Bulletin of the National Research Centre

REVIEW Open Access

# Microbial delignification and hydrolysis of lignocellulosic biomass to enhance biofuel production: an overview and future prospect

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## Abstract

**Background:** The depletion of fossil fuel and its huge environmental problem are currently a concern for a scientific community in the area of energy engineering. This opened research opportunities for searching alternate renewable energy sources especially biofuel production from lignocellulose biomass resources. The main objective of this paper is to review the delignification and hydrolysis capabilities of microorganisms (bacteria and fungi).

**Results:** Currently, different types of lignocellulose biomass pretreatment technologies are available. All of the technologies are either in lab scale or in pilot scale. Among the pretreatment technologies, biological pretreatments attract many attentions because of their eco-friendly advantages, performed at a mild temperature and do not produce inhibitory compounds during the pretreatment process. Industrial-scale biofuel production using biological delignification and hydrolysis process is still at lab scale, and intensive research works are required. The cost of biofuel production from lignocellulose biomass is currently expensive.

**Conclusion:** Searching for the best microbial strains having efficient lignin-degrading and polysaccharide-hydrolyzing capabilities is vital to realize industrial-scale biofuel production from lignocellulose biomass. Process optimization along with genetic engineering of microorganisms is seen as a potential for biofuel production from lignocellulose biomass.

**Keywords:** Biological pretreatment, Lignocellulose biomass, Delignification, Fungi, Bacteria, Hydrolysis

## Introduction

In our today's world, fossil fuel (petroleum, natural gas, and coal) is one of the major sources of energy. The global demand for energy is growing each year along with population growth. However, climate changes caused by the use of fossil fuels and its limited availability and sustainability are driving for searching a sustainable supply of energy. According to global energy statistics, the total energy consumption of the world was 13,903 million tons of oil equivalent or $5.82 \times 10^{20}$ J in 2016 alone which was dominated by fossil fuels (Enerdata 2017). According to Shafiee and Topal's report, oil, gas, and coal reserves in the world are estimated to end within the next 27, 29, and 99 years, respectively (Shafiee and Topal 2009; Vohra et al. 2014). Therefore, sustainability problem and combustion emission of greenhouse gas open the door for scientists to search for a sustainable and relatively safer supply of energy to the world.

Biological materials, energy crops, and agricultural by-products are identified as sustainable and alternative energy sources for biofuel production. Bioenergy reduces adverse environmental impact (reduce the emission of greenhouse gases) caused by the use of fossil fuels, and at the same time, they are sustainable. The use of energy crops for biofuel production creates a fuel-food crisis by increasing the price of food across the globe (Mohapatra et al. 2017). Hence, the production of second-generation biofuels has been suggested as a desirable biofuel source than first-generation fuels (Haider 2013; Naik et al. 2010). According to the US Department of Energy,

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blending ethanol with a gasoline can reduce 25–30% emission of $CO_2$ (US Department of Energy 2017). To meet this demand, the industrial-scale production of ethanol from renewable biomass sources (lignocellulose) is required, since they are environmentally sound and economically viable (Hui et al. 2010).

Lignocellulose biomass contains lignin and polysaccharides such as cellulose, hemicellulose, pectin, ash, minerals, and salts. Cellulose is a chain of monomers of D-glucose linked to each other by linear β (1–4) linkage constituting 20–50% of the plant biomass. Hemicellulose is assembled from diverse polymers of short chains of polysaccharide molecules constituting 15–35% of lignocellulose biomass. They are composed of monomers of five different sugars (i.e., D-xylose, L-arabinose, D-galactose, D-mannose, and D-glucose). Lignin has an aromatic and amorphous nature constituting 18–35% of plant biomass. The chemical composition of different lignocellulose biomass is given in Table 1. The structure of lignin varies depending upon biomass type and species (Kulasinski et al. 2014). Perennial grasses, agricultural by-products, agro-industrial by-products, wood, and vegetable residues are categorized as lignocellulosic feedstock. They are rich in hemicellulose and cellulose, which are ideal raw materials for the production of biofuel. However, these polysaccharides are wrapped in a lignin matrix, which prohibits microorganisms to access it. This is a major barrier for hydrolysis and fermentation of lignocellulose biomass.

Pretreatment process is required for biofuel production from lignocellulose biomass. The primary objective of biomass pretreatment is to remove lignin and enhance the availability of cellulose and hemicellulose for hydrolysis and fermentation. Pretreatments can yield up to 90% of sugar while its absence can result in a yield of less than 20% of the total available sugars. Currently, there are different pretreatment mechanisms of lignocellulose biomass to enhance cellulose and hemicellulose by deconstructing the biomass (Ohgren et al. 2007; Hendriks and Zeeman 2009; Singh et al. 2014; Tsegaye et al. 2017). Physicochemical pretreatment, chemical pretreatments, thermochemical pretreatments, and biological pretreatments are among the mainly studied processes. Lignin shields the polysaccharides in lignocellulose biomass making them difficult to access and reluctant for microbial and enzymatic hydrolysis. Hence, pretreatment is used to increase the availability of cellulose and hemicellulose by increasing cellulose crystallinity, by removing lignin, and by increasing the porosity and surface area of the biomass structure (Carvalheiro et al. 2008; Pellera and Gidarakos 2017). Among the pretreatment processes, alkali pretreatments were found to be more effective in terms of solubilizing lignin and hemicellulose and cellulose yield (Carvalheiro et al. 2008; Foston and Ragauskas 2010; Pu et al. 2013; Tsegaye et al. 2017). The effectiveness of the methods is analyzed by their abilities to preserve and depolymerize celluloses, depolymerize hemicelluloses, and restrict inhibitory formation which reduces carbohydrate hydrolysis, low energy input, and ease of product recovery or separation (Mohapatra et al. 2017).

Alkali pretreatment method releases a relatively high yield of fermentable sugar compared to other pretreatment methods. The production of fermentation inhibitors, high energy requirement, equipment corrosiveness, high cost, need of the high amount of chemicals, long residence time, and destruction of a portion of pentose and hexose sugar make alkali method less desirable for industrial-scale production (Martínez et al. 2009). On the other hand, biological pretreatment, which needs no

**Table 1** Chemical compositions of various lignocellulose biomass (percentage in dry weight basis)

| Lignocellulose biomass type | Composition | | | | Reference |
|---|---|---|---|---|---|
| | Cellulose | Lignin | Hemicellulose | Arabinose | |
| Corn stover | 36 | 17.2 | 21 | 3.5 | Ohgren et al. 2007 |
| Olive tree | 25 | 19 | 15 | 2.4 | Cohen et al. 2017 |
| Rice straw | 41 | 10 | 15 | 5 | Niladevi et al. 2007 |
| Switch grass | 32 | 23 | 20 | 4 | Foston and Ragauskas 2010 |
| Wheat straw | 32 | 15 | 37 | 4–8 | Tsegaye et al. 2017 |
| Poplar wood | 40 | 29 | 15 | 1 | Foston and Ragauskas 2010 |
| Eucalyptus | 50 | 28 | 11 | < 1 | Feijoo et al. 2008 |
| Pine wood | 45 | 28 | 6 | 2 | Perestelo et al. 1989 |
| Sorghum straw | 33.5 | 18 | 25.5 | – | Mishra et al. 2017 |
| Barley hall | 34 | 16.5 | 36 | – | Zimmermann and Broda 1989 |
| Barley straw | 39 | 8 | 28 | – | Zimmermann and Broda 1989 |
| Rice husk | 32 | 18 | 20.5 | – | Haider 2013 |
| Conifers | 43–46 | 27–32 | 5–10 | 0.5–2 | Wagner et al. 2009 |

chemicals and performed in a mild environment, is considered as an eco-friendly, efficient, and cheap alternative for biofuel production (Wan and Li 2012). Biological pretreatments are usually performed by employing lignolytic and cellulolytic microorganisms, which synthesize potent lignolytic and cellulolytic enzymes during hydrolysis (Ruqayyah et al. 2013; Kadri et al. 2016; Neamah et al. 2016). The efficiency of biological delignification depends upon the type of microorganism used, nature and type of substrate used, and the cultivation methods and conditions used (Liu et al. 2017; Narra et al. 2017; Tsegaye et al. 2018a, b).

Bioethanol can be acquired from lignocellulose biomass after successive processes including pretreatments to remove lignin and releases the entangled polysaccharides and fermentation (Silveira et al. 2015; Oonkhanond et al. 2017). Oonkhanond et al. (2017) obtained highly accessible cellulose for enzymatic hydrolysis after pretreating sugarcane bagasse by green solvents under supercritical carbon dioxide condition. Separated hydrolysis and fermentation (SHF) and simultaneous hydrolysis and fermentation (SSF) are the most commonly used techniques for bioethanol production. But the concept of integration of filtration in simultaneous hydrolysis and fermentation provides an additional advantage over the common techniques used (Ishola et al. 2013). It eliminates the risk of inhibition and helps the recovery of the microorganisms for further reuse. Besides this, the use of pentose-sugar-fermenting microorganisms can enhance ethanol yield.

The main objective of this review paper is to present insight studies conducted on microbial delignification and hydrolysis of lignocellulosic biomass for biofuel production. The mechanism of the delignification process was also reviewed.

## Overview of biological pretreatments

Compared to other pretreatment methods, biological pretreatments are an eco-friendly, cheap, and efficient alternative method. The advantage and limitation of biological pretreatments compared to other pretreatment methods are given in Table 2. Lignocellulose biomass conversion to biofuel has done by employing different microbial strains and combinations of enzymes. Many scholars reported that various species of bacteria and fungi have the capabilities to degrade lignocellulose biomass. Fungi are known by degrading lignin components of lignocellulose biomass through the production of enzymes such as laccase and peroxidases. The overall scheme of biological conversion of lignocellulose biomass to biofuel is given in Fig. 1.

There are many common fungi strains used for pretreatments of lignocellulose biomass, such as *Ceriporiopsis subvermispora*, *Ceriporia lacerate*, *Cyathus stercoreus*,

**Table 2** Comparison of biological pretreatment with other pretreatment methods

| Pretreatment type | Merits or advantages | Common chemicals/ solvents used | Constraints/limitation | References |
|---|---|---|---|---|
| Biological | ✓ Low use of energy and chemicals<br>✓ Able to degrade hemicellulose and lignin<br>✓ Environmentally sound | – | Have lower hydrolysis rate | Dunlop 2011; Monavari et al. 2009; Dionisi et al. 2014 |
| Organosolv | Able to depolymerize lignin and hemicelluloses | Acetone, formic acid, methanol, ethylene glycol, butanol, ethanol | ➢ Needs solvent recycling and draining<br>➢ Expensive<br>➢ Inhibitors are produced | Monavari et al. 2009 |
| Steam explosion | Able to depolymerize lignin and hemicelluloses | Steam | ➢ Xylan loss<br>➢ Partial depolymerization of components<br>➢ Inhibitors are produced | Galbe and Zacchi 2002; Wyman et al. 2005 |
| Alkali treatment | ➢ Able to take out lignin and hemicelluloses<br>➢ Increases the accessibility of the surface | Sodium hydroxide, calcium hydroxide, ammonia | ➢ Washing is required<br>➢ Salt formation causing fouling problems | Alexandropoulou et al. 2017; Narra et al. 2017 |
| Ozonolysis | ➢ Able to depolymerize lignin<br>➢ No inhibitory production | Ozone | ➢ High amount of ozone is required<br>➢ Expensive | Sun and Cheng 2002 |
| Ammonium fiber explosion | ➢ Increases the accessibility of the surface<br>➢ Able to depolymerize lignin and hemicellulose | Ammonia, water | ➢ Efficient problem<br>➢ Inhibitors are produced | Gupta and Lee 2009 |
| Acid treatment | ➢ Able to hydrolyze hemicellulose<br>➢ Modifies lignin structure | Sulfuric acid, nitric acid | ➢ Expensive<br>➢ Corrosive to equipment<br>➢ Inhibitors are produced | Pu et al. 2013; Mohapatra et al. 2017 |

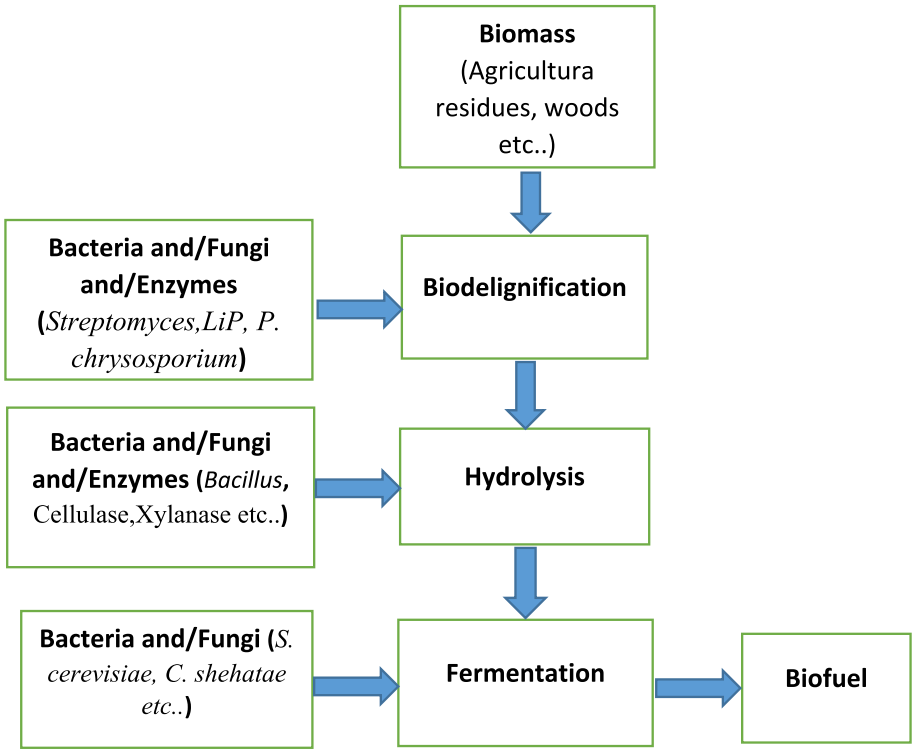


**Fig. 1** Overall biological conversion scheme of lignocellulose biomass to biofuel

*Pleurotus ostreatus*, *Pycnoporus cinnabarinus*, *Phanerochaete chrysosporium*, *Coniophora puteana*, *Laetiporus sulphureus*, *Serpula lacrymans*, *Gloeophyllum trabeum*, *Paecilomyces* sp., *Daldinia concentrica*, and *Cadophora* spp. (Kumar et al. 2009; Maurya et al. 2015; Masran et al. 2016; Shirkavand et al. 2017). Few scholars have reported on biological pretreatments using bacteria. Limited bacterial strains showed lignin-degrading ability. Some of the strains which are capable to degrade lignin are *Bacillus circulans*, *Zymomonas* spp., *Bacillus* sp. AS3, *Cellulomonas*, and *Sphingomonas paucimobilis* (Lynd 1989; Lynd et al. 2002). In general, current research findings showed that bacteria have poor lignin degradation capabilities than fungi.

## Degradation of lignin microorganisms

### Lignin-degrading fungi

Filamentous fungi are one of the most known types of lignin-degrading fungal species. They are ubiquitously available in lignocellulosic waste material and in soil and plants. Numerous studies identified that white- and brown-rot fungi are effective in degrading lignocellulose biomass such as Bermuda grass, wood chips, wheat straw, and softwoods (Alexandropoulou et al. 2017; Cohen et al. 2017; Liu et al. 2017; Mishra et al. 2017). White-rot fungi have the capability to degrade hemicellulose, cellulose, and lignin whereas brown-rot fungi are limited to hemicellulose and cellulose without affecting lignin. They are known as the major degrader of forest wood in the ecosystem. Lignin-degrading efficiencies of various types of fungal species are given in Table 3.

*Trametes versicolor* removed about 57.4% of lignin from beech wood within 120 days of pretreatment (Bari et al. 2016). About 28% of lignin from cotton stalks were removed by *Phanerochaete chrysosporium* after 14 days of pretreatment (Shi et al. 2008). The removal of lignin from cotton stalks was further increased to 60% after 30 days of pretreatment (Kerem et al. 1992). This is the maximum amount of lignin removal reported so far by using fungi. In addition, 40% of lignin removal was reported by using fungi species *Pleurotus ostreatus* within 30 days of pretreatment (Adebayo 2015; Kerem et al. 1992). Even though fungi have a greater potential for lignin degradation, the long residence time requirement makes them not feasible for large-scale production. The long residence time increases production costs and requires large space. However, the mild temperature operation, the eco-friendly nature, and the requirement of no chemicals make biological pretreatment a cheap alternative for biofuel production. If much focus and research are done on different fungi species using various lignocellulose biomass, there is a possibility of novel strain isolation and discovery.

**Table 3** Fungi degradation of lignin on different feedstock

| Fungi species | Category | Feedstock used | Lignin degradation (%) | Time (days) | Reference |
|---|---|---|---|---|---|
| *Pleurotus ostreatus* | Mushroom | Cotton stalks | 40 | 30 | Kerem et al. 1992 |
| *Phanerochaete chrysosporium* | White-rot fungus | Cotton stalks | 60 | 30 | Kerem et al. 1992; Shi et al. 2008 |
| *Trametes versicolor* | White-rot fungus | Beech wood | 57.4 | 120 | Bari et al. 2016 |
| *Phanerochaete chrysosporium* | White-rot fungus | Cotton stalks | 28 | 14 | Shi et al. 2008 |
| *Irpex lacteus* | White-rot fungus | Cornstalks | 15 | 11.84 | Du et al. 2001 |
| *Echinodontium taxodii* 2538 | White-rot fungus | Bamboo culms | 24 | 28 | Suhara et al. 2012 |
| *Pleurotus ostreatus* | White-rot fungus | Beech wood | 56.5 | 120 | Kerem et al. 1992; Patel et al. 2009 |
| *Phlebia* sp. MG-60 | White-rot fungus | Oak wood | 40.6 | 56 | Kamei et al. 2012 |
| *Trametes versicolor* spp. | White-rot fungus | Bamboo culms | 9–24 | 28 | Suhara et al. 2012; Shirkavand et al. 2017 |
| *Ceriporia lacerata* | White-rot fungus | Red pine | 13 | 56 | Lee et al. 2007 |
| *Stereum hirsutum* | Brown-rot fungus | Red pine | 15 | 56 | Shirkavand et al. 2017 |
| *Ceriporiopsis subvermispora* | White-rot fungus | Corn stover | 39.2 | 42 | Ohgren et al. 2007; Liu et al. 2017 |

## Mechanism of fungi delignification

The main mechanisms of lignocellulose biomass degradation in fungi are broadly categorized into hydrolytic and oxidative type. Free radicals of reactive oxygen species mainly hydroxyl types are produced during lignin degradation in oxidative type mechanism (Hammel et al. 2002). Hydrogen peroxides are produced by many fungi through the action of enzymes like aryl-alcohol oxidase, pyranose-2 oxidase, and glyoxaline oxidase (Martínez et al. 2009). The hydroxyl radicals, which are produced by the reaction of iron with hydrogen peroxide (Fenton reaction), degrade lignin into lower molecular weight products (Hammel et al. 2002). Glycosidic linkages are broken down by hydrolytic enzymes from fungi in hydrolytic type mechanism (Feijoo et al. 2008).

Another group of enzymes such as manganese peroxidase (MnP) and laccases catalyzes the oxidative type mechanism of lignin degradation. Multicopper oxidase laccase can catalyze lignin degradation, which is mediated by free radicals (Eggert et al. 1997). The hydrolysis of hydrogen peroxide by manganese peroxidase oxidizes $Mn^{2+}$ into $Mn^{3+}$ through hydrolyzing hydrogen peroxide (Hofrichter 2002).

### Lignin-degrading bacteria

*Streptomycetes*, a group of bacterial genius which compromises over 500 species, is one of the most important lignolytic microorganism playing a crucial role in nutrient recycling and plant biomass degradation in the terrestrial ecosystem. When these filamentous bacteria grow on lignocellulose residue, they solubilize and produce several oxidative enzymes such as peroxidases (Tuncer et al. 2004) and laccases (Hernández et al. 2001; Niladevi et al. 2007). Even though the enzymes are well known for lignin degradation, the specific roles of each enzyme of *Streptomycetes* on native lignin degradation have not yet demonstrated but it has been approved on lignin model compounds (Munk et al. 2015).

Many bacteria species (*Actinomycetes*, *Nocardia*, *Streptomyces*, *Eubacteria*) are identified by their role in modifying, solubilizing, and degrading lignin structures to some extents. About 3.2% of milled wood lignin (MWL) were mineralized by *Streptomyces badius* within 30 days of pretreatment time. It was further increased to about 11% if enriched with yeast extract and cellulose (Crawford et al. 1993). About 15% of lignin were mineralized by *Streptomyces*, one genus of filamentous bacteria, and produced acid-precipitable and water-soluble polymeric lignin as end products (Tuor et al. 1992; Crawford et al. 1993). It has been observed that *Pseudomonas* spp. showed up to 52% of lignin degradation within 30 days on poplar wood (Dionisi et al. 2014). In addition, *Acinetobacter* removed about 47 to 57% of lignin from poplar wood within 30 days of pretreatment (Odier et al. 1981; Dionisi et al. 2014). This is the maximum lignin removal reported so far by using bacteria. *Streptomyces cyaneus* and *Thermomonospora mesophila* are also able to degrade 50% of lignin in barley straw within 21 days. Some bacterial strains show good capabilities of delignification on selected lignocellulose biomass, and further researches are required to test their abilities of delignification on different lignocellulose biomass for biological pretreatment. Even though many research showed bacterial abilities of lignin degradation, their efficiencies are not satisfactory and need improvement. Much research works are required to identify and isolate the best bacterial strains from various sources on different lignocellulose biomass. Bacteria have great potential and advantage over fungi in the biotreatment of lignocellulose biomass because of their faster growth rate. The degradation efficiencies of different types of bacterial species on different substrate are given in Table 4.

**Table 4** Bacteria degradation of lignin on different feedstock

| Bacteria species | Availability | Gram stain | Feedstock used | Lignin degradation (%) | Culturing time (days) | Reference |
|---|---|---|---|---|---|---|
| *Pseudomonas* spp. | Water, plant seeds | Gram negative | Kraft lignin | 39 | 52 | Shi et al. 2008 |
| *Acinetobacter* spp. | soil | Gram negative | Poplar wood | 47–57 | 30 | Odier et al. 1981; Dionisi et al. 2014 |
| *Pseudomonas* spp. | Water, plant seeds | Gram negative | Poplar wood | 40–52 | 30 | Dionisi et al. 2014 |
| *Xanthomonas* spp. | Plants | Gram negative | Poplar wood | 39–48 | 30 | Odier et al. 1981; Dionisi et al. 2014 |
| *Pseudomonas* spp. | Water, plant seeds | Gram negative | Kraft lignin | 20 | 40–60 | Shi et al. 2008 |
| *Streptomyces badius* | Soil | Gram positive | Indulin lignin | 3–4 | 35 | Giroux et al. 1988 |
| *Streptomyces viridosporous* | Soil and decays | Gram positive | Indulin lignin | 3–4 | 35 | Giroux et al. 1988 |
| *Streptomyces cyaneus* | Soil and decays | Gram positive | Barley straw | 29–52 | 21 | Zimmermann and Broda 1989 |
| *Thermomonospora mesophila* | Decays | Gram positive | Barley straw | 36–48 | 21 | Zimmermann and Broda 1989; Dionisi et al. 2014 |

### Actinobacteria

*Actinobacteria* are a group of gram-positive bacteria, which plays an important role in decomposing plant biomass, and mostly exist in the soil. From this group of bacteria, the genus *Streptomyces* are common in degrading lignin-containing biomass. *S. viridosporus* T7A are capable of degrading synthetic lignin, kraft lignin, aromatic dyes, and polyethylene plastic. *Streptomyces flavovirens*, *Streptomyces badius* ATCC 39117, *Streptomyces cyaneus* CECT 3335, *Streptomyces psammoticus*, and *Amycolatopsis* sp. ATCC 39116/75iv2 are some of the bacteria from *Streptomyces genus* which showed lignin depolymerization and mineralization activities on lignin derivatives (Sutherland et al. 1979; McCarthy 1987; Niladevi and Prema 2005; Moya et al. 2010; Brown and Chang 2014). *Mycobacteria* (a genus of *Actinobacteria*) had also shown aromatic compound degradation by producing peroxidase and/or catalase (Le Roes-hill et al. 2011). *Mycobacterium tubercolosis* and *Mycobacterium smegmatis* are also involved in the catabolism of aromatic compounds (Heym et al. 1995; Magliozzo and Marcinkeviciene 1997).

### Firmicutes

*Firmicutes* are a phylum of bacteria, and mostly, they are gram-positive. They have round cells, called cocci (singular coccus), or rod-like forms (*Bacillus*). From this group of bacterial phylum, *Bacillus* class shows lignolytic activity. *Bacillus megaterium* and *Bacillus pumilus* which are isolated from kraft pine and forest soil showed the capability of degrading poplar wood lignin and kraft lignin (Perestelo et al. 1989; Huang et al. 2013). Similar activities have been observed in different bacterial strains. For examples *Paenibacillus* sp. KBC101, *Bacillus licheniformis*, and *Paenibacillus* sp. are some of the bacteria in this class that showed the production of key lignolytic enzymes (Sakai et al. 2005; Chandra et al. 2008; Koschorreck et al. 2008).

### Proteobacteria

*Proteobacteria* is a phylum of the higher classification of gram-negative bacteria including a wide range of pathogens such as *Helicobacter*, *Escherichia*, *Vibrio*, *Salmonella*, and *Yersinia* and other free-living bacteria responsible for nitrogen fixation. Several strains of bacteria from the genera of *Brucella*, *Ochrobactrum*, *Sphingomonas*, and *Sphingobium* have the capacity to degrade aromatic compounds. Bacterial strain *O. anthropi* from the genera of *Ochrobactrum* isolated from termite gut showed the ability to catabolize 2, 2′-dihydroxybiphenyl and benzylvanillin (Kuhnigk and König 1997). Gonzalez et al. (1997) showed the mineralization and solubilization of synthetic and kraft lignin by bacterial strain *Sagittula stellata* isolated from the coastal area of sea. Currently, many bacterial strains of this class are identified, which have the capabilities to degrade lignin and lignin model compounds. *Pseudomonas* sp., *E. aerogenes*, and *Aeromonas* spp., *Pandoraea* sp. are some of them (Deschamps et al. 1980; Dhindwal et al. 2011).

## Mechanism of lignin degradation in bacteria

It has been observed that various bacterial genera metabolize and depolymerize lignin and release metabolites such as acid-precipitable polymeric lignin (APPL), i.e., a high molecular weight metabolites (Crawford 1978; Ramachandra et al. 1988; Chen et al. 2012). Bacteria can degrade lignin into high molecular weight metabolites by extracellular enzymes and import lower molecular weight lignin for aromatic catabolism (Kanaly and Harayama 2000; Chakraborty and Coates 2004). Isolation of extracellular oxidative enzymes from bacteria, *Streptomyces viridosporus* T7A, that secretes heme peroxidase enzyme for metabolizing lignin was the first report on molecular information of bacterial capabilities of delignification, which produced acid-precipitable polymeric lignin (Ramachandra et al. 1988; Thomas and Crawford 1998). Generally, the mechanism of lignin

catabolism in bacteria is not well known, and it is one of the current research focus.

## Delignification enzymes and their mechanisms

There are no microorganisms producing all lignolytic enzymes simultaneously (laccase, manganese peroxidase (MnP), lignin peroxidase (LiP), versatile peroxidase (VP)). Some microorganisms are capable of producing two or three lignolytic enzymes. This gives them a higher level of delignifying capacity. Enzymes produced by microorganisms and showed lignin-degrading abilities are discussed in the following sections.

### Lignin peroxidase

Lignin peroxidases are glycosylated enzymes of molecular weight between 38 and 50 kDa with about 340 amino acids having two calcium ions and a single heme group. It is mainly extracted from fungi strains of *Phanerochaete chrysosporium*, brown- and white-rot fungi, and *Aspergillus* strains and bacterial strains of *Streptomyces viridosporus*, *Acinetobacter*, *Streptomyces lividans*, and *Calcoaceticus*.

Because of the complex structure of lignin, the delignification process takes place on the outer side of the cell and the enzyme lignin peroxidases are found in the peripheral region. Two sites of substrate interactions have been observed on LiP: the classical heme edge and glutamine 146 site that plays a major role in lignin-derived compound hydrolysis. Lignin peroxidases depolymerize lignin through $H_2O_2$ using a series of steps (Renganathan et al. 1985; Wong 2009):

- Formation of intermediate, oxo-ferryl intermediate through the reaction between $H_2O_2$ and heme cofactor
- Electron reduction through two consecutive steps: (i) formation of substrate radical cation and compound II by the reduction of one electron from LiP and (ii) further one electron reduction, which completes the cycle of catalysis by returning the enzyme in the state of ferric oxidation
- The radical produced in the first step undergoes non-enzymatic lignin hydrolysis via a set of reaction.

The lignin degradation pathways of lignin peroxidase enzyme are shown in Fig. 2 (Renganathan et al. 1985; Wong 2009).

### Manganese peroxidase

Manganese peroxidase shares several lignin peroxidase features except the amino acid length is 350 and the molecular weight is 40 kDa. Manganese peroxidases are primarily extracted from *P. chrysosporium*, *Ceriporiopsis subvermispora*, *Schizophyllum* sp., *Lentinula edodes*, *Panus tigrinus*, *Bjerkandera adusta*, *Nematoloma frowardii*, *Dichomitus Squalens*, and *T. versicolor* (Kanayama et al. 2002; Martínez et al. 2009). The production of manganese peroxidases depends on (i) microbial strain and species, (ii) carbon sources and type, and (iii) aromatic compound presence (Elisashvili and Kachlishvili 2009). Manganese peroxidases degrade lignin in a similar series of cycles as lignin peroxidases (Tuor et al. 1992; Wong 2009):

- Formation of the intermediate of radical cation of Fe(IV)-oxo-porphyrin through the reaction between $H_2O_2$ and enzyme
- Reduction of intermediate I to intermediate II by producing $Mn^{3+}$
- Regeneration of enzyme
- Oxidation of phenolic substrates by $Mn^{3+}$ producing phenoxy radicals, which activates reactions for lignin hydrolysis

The enzyme manganese peroxidase has only one binding site for $Mn^{2+}$ near the heme site, through the loss of one $H_2O_2$ equivalent, and two $Mn^{3+}$ equivalents are gained in a reaction acquiring proper manganese chelator (Timofeevski and Aust 1997; Wariishi et al. 1999). The reaction between $Mn^{3+}$ and $H_2O_2$ is activated by metal chelator $Cu^{2+}$. Analysis of crystal structure and the active site of manganese peroxidase enzyme from *P. chrysosporium* has shown that acidic amino acids (glutamic and aspartic acid) are involved in $Mn^{2+}$ binding at positions 35, 39, 45 and 179, and arginine at 42 while serine at 172 (Ambert-balay et al. 2000; Sundaramoorthy et al. 2010). The general pathway of lignin modification by manganese peroxidases on lignin model compound (phenolic aryglycerol β-aryl ether) is given in Fig. 3 (Renganathan et al. 1985; Wong 2009).

### Laccases

Laccases are a group of enzymes found in insects, plants, fungi, and recently in bacteria which are the most widely distributed enzyme in nature. Laccases are recognized biocatalysts, which have the capacity to oxidize different phenolic compounds by using oxygen as an electron acceptor (Majumdar et al. 2014). Recently, laccases characterized by the presence of two cupredoxine domains were identified in *Streptomycetes* (Molina-guijarro et al. 2009; Trubitsina et al. 2015). Their ability to withstand harsh conditions like high temperature and a range of pH draws the attention for biotechnological purposes.

The presence of laccases has been reported in various bacteria and fungi species. In fungi, the enzymes have been reported in *Pycnoporus cinnabarinus*, *Trametes versicolor*, *Myceliophthora thermophile*, *Trametes pubescens*, *Cerrena unicolor*, *Pleurotus eryngii*, *Pleurotus*

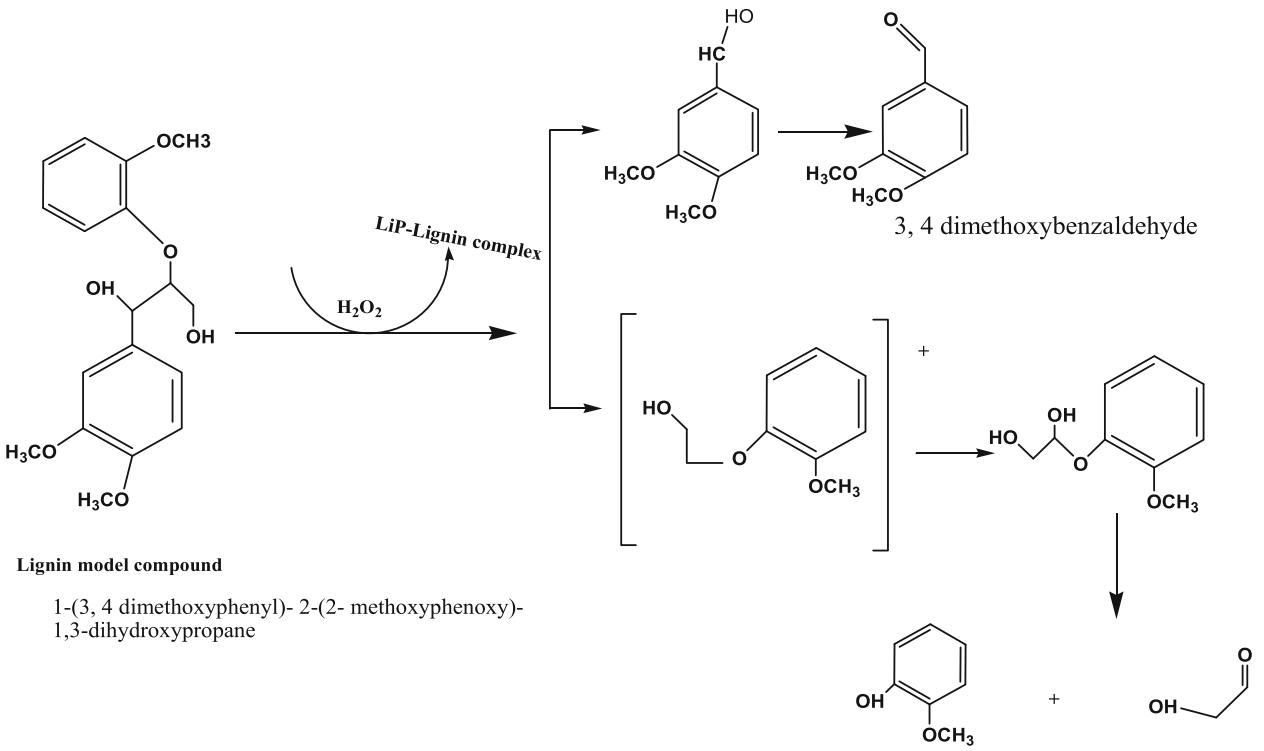


**Fig. 2** Lignin peroxidase-catalyzed oxidation of lignin model compound (veratrylglycerol beta-guaiacyl ether)

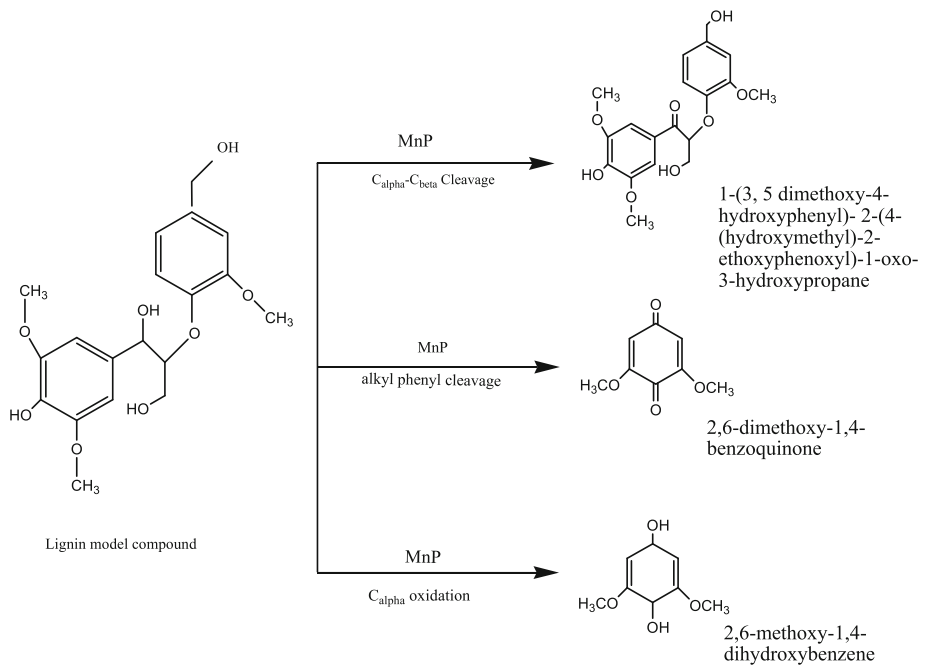


**Fig. 3** Manganese peroxidase-catalyzed oxidation of lignin model compound (phenolic aryglycerol β-aryl ether)

*astreatus*, *Lentinula edodedes*, *Pleurotus ferulae*, *Agaricus blazei*, and *Cyathus bulleri* among others. They have been also reported in bacteria like *Marinomonas mediterranea, Bacillus subtilis*, *Azospirrullum lipoferum*, *Haloferax volcanii*, and *Streptomyces griseus.*

Laccase catalyzes the oxidation of non-phenolic and phenolic compounds to their equivalent active free radicals in a reaction facilitated by four copper atoms positioned at the catalytic core. Losses of one molecule of oxygen to two molecules of water and generation of four free radicals were observed when laccase oxidizes phenolic substrates (Arora and Sharma 2010). The Cu atoms are organized into three diverse groups: blue Cu center or type 1, normal Cu center or type 2, and coupled binuclear Cu center or type 3. Lignin degradation is performed in a three-stage reaction pathway: (i) copper is reduced by lignin oxidation, (ii) electron is moved from a reduced Cu atom in step one to the two groups of Cu atom, and (iii) oxygen is reduced to water at the centers of type 3 and type 2 Cu (Riva et al. 2006; Dwivedi et al. 2011). The toxic effect of intermediate compounds to the cell can be eluded in case of laccase oxidation since the early stage of delignification process uses oxygen instead of $H_2O_2$ (Sterjiades et al. 1993). Laccase has the capability to oxidize a variety of substrates as well as aromatic diamines, polyphenols, and methoxy-substituted phenols by cleaving Cα-Cβ and alkyl-aryl bonds by oxidation (Molina-guijarro et al. 2009; Wong 2009; Gillet et al. 2017). The mechanism of laccase-catalyzed reactions is shown in Fig. 4 (Renganathan et al. 1985; Kawai et al. 2002; Wong 2009).

## Hydrolysis of polysaccharides in lignocellulose biomass

Hydrolytic microorganisms can have a capability to establish synergistic relationships with each other to degrade polysaccharides in lignocellulosic biomass. Cellulase and xylanase are the best examples for the complete degradation of cellulose and hemicellulose in biomass (Tsegaye et al. 2018a, 2018b). Cellulase is responsible for decomposing cellulose into its constituents, and xylanase decomposes hemicellulose. Cellulase is a complex enzyme mixture having different specificities. The three main activities of cellulase are cellobiohydrolase, endoglucanases (endo-1-4-β-glucanase), and β-glucosidase. Endoglucanases attack randomly different internal sites of the amorphous region of cellulose opening up a root for cellobiohydrolase attack (Lynd et al. 1991). Cellobiohydrolase degrades the crystalline cellulose regions (Esterbauer et al. 1991; Rowell 1992). Cellobiohydrolases and endoglucanases operate synergistically during cellulose hydrolysis.

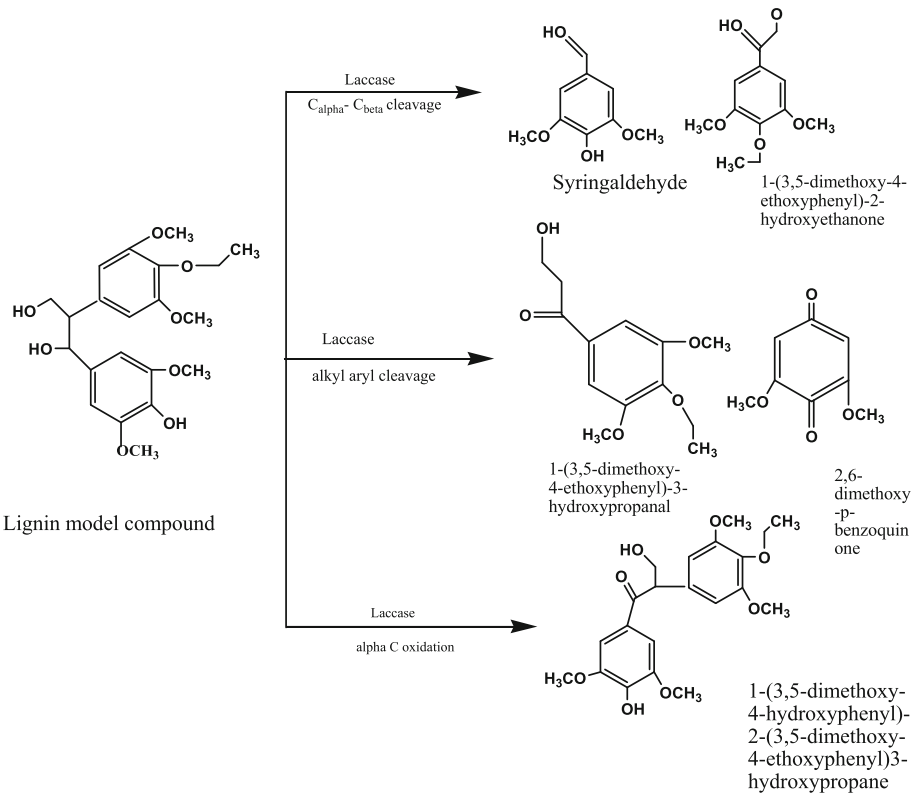


**Fig. 4** The laccase-catalyzed reaction of phenolic β-1 lignin model compound

Depending upon the action they perform on specific substrates, hemicellulase enzymes are also classified into endo-1,4-β-xylanase which cleaves xylan from hemicellulose to lower molecular weight oligosaccharides. Xylan 1,4-β-xylosidase further cleaves oligosaccharides to xylose. For the efficient hydrolysis of wood xylan, different additional enzymes have to act synergistically, such that the synergistic action of ferulic and p-coumaric esterases, xylan esterases, α-4-*O*-methyl glucuronosidases, and α-1-arabinofuranosidases is required for complete degradation (Jeffries 1994). Therefore, combinations of proper type and amount of hydrolytic enzymes are required in order to hydrolyze lignocellulose biomass. Searching unique strains of microorganisms which are capable of producing more than two hydrolytic enzymes realizes the biological conversion of lignocellulose biomass to biofuels.

### Fermentation

Fermentation is a very important phase for biofuel (bioethanol) production. The hydrolysate product obtained after delignification and hydrolysis is converted to biofuel through fermentation (Kiran et al. 2014; Wei et al. 2013). Various kinds of microorganisms (bacteria, fungi, and yeast) are used in fermentation but *Saccharomyces cerevisiae* is the most commonly used. However, the selectivity (limited to hexose sugar only) and lower activity at higher ethanol concentration make them inefficient microorganism in the fermentation of lignocellulose biomass. This creates the difficulty in using lignocellulose biomass for biofuel production using this microbe. Industrial-scale production of bioethanol from lignocellulose biomass is still not in a satisfactory stage due to lack of microorganisms that efficiently utilize pentose and hexose sugars simultaneously (Gabriel and El-halwagi 2013). Theoretically, about 90% of ethanol yield was produced from glucose using *Saccharomyces cerevisiae* (Gabriel and El-halwagi 2013). The uses of pentose-fermenting microorganisms such as *C. shehatae*, *P.stipitis*, and *P. tannophilus* can improve the efficiency of the fermentation of lignocellulose biomass (Rubin 2008).

The development of new ways of hydrolysis and fermentation (separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF)) improved ethanol yield. Higher ethanol yield (13% more) was reported in simultaneous saccharification and fermentation process after comparing it with separate hydrolysis and fermentation. About 0.49 g/g of ethanol yield was obtained after the enzymatic hydrolysis of *Prosopis juliflora* biomass (Gupta et al. 2009). Further research work is required to search for the better microorganisms as well as the development of an efficient process for biofuel production.

## Effects of delignification on the efficiency of biofuel production

The presence of lignin in lignocellulose biomass shields the available polysaccharides that have an adverse effect on enzymatic and/or microbial hydrolysis and fermentation. It regulates the extent and rate of hydrolysis and fermentation (Chang and Holtzapple 2000). Therefore, proper pretreatment is required to remove the maximum possible lignin and to preserve the maximum possible polysaccharides in the biomass. Recent studies show that the use of alkali pretreatment along with microbial hydrolysis of the pretreated biomass can greatly remove lignin and preserve polysaccharides. By this method, about 69.5% of lignin was removed and 72.67% of cellulose was obtained from a wheat straw after pretreating with 10% NaOH (Tsegaye et al. 2017). Hydrolyzing the alkali pretreated wheat straw, about 83.68% of total reducing sugars (glucose and xylose) were obtained by the microbial hydrolysis of cellulose and hemicellulose. This process increased the accessible cellulose for enzymatic hydrolysis. Recent work on fungi isolates showed their ability to selectively depolymerize lignin. Pretreatment of bamboo culms with *Punctularia* sp. TUFC20056, which belongs to white-rot basidiomycete, removed about 50% of lignin (Suhara et al. 2012). Due to this pretreatment, the hydrolysis efficiency and bioethanol yield were improved. Corn stalk pretreatment with white-rot *Irpex lacteus* fungus improves hydrolysis efficiency up to 82% after 28 days of pretreatment (Du et al. 2011). These show how fungi are effective in pretreatment. Besides the advantages of biological pretreatment (mainly removing inhibitory compounds and mild temperature operation), the slow growth rate and yield are still the problems remained unsolved.

Even though various pretreatment methods are giving promising results in terms of lignin removal and cellulose release, the solubilization of parts of hemicellulose and the production of inhibitory compounds remain a problem for scale up. The loss of hemicellulose has directly affected the yield of biofuel production. The inhibitory compounds such as furfural and hydroxymethylfurfural decrease the efficiency of fermentation by suppressing cell growth (Liu et al. 2004). Most of the fermentative microorganisms such as *S. cerevisiae* and *P. stipitis* are sensitive to the inhibitory compounds (Liu et al. 2004). The growth of *P. stipitis* was reduced by 43% in the presence of 0.5 g/L of hydroxymethylfurfural and by 70% in 0.75 g/L of hydroxymethylfurfural. The growth was completely stopped (100%) in the presence of 1.5 g/L of hydroxymethylfurfural (Delgenes et al. 1996; Nigam 2001). Therefore, to overcome these problems, detoxification is a necessary and important step, but the high cost of detoxification process makes it not feasible for large-scale biofuel production.

Searching for special strains of microorganism that can withstand the toxic nature might be a possible alternative. In addition, research work on genetic modification of microorganisms to remove or adapt the inhibitory compounds should be considered to solve the problems.

## Factors affecting biological pretreatments

Optimization of process parameters and screening of the most effective strains of microorganisms will give a better yield of reducing sugars, which enhance biofuel production (Van Kuijk et al. 2015). The type of microbial strain used, nature and type of the biomass, pH, culturing temperature, culturing time, moisture content, concentration of inoculums used, and aeration rate are the most important factors affecting biological pretreatments.

### Moisture content and substrate concentration

In biological pretreatments, high substrate concentration should be used for the economically viable process but it leads to the increased accumulation of inhibitory compound, which adversely affects reducing sugar yields. In case of fungi, enzyme production and growth of microorganism are significantly affected by initial moisture content, which affects the rate of lignin degradation. High lignin degradation was observed between 75–80% than 65% moisture content in cotton stalk pretreatments with *Penicillium chrysogenum* (Shi et al. 2008). Lower solid to liquid ratio contributed to higher lignin peroxidase and manganese peroxidase production. The optimum moisture content depends upon the type of microorganism involved and the nature and type of biomass used. Therefore, the optimization of moisture content and substrate concentration is required for biological pretreatments (Van Kuijk et al. 2015).

### Nature and type of lignocellulosic biomass

The complex structure of lignocellulose biomass is formed by hydrogen and covalent bond interactions between hemicellulose and cellulose in which both are linked to lignin. Hardwood contains between 30 and 50% lignin, whereas softwood contains between 30 and 60% lignin. Agricultural residues contain a lower amount of lignin (5–25%) relative to other biomass (Limayem and Ricke 2012). The varying proportion of these components in the biomass determines its application, nature, and strength. A higher proportion of lignin provides stability and stiffness to the polysaccharides against hydrolytic enzymes and microbes. Therefore, accessing the polysaccharides without prior pretreatments is very difficult since the carbohydrates are wrapped with lignin bond. So, proper pretreatment is required to remove lignin for efficient hydrolysis and fermentation.

Hemicellulose contains heterogeneous mixtures of pentose (arabinose and xylose) and hexose sugars (galactose, glucose, and mannose) along with sugar acids such as uronic acid and galacturonic acids (Saxena et al. 2009; Limayem and Ricke 2012). The predominant monomers of lignocellulosic biomass hemicellulose in hardwood and agricultural residue are xylan linked by β−1, 4 linkages of D-xylose (about 90% of monomers are xylose). Therefore, selecting appropriate types of lignocellulosic biomass helps for efficient biofuel production.

Cellulose is a chain of monomers of D-glucose linked to each other by linear β (1–4) linkage constituting 20–50% of the plant biomass. Van der Waals and hydrogen bonds bind between the cellulose chains. Microfibrils are groups of chains of cellulose, and when they are merged together, they form cellulose fiber. The microfibrils are wrapped in lignin and hemicellulose. Therefore, selecting lignocellulose biomass having lower lignin content and higher carbohydrates is vital for biofuel production (Table 1).

### Culturing temperature

It is important to optimize and maintain the optimum culture temperature for each type of microorganism involved in lignocellulosic degradation since it affects the growth and enzyme secretion ability of the microorganisms. For example, most of the class basidiomycetes of white-rot fungi grow optimally between 25 and 30 °C while the class of ascomycetes grows around 39 °C. The growth rate is highly affected by the temperature that has an effect on delignifying capacity. Therefore, the optimal culturing temperature for each microorganism is required for proper pretreatments of the biomass.

### Culturing time and types of microbial strains

The pretreatment time required for the depolymerization of lignocellulose biomass depends on the types of microbial strains used. Prolonged time is required for strains having a low rate of delignification ability, and it is the major barrier in biological pretreatment. Lignin degradation yield (37.6%) was observed in *Irpex lacteus* when treated with corn stalks for 42 days (Du et al. 2011). It has been observed that *Pseudomonas* sp. showed up to 52% of lignin degradation within 30 days on poplar wood (Dionisi et al. 2014). On the other hand, *Acinetobacter* removed about 47 to 57% of lignin from poplar wood within 30 days of pretreatment (Odier et al. 1981; Dionisi et al. 2014). This is the maximum lignin removal reported so far by using bacteria. On the other hand, the maximum amount of lignin removal (about 60% removal) was observed during cotton stack pretreatment with fungi strain *Phanerophyte chrysosporium* after 30 days of pretreatment (Shi et al. 2008). *Trametes versicolor* removed about 57.4% of lignin from beech wood within 120 days of pretreatment (Bari et al. 2016).

Many reports suggest that using microbial consortium can degrade lignin faster and increases yields. A microbial consortium of *P. chrysogenum*, *Tinea versicolor*, and *Pleurotus sajor-caju* showed an improved efficiency from 5 to 16% of lignin removal on spruce saw (Asiegbu et al. 1996). Selecting microorganisms having a higher growth rate and higher delignifying ability is important to increase the rate of delignification.

### Aeration

The activity of lignolytic enzymes and its production is highly affected by aeration during biological pretreatment. It helps to remove $CO_2$, heat, and oxygen transport as well as to maintain humidity during metabolism (Millati et al. 2011). Oxygen circulation is crucial during lignin degradation by microorganisms because the process is oxidative. Increasing the rate of aeration could increase the productivity of lignin peroxidase (Couto et al. 2002). Therefore, controlling and optimizing the rate of aeration are important for biological delignification.

### pH

Biological delignification of lignocellulosic biomass is significantly affected by pH because it alters the three-dimensional structure of enzymes, which directly affects the functions and activity of microbial enzymes. Changing the pH of the medium could affect significantly the laccase production (Patel et al. 2009). Most white-rot fungi grow well at a pH range of 4.0 to 5.0. Therefore, optimal pH is required for the proper functioning of microbial enzymes during biological pretreatment process.

## Lignocellulose biofuel economy

The availability of various production technologies for lignocellulose biofuel production makes it very difficult to estimate the total production costs. The production cost of biofuel from lignocellulose biomass needs intensive capital investment. The production cost of a barrel of biofuel from lignocellulose biomass was estimated at about 180 USD, which is more expensive than the current oil price (De Wit et al. 2010). It was estimated that about 15% of total production cost goes to simultaneous saccharification and fermentation, about 17% for pretreatments, and about 36% for energy expenses to produce ethanol. The total production cost for producing a liter of ethanol from pentose sugar is about 0.48 USD (Von Sivers et al. 1994). In addition, the high cost of hydrolytic enzymes (0.15 USD per gallon of bioethanol produced) contributes to the high production cost of biofuel from lignocellulose biomass (Wyman et al. 2005). Currently, there are no literature data assessing the production cost of biofuel production from lignocellulose biomass using microbes in the whole production stages (delignification, hydrolysis, and fermentation). The work is still on a lab scale. The use of microorganisms for delignification and hydrolysis could reduce ultimately the production cost if the low yields and long residence time are solved. Intensive research on the optimization of process parameters and investigation of the best strains of microorganisms along with genetic engineering are greatly required to breakthrough current problems.

## Future prospective

Many researchers showed the possibility of biological pretreatments of lignocellulosic biomass to biofuel by using different species of bacteria and fungi. Bacteria and fungi are the main microorganisms playing a great role in lignin degradation during biological pretreatments. Their ability to eliminate the production of inhibitory compounds and low operating cost, as well as environmentally sound process, open the possibilities to scale up the process into industrial scale. This is a promising way of transforming the abundantly available natural resource into biofuel by eliminating the risk of environmental problem posed by the use of fossil fuels. Although this process is possible, the problems of low productivity, long time requirement, and low yield should be solved for industrial application. In addition, research works on the optimization of process parameters and appropriate selection of the best microbial strains are to be done for realizing the biological conversion of lignocellulose biomass to biofuel at industrial scale.

On the other hand, the use of genetic engineering to alter the genetic makeup of microbial strains and to manipulate the biosynthesis of plant biomass showed promising results. A higher ratio of syringyl (S) to guaiacyl (G) unit of lignin and lower content of lignin is always easier for pretreatment (Lu et al. 2010). Therefore, altering this ratio using advanced molecular biology techniques will improve the biological pretreatment efficiency and yield. Wagner et al. (2009) developed 36–50% less lignin-containing *Pinus radiata* by suppressing the gene that involved in monolignol synthesis (the 4-coumarate-coenzyme A ligase).

The cellulose and hemicellulose content can also be altered by genetic engineering. Microbial strains are also engineered to overcome the inhibiting effect of biofuel end products of biological pretreatments (Dunlop 2011). This can be done by using techniques such as activation of stress response genes, modification of membrane proteins and heat shock proteins, or heterologous expression of efflux pumps. This advancement in genetic engineering will lead us to treat lignocellulose biomass biologically to produce biofuel on an industrial scale in the near future.

## Conclusions

The structural configuration of lignocellulose biomass creates a reluctant nature for hydrolysis, especially for enzymatic and microbial hydrolysis. Intensive research works have been done to convert lignocellulose biomass into biofuel specifically to bioethanol using different approaches. The productions of inhibitory compounds such as furfural and furfural derivative compounds and hemicellulose solubilization are the main challenges for all pretreatment technologies except for biological pretreatment. The problems of low yield, low productivity, and long residence time for microbial delignification and hydrolysis are the main challenge for scale up (industrial scale production). Therefore, isolation and identification of appropriate microorganisms, proper selection of raw materials (biomass), and optimization of process parameters (temperature, pH, aeration, particle size, time substrate concentration, and inoculum concentration) are compulsory for efficient utilization and conversion of the abundantly available resources. This shows the possibility of microbial ability for the delignification of lignocellulose biomass, and it needs further investigation and isolation of microorganisms from different sources.

#### Acknowledgments
Not applicable.

#### Funding
This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

#### Availability of data and materials
Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

#### Authors' contributions
BT initiated the idea and drafted the manuscript. CB participated in the design and coordination as well as refined and edited the manuscript. PR participated in design and coordination as well as refined and edited the manuscript. All authors read and approved the final manuscript.

#### Ethics approval and consent to participate
Not applicable.

#### Consent for publication
All the participant researchers are consent for publication.

#### Competing interests
The authors declare that they have no competing interests.

## Publisher's Note



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Received: 5 January 2019 Accepted: 14 March 2019
Published online: 28 March 2019

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