligninolytic enzymes production and was the most efficient inducer for Lac (Palmieri et al. 2000). Addition of Cu^{2+} (25.0 mM) increased Lac activity from 270 to 1,420 U/L using *Pleurotus pulmonarius* (Tychanowicz et al. 2006). Addition of 1 mM Cu^{2+} increased Lac production eight-fold using *P.*

ostreatus cultivated in liquid nitrogen-limited medium (Baldrian and Gabriel 2002). Other results suggest (Stajic et al. 2006b) that optimum addition of Cu^{2+} for Lac production using *P. ostreatus* is 1 mM. Addition of Cu^{2+} more than 0.3 mM inhibited fungal growth and decreased Lac activity with *P. ostreatus* (Patel et al. 2009b). Simultaneous addition of Cu^{2+} and lignin could significantly increase Lac activity from 8 U/mL (only Cu^{2+} added) to 12 U/mL (Cu^{2+} and lignin added) using *Pleurotus ostreatus* (Tinoco et al. 2010). Nano particles of copper and iron induced production of ligninolytic enzymes and reduced hydrolytic enzyme (β-glucosidase, β-xylosidase and cellobio-hydrolase) significantly (Shah et al. 2010).

Addition of Mn^{2+} and Cu^{2+} with particular concentration to culture of white-rot fungi can induce and control ligninolytic enzymes production. Mn^{2+} concentration can affect MnP and LiP activities, whereas Cu^{2+} can affect Lac activities.

Aeration

Aeration is one of the most important parameters that affect production and activity of ligninolytic enzymes. The functions of aeration are e.g. oxygenation, CO_2 removal, heat dissipation, distribution of water vapour for regulating humidity, and distribution of volatile compounds produced during metabolism. The porosity of the medium affects the aeration rate, and therefore, pO_2 and pCO_2 should be optimised for each type of medium, microorganism, and process (Graminha et al. 2008). Lignin degradation is an oxidative process, and replacing air with an atmosphere of O_2 stimulates lignin degradation by many white-rot fungi growing on straw and wood (Zadražil et al. 1991). Oxygen enrichment of the atmosphere also stimulates degradation of non-lignin component as well as lignin degradation (Reid 1989). A study on LiP productivity using *P. chrysosporium* (Couto et al. 2002) shows that the productivity can be increased by increasing the aeration rate. On the other hand, productivity of MnP was not significantly affected by the aeration. Another study showed that batch operation at an aeration level of 0.5 vvm led to maximum MnP and LiP activities of 574 and 116 U/L, respectively. It was also shown that aerated *P. chrysosporium* culture with pure O_2 could improve intracellular production of LiP and MnP (Belinky et al. 2003). Biotrans-formation of lignocellulosic wastes into compost using *Coriolus versicolor* and *P. flavido-alba* were enhanced at low aeration condition (Lopez et al. 2002).

Moisture Contents

Moisture content of the solid state fermentation is a critical factor for fungal growth and activities, and significantly affects lignin degradation (Shi et al. 2008). Moisture content is defined during the initial substrate preparation before inoculation with white-rot fungi. The range of moisture content of substrate for SSF using white-rot fungi is usually between 60 and 80% (Karunanandaa and Varga 1996). Different reports (Xu et al. 2001) emphasise that lower solid/liquid ratio is more beneficial to the production of MnP and LiP. SSF of straw is optimum in a medium with water content of 75 mL/25 g substrate (Zadražil and Brunnert 1981). However, most of the fungi tested could digest straw over a wide range of water content. At higher water contents (125-150 mL/25 g of substrate), an increased production of aerial mycelium was observed. Laccase production using *P. pulmonarius* was positively affected by increasing the initial

moisture content from 40% to 60% (Patel et al. 2009b). The effects of substrate moisture contents, inorganic salt concentrations, and culture times on the biological pretreatment of cotton stalks using *P. chrysosporium* was investigated (Shi et al. 2008). Moisture content and time significantly affected lignin degradation. Higher moisture content of the culture (75% and 80%) resulted in degrading approximately 6% more lignin than 65% moisture content. However, optimum moisture content depends upon the organism and the substrate used for SSF. Increasing the moisture content will reduce the porosity of the substrate and limits oxygen transfer. Lac activity using *P. pulmonarius* decreases when moisture content increases from 60% to 80% (Patel et al. 2009b).

Acidity (pH)

pH is one of the important parameters in fungal cultivation that is difficult to control in solid-state fermentation (Hölker et al. 2004). Most white-rot fungi grow well on slightly acidic substrate pHs between 4 and 5 (Reid 1989). Many white-rot fungi reduce acidity of the substrate during their growth (Zadražil and Brunnert 1981; Agosin et al. 1985). Ligninolytic enzyme activity and production are affected by the starting pH of SSF. The starting pH for production of LiP and MnP using *P. chrysosporium* was 4.0 and 5.5, respectively, which resulted in the respective maximum activities of the enzymes of 2600 U/L and 1375 U/L (Xu et al. 2001). SSF of wheat straw using selected white-rot fungi showed a decrease in pH during fermentation. *Vararia effuscata* and *D. squalens* had very similar growth patterns, and the pH values at the inflexion point were 4.9 and 4.2, respectively (Agosin et al. 1985). Optimal pH for maximum Lac production using *P. ostreatus* was observed at pH 5.0. However, Lac production decreased when the initial pH increased to more than 5.0. A change in pH will alter the tree-dimensional structure of the Lac and may reduce their activity (Patel et al. 2009b).

Temperature

The effect of temperature on the rate and selectivity of delignification varies from one genus to another. Most white-rot fungi are mesophiles, with optimum temperature between 15^{o} to 35 ^{o}C (Reid 1989). Various optimal temperatures have been reported for SSF in the production of ligninolytic enzyme using white-rot fungi. The optimal temperature for producing the enzyme using *P. chrysosporium* was 39 ^{o}C (Xu et al. 2001). A report (Asther et al. 1988) mentions that 37 ^{o}C is the optimum for the mycelium-growing phase, while 30 ^{o}C is optimum for the lignin peroxidase-producing phase using *P. chrysosporium*. However, *G. applanatum*, *Pleurotus ostreatus*, and *Pleurotus serotinus* lignin degradation, even on an absolute scale, was less at 30 ^{o}C than at 22 ^{o}C (Zadražil and Brunnert 1981). Only *T. hirsuta* enhanced degradation at elevated temperature of 30 ^{o}C.

Different optimal temperature at SSF for biological pretreatment of lignocellulosic biomass is related to fungal physiology, fungal strain, and type of substrate. Optimum temperature for Lac activity using *P. ostreatus* was 28 ^{o}C (Patel et al. 2009b). The metabolism of the white-rot fungi during delignification generates heat and it may raise the fermenting material to temperatures that inhibit the growth of the fungi.

APPLICATION OF BIOLOGICAL PRETREATMENT USING WHITE-ROT FUNGI IN SOLID-STATE FERMENTATION

The combination of solid-state fermentation (SSF) technology with the capability of white-rot fungi to selectively degrade lignin has made industrial-scale application of lignocellulose-based biotechnologies possible. One of the most important aspects of white-rot fungi is related to the use of their ligninolytic system for a variety of applications (Fig. 2).

A review, covering advantages and drawbacks of SSF (Hölker et al. 2004), shows SSF as a robust technology that outperforms conventional fermentation technologies with respect to simplicity, cost effectiveness, and maintenance requirements. These advantages make SSF an attractive technology for environmental problems, where money and highly educated people are limited (Bhatnagar et al. 2008; Rivela et al. 2000). In this section, biotechnological applications and potential of pretreatment of lingo-cellulose using white-rot fungi in SSF is described.

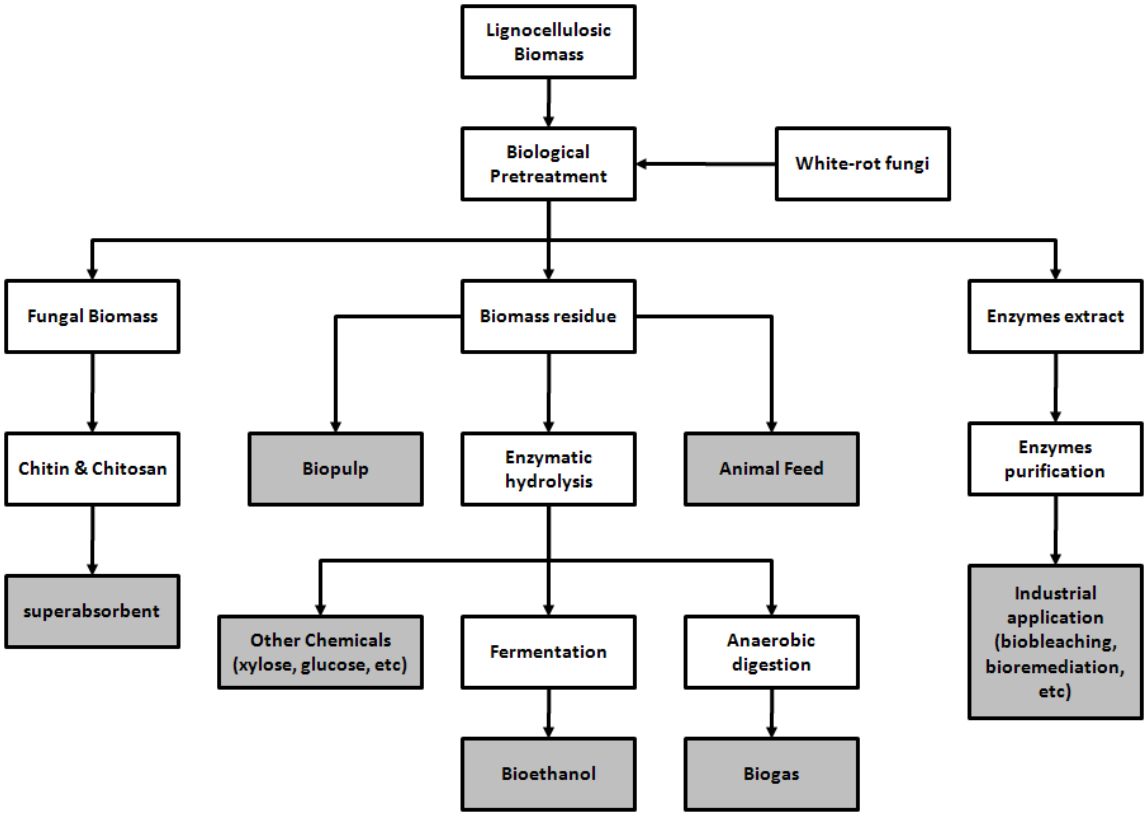

Fig. 2. Suggestion for biological pretreatments of lignocellulosic biomass with white-rot fungi and alternative application routes

Table 1. Application of Biological Pretreatment of Lignocellulosic Biomass with White-Rot Fungi in Solid-State Fermentation

Purpose	White-rot fungus	Substrates	References
Enzymatic Hydrolysis			
	Ceriporia lacerata, Stereum hirsutum and *Polyporus brumalis*	Japanese red pine	(Lee et al. 2007)
	Coriolus versicolor	bamboo residues	(Zhang et al. 2007a)
	Echinodontium taxodii	softwoods and hardwoods	(Yu et al. 2009a)
	Irpex lacteus	wheat straw	(Dias et al. 2010)
	I. lacteus	cornstalks	(Yu et al. 2010a)
	Phanerochaete chrysosporium	*Achras zapota*	(Ganesh Kumar et al. 2006)
	Pleurotus ostreatus	rice straw	(Taniguchi et al. 2005)
	Trametes versicolor G20 and *Echinodontium taxodii* 2538	bamboo culms	(Zhang et al. 2007b)
	T. versicolor, Ganoderma lucidum and *E. taxodii*	corn straw	(Yu et al. 2010b)
	Various species of white-rot fungi	wheat straw	(Hatakka 1983)
Biofuel (Bioethanol, Biogas and Pyrolysis)			
	Ceriporiopsis subvermispora	corn stover	(Wan and Li 2010)
	C. subvermispora, Dichomitus squalens,Pleurotus ostreatus and *Coriolus versicolor*	beech wood	(Itoh et al. 2003)
	E. taxodii	water hyacinth	(Ma et al. 2010)
	P. chrysosporium	cotton stalks	(Shi et al. 2008)
	P. chrysosporium	rice straw	(Bak et al. 2009)
	P. chrysosporium	wheat straw	(Zeng et al. 2011)
	Pleurotus florida	corn straw	(Zhong et al. 2011)
	Pleurotus ostreatus BP2*, E. taxodii* 2538 and *I. lacteus* CD2	corn stover	(Yang et al. 2010)
	Various species of white-rot fungi	wheat straw	(Muller and Trosch, 1986)
Biopulping & Biobleaching			
	C. subvermispora	rice, wheat and barley straw	(Yaghoubi et al. 2008)
	C. subvermispora	*Eucalyptus grandis*	(Ferraz et al. 2008)
	C. subvermispora and *P. chrysosporium*	wood	(Akhtar et al. 1998)
	C. subvermispora SS-3	*E. grandis*	(Mosai et al. 1999)
	P. chrysosporium	wheat straw	(Chen et al. 2002)
Biopulping & Biobleaching			
	Bjerkandera sp. strain BOS55	Kraft-Pulp	(Moreira et al. 1997)
	P. chrysosporium	wheat straw	(Jiménez et al. 1997)
	P. chrysosporium and *T. Versicolor*	Kraft-pulp	(Katagiri et al. 1995)

Table 1. - *continued*

Purpose	White-rot fungus	Substrates	References
	P. chrysosporium ME446	wheat straw	(Qin et al. 2009)
	P. chrysosporium,	Douglas-Fir	(de Jong et al. 1997)
	P. sordida YK-624	Kraft-pulp	(Kondo et al. 1994)
	Pleurotus eryngii	wheat straw	(Martínez et al. 1994)
	Several white-rot fungi	Loblolly pine	(Levin et al. 2007)
Ruminant Feed			
	C. subvermispora	madake bamboo	(Okano et al. 2009)
	C. subvermispora and *Cyathus stercoreus*	Various biomass	(Akin et al. 1996)
	P. chrysosporium	wheat straw	(Basu et al. 2002)
	Phlebia floridensis	wheat straw	(Sharma and Arora 2010)
	Pleurotus eryngii	bagasse	(Zadražil and Puniya 1995)
	Pleurotus ostreatus	cottonseed hull	(Li et al. 2001)
	Pleurotus ostreatus	barley straw	(Ortega Cerrilla et al. 1986)
	Pleurotus ostreatus	rice husk	(Beg et al. 1986)
	Pleurotus ostreatus, D. squalens and *B. adusta*	wheat straw	(Agosin and Odier 1985)
	Pleurotus sajor-caju	cotton plant stalk	(Hadar et al. 1992)
	Pleurotus sajor-caju and *Potyporus hirsutus* 534	bagasse	(Kewalramani et al. 1988)
	Pleurotus sp	bagasse	(Ortega et al. 1992)
	*Pleurotus tuber-regium (*Fr.) Sing.	wheat straw	(Jalc et al. 1999)
Enzyme production			
	P. chrysosporium	Barley Straw	(Rodríguez et al. 1997)
	Pleurotus sajor-caju PS 2001	bagasse	(Camassola and Dillon 2009)
	P. chrysosporium	steam-exploded straw	(Fujian et al. 2001)
	Pleurotus ostreatus strain 10969	Juncao	(Liu et al. 2009)
	Pleurotus ostreatus		(Téllez-Téllez et al. 2008)
	Pleurotus sp	wheat straw	(Bhattacharya et al.)
Others			
	P. chrysosporium	composting	(Taccari et al. 2009; Zeng et al. 2010)

Enzymatic Hydrolysis of Lignocellulose

Polysaccharides in lignocellulosic biomass, including cellulose and hemicelluloses, can be hydrolysed to monomeric sugars such as glucose and xylose, which can be further used for the production of ethanol, xylitol, organic acid, and other chemicals. The cellulose polymers in the cell wall are directly associated with lignin and hemicellulose moieties, resulting in even more complex physical and morphological structures, so that the enzymatic hydrolysis is obstructed. The limiting factors that affect enzymatic hydrolysis of biomass have been traditionally divided into two groups: (a) biomass structural features and (b) enzymatic mechanisms. Conventionally, structural features have been divided into two groups and classified as physical or chemical. The chemical structural features are the compositions of cellulose, hemicellulose, lignin, and acetyl groups bound to hemicellulose. The physical structural features consist of accessible surface area, crystallinity, the physical distribution of lignin in the biomass matrix, degree of polymerisation, pore volume, and biomass particle size. In order to improve the rate of enzymatic hydrolysis and to increase the yield of fermentable sugar, the process of pretreatment is absolutely essential. Pretreatment is required to alter the structural and chemical composition of lignocellulosic biomass in order to facilitate rapid and efficient hydrolysis of carbohydrates into fermentable sugars (Chang and Holtzapple 2000). The main focus of most studies dealing with lignocellulosic biomass conversion has been to maximise the availability of the cellulose to cellulase.

Pretreatment of lignocellulose with white-rot fungi for enzymatic hydrolysis has been studied for a long time (Hatakka 1983). Different species of white-rot fungi have been used with various lignocellulosic biomass for enzymatic hydrolysis (see Table 1). Biological pretreatment of lignocelluloses could increase accessibility of enzyme into biomass and increase the sugar yield. An evaluation of biological pretreatment of wheat straw using nineteen white-rot fungi followed by enzymatic hydrolysis (Hatakka 1983), shows that after pretreatment with *Pycnoporus cinnabarinus* for five weeks, as much as 54.6% of the residue could be converted into reducing sugar by enzymatic hydrolysis. A recent paper (Dias et al. 2010) revealed that wheat straw biologically pretreated with two white-rot fungi (Euc-1 and *I. Lacteus*) could improve the hydrolysis yield by approximately four and three times compared with untreated straw, respectively. In addition, biological pretreatment of corn stover using *P. chrysosporium* improved enzymatic hydrolysis three- to five-fold in comparison to that of untreated corn stover and reduced the energy requirement for its milling (Keller et al. 2003). Similar enhancements with biological pretreatment on rice straw using four white-rot fungi *P. chrysosporium*, *T. versicolor*, *C. subvermispora*, and *Pleurotus ostreatus* was reported (Taniguchi et al. 2005). An enhanced degree of enzymatic hydrolysis of straw was observed as the content of Klason lignin decreased. Biological pretreatment of bamboo using a white-rot fungus *Coriolus versicolor* B1 under different conditions and saccharification was studied (Zhang et al. 2007a). Their study shows that the saccharification rate was significantly enhanced and a maximum saccharification rate of 37.0% was achieved after the pretreatment.

Biofuel: Bioethanol, Biogas and Pyrolysis

Bioethanol can be produced from lignocellulosic biomass after hydrolysis of poly-

saccharide components (hemicelluloses and cellulose) into monosaccharides. Increase of sugar yield by enzymatic hydrolysis after biological pretreatment indicates a high bio-ethanol yield. Biological pretreatment of corn stover using *C. subvermispora* for 35 days is able to improve the overall ethanol yield by up to 57.8% (Wan and Li 2010). A similar result was obtained when rice straw was biologically pretreated using *D. squalens*. The ethanol production yield and productivity were 54.2% of the theoretical maximum and 0.39 g/L/h, respectively, after 24 h (Bak et al. 2010). The ethanol yield achieved 0.192 g/g dry matter from water hyacinth when pretreated with a combination of biological and mild acid pretreatment (Ma et al. 2010).

Biological pretreatment has been used for biogas production. Biogas production from biologically pretreated wheat straw increased from 0.293 L/g (untreated) to 0.343 L/g (pretreated one) using *Pleurotus ostreatus* (Muller and Trosch 1986). However, biological pretreatment of corn straw using *Pleurotus florida* resulted in 16.58% less biogas than after a chemical pretreatment (Zhong et al. 2011).

Biological pretreatment has been used before pyrolysis of biomass to produce fuel. Biological pretreatment of corn stover can optimise the thermal decomposition, decrease the reaction temperature and reduce the gas contamination (SO_x), making the biomass pyrolysis more efficient and environmentally friendly (Yang et al. 2010). Biological pretreatment can decrease the activation energy and reacting temperature of the hemicellulose and cellulose pyrolysis (up to 36 ^oC), shorten the temperature range of the active pyrolysis (up to 14 ^oC), and increase the thermal decomposition rate.

Biopulping and Biobleaching

Biopulping is a SSF process in which wood chips are treated with white-rot fungi to improve the delignification process. Biological pulping has the potential to reduce energy costs and environmental impact relative to traditional pulping operations (Scott et al. 2002). The benefits of biopulping was demonstrated (Scott et al. 2002) using 50-ton scale experiments. The tensile, tear, and burst indexes of the resulting papers were improved, indicating a higher degree of cellulose conservation during the pulping process. In addition, the brightness of the pulp was also increased, indicating an improved lignin removal. Moreover, an improved energy savings of 33% for thermomechanical pulping (TMP) was reported. Biological pretreatment of wheat straw using *P. chrysosporium* ME466 could alter degradation of lipophilic and hydrophilic extractives. Obviously, the biological pretreatment of wheat straw was beneficial to pitch control in pulping and papermaking processes, in view of the degradation of the more lipophilic substances (van Beek et al. 2007). Variable optimisation for biopulping of agricultural residues using *C. subvermispora* was also investigated (Yaghoubi et al. 2008). Biological pretreatment could increase the physical properties (kappa number, tensile strength, and burst factor) and the quality of the pulp from barley straw.

Production of biopulp with *P. chrysosporium* using steam-exploded wheat straw as substrate was considered (Chen et al. 2002). Its hemicellulose was partially degraded and became partly water-soluble sugar during the steam explosion process. These sugars could be used as a carbon resource for growth of the fungus. Compared with non-treated wheat straw, degradation of cellulose was decreased and degradation of lignin was increased for the steam-exploded wheat straw cultured with *P. chrysosporium*. Fermented

straw could be used directly as the material for pulp making.

Some researchers have investigated the use of white-rot fungi for biobleaching pulp. Pretreated pulp with white-rot fungi could improve brightness and strength properties of the pulp (de Jong et al. 1997; Bajpai 2004). Besides the direct use of fungi in biological pretreatment for biobleaching of pulp, application of ligninolytic enzymes also has been intensively investigated. Ligninolytic enzymes, mainly Manganese peroxidase (MnP) are the key enzyme for biobleaching of the pulp. Various screening experiments have demonstrated that MnP activities and production are correlated to the bleaching of the pulp. Semi-purified MnP can also delignify pulp and improve the brightness of the pulp (Kondo et al. 1994). Furthermore, application of Lac in totally-chlorine-free (TCF) sequence processes using a laccase-mediator system could improve the brightness up to 82% ISO brightness (compared with 37% in the initial pulp and 60% in the peroxide-bleached control) and result in very low kappa number (Camarero et al. 2004). Lac have been used commercially as a biobleaching agent for pulp and have been well reviewed (Call and Mücke 1997).

Ruminant Feed

The direct use of lignocellulosic residues as ruminant animal feed, or as a component of such feeds, represents one of the oldest and most widespread applications of biomass utilisation. The idea of using white-rot fungi to improve the digestibility of lignocellulosic waste for ruminants was first developed in 1902 by Falck (Cohen 2002), who suggested the use of fungi for the improvement of lignocellulosic wastes. Since then, a considerable amount of work has been conducted on the upgrading of lignocellulosic matter to feed using white-rot fungi. The concept of preferential delignification of lignocellulose waste with white-rot fungi has been applied to increase the nutritional value of forages (Agosin and Odier 1985; Zadražil and Puniya 1995; Okano et al. 2009). A wide range of lignocellulosic biomass have been pretreated with white-rot fungi and used as ruminant feed (See Table 1). Biological pretreatment of lignocellulose could improve the nutritional value (Okano et al. 2009) and *in vitro* digestibility (Zadražil and Puniya 1995), increase bioavailability of nutrients, and decrease anti-nutritional factors (Mandebvu et al. 1999).

Enzyme Production

The ability of ligninolytic enzymes to oxidise both phenolic and non-phenolic lignin related compounds as well as highly recalcitrant environmental pollutants makes these enzymes very useful for their application to several biotechnological processes (Mayer and Staples 2002; Minussi et al. 2002; Regalado et al. 2004; Couto and Herrera 2006). Production and application of Lac has been investigated more intensively than other ligninolytic enzyme during the last few decades, and such literature has been reviewed (Call and Mücke 1997; Leonowicz et al. 2001). Lac can be implemented in the food industry, pulp and paper industry, and textile industry (Couto and Herrera 2006; Call and Mücke 1997; Riva 2006; Cañas and Camarero 2010). SSF for enzyme production has more advantages than SF, since several studies have shown high product yield and simplified downstream processing compared with SF (Hölker and Lenz 2005; Couto and Sanroman 2006). Lignocellulosic wastes are generally used as substrate for

enzyme production (see Table 1).

Other Applications

The white-rot fungus *P. chrysosporium*, combined with other microorganisms, can be used as compost inoculants for lignocellulosic waste composting materials (Zeng et al. 2010; Taccari et al. 2009). When the fungi are inoculated during the second fermentation phase, *P. chrysosporium* induced significant changes on all parameters of compost maturity except C/N ratio. Composting methods using white-rot fungi have also been used for pollutant degradation (Zeng et al. 2007). Inoculation of the benzo[a]pyrene contaminated soil composting system with the white-rot fungus *P. chrysosporium* increased the rate of bound residue formation of contaminant carbon. Bound residue formation was found to be the predominant transformation mechanism for benzo[a]pyrene in the microbially active compost systems, accounting for nearly 100% of the benzo[a]pyrene removed (McFarland and Qiu 1995).

COMBINATION OF BIOLOGICAL PRETREATMENT WITH OTHER PRETREATMENT METHODS

The main drawbacks of biological pretreatment are loss of polysaccharides (hemicelluloses and cellulose) and the longer pretreatment duration than chemical/ physical pretreatment. In order to reduce the time for pretreatment, polysaccharides loss, and to enhance the yield of fermentable sugar, biological pretreatment can be combined with chemical/physical pretreatments. Combinations of pretreatment methods between biological and chemicals/physical pretreatments can enhance performance of the pretreatment compared to sole pretreatment methods. Chemical/physical pretreatment prior to biological treatment allows the substrate to be easily assessable for fungus to degrade the lignin component (Reid 1989). Optimisation of these combination methods leads to maximum sugar yield and reduces the overall pretreatment cost, i.e. incubation time, acid concentration, and/or energy used. These combination methods could significantly decrease the time of biological pretreatment and increase the sugar yield after enzymatic hydrolysis. When rice straw was pretreated with a steam explosion prior to biological treatment using *Pleurotus ostreatus*, the treatment time required for obtaining a 33% net glucose yield was reduced from 60 days to 36 days (Taniguchi et al. 2010). When rice straw was pretreated with H_2O_2 (2%, 48 h), the treatment time was reduced from 60 days to 18 days with comparable sugar yield (Yu et al. 2010b). The reduction time is probably due to partial degradation of the networks of lignin with sugar moieties as well as partial breakdown of the structure during the biological treatment.

The combined pretreatment of water hyacinth (*Eichhornia crassipes*) with white-rot fungi *E. taxodii* (10 days) and 0.25% H_2SO_4 was shown to be more effective than the sole acid pretreatment method. The reducing sugar yield from enzymatic hydrolysis increased by a factor of 1.13 to 2.11 compared to that of acid treatment under the same conditions (Ma et al. 2010). Biological pretreatment of beech wood chips prior to organosolv pretreatment could increase the ethanol yield by 1.6 times more than without biological pretreatment (Itoh et al. 2003). Brown-rot fungi combined with organosolv pretreatment has also been used (Monrroy et al. 2010). The biological pretreatment of

Pinus radiata wood chips prior to the organosolv pretreatment resulted in improved solvent accessibility. A similar result (Yu et al. 2010b) showed that biological pretreatment of corn straw for 15 days using *E. taxodii* followed by alkali/oxidative pretreatment could lead to an increase of 50.7% in reducing sugar compared to alkali/oxidative pretreatment alone. Biological pretreatment of cornstalks followed by mild alkaline pretreatment with *I. lacteus* could increase the digestibility of cellulose. The biological pretreatment enhanced delignification and glucan digestibility more significantly when the alkaline pretreatment was performed at lower severity (Yu et al. 2010a).

CONCLUDING REMARKS

Biological pretreatments of lignocellulosic biomass have been successfully implemented for animal feed and biopulping processes. Biological pretreatment has also been extensively examined for other purposes, such as enzymatic hydrolysis of lignocelluloses. Biological pretreatment has several advantages over conventional physical/chemical pretreatment. However, the challenges of biological pretreatments are the relatively long time of the pretreatment compared to physical/chemical methods, and incurring the risk of sugar loss. Consequently, biological pretreatment requires more space and longer processes, which increase the operating costs. This means that this method will be beneficial, where it could decrease biomass recalcitrance with a minimum loss of polysaccharides and a short time for incubation. Overcoming these challenges, i.e. slow process and sugar loss will most likely be the future developments of biological pretreatments.

One way to decrease pretreatment time is by applying a combination of biological and chemicals/physical methods. Many genetic, metabolic, physiological, and process factors that can be manipulated to improve lignin degradation and reduce sugar loss by, e.g. altering lignocellulosic structure and ligninolytic or cellulolytic enzymes, have already been investigated, but there is a need for further improvements. Minimization of carbohydrate loss during biological pretreatments could be achieved by manipulating the culture conditions, addition of certain substrates that can suppress the activity of hydrolytic enzymes, or by genetic engineering of white-rot fungi to lower the activity of such enzymes. Moreover, the structural differences of various lignocelluloses influences the success of biological pretreatment, as therefore, understanding the combination of the biological pretreatments and the structural changes of the lignocelluloses during the pretreatments will probably be a hot research topic in this field in the future.

ACKNOWLEDGEMENTS

This work was financially supported by Directorate General of Higher Education, Ministry of National Education of Republic of Indonesia through Competitive Research Grant of International Joint Research for International Publication (Grant No. 425/SP2H/PP/DP2M/VI/2010), European Commission program EM-EuroAsia and

Swedish International Development Cooperation Agency. We gratefully acknowledge Professor Zaenal Bahrudin for a critical reading of the manuscript.

All the authors were deeply saddened by loss of our colleague Prof. Knut Lundquist who passed away on the first of July 2011 during the final revisions of this paper, and would like to extend our deepest condolences to his family.

Professor Knut Lundquist received his scientific education from the late professor Erich Adler, one of the well-known pioneers in lignin chemistry research. Knut Lundquist was thus attracted by wood chemistry problems and became one who successfully continued the traditional ligninchemical studies also after retirement.

ABBREVIATIONS

SSF, Solid-state fermentation; SF, Submerged Fermentation; LiP, Lignin peroxidase; LiPs, Lignin peroxidases; Lac, Laccase; MnP, Manganese peroxidase; MnPs, Manganese peroxidases; VP, Versatile peroxidase; GLOX, Glyoxal oxidase; AAO, aryl alcohol oxidase; H, *p* -hydroxyphenyl; G, guaiacyl; S, syringyl.

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Article submitted: April 18, 2011; Peer review completed: May 16, 2011; Revised version received: June 27, 2011; Accepted: August 4, 2011; Published: August 6, 2011.