



Ionizing radiation and a wood-based biorefinery



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HIGHLIGHTS

- Ionizing radiation reduces the crystallinity of cellulose.
- Ionizing radiation reduces cellulose's degree of polymerization.
- The amount and rate of enzymatic hydrolysis of lignocellulosic materials, including wood, are increased with increasing radiation dose.
- Wood and other lignocellulosic materials have the potential to be a renewable material for the production of chemicals and fuels.

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ABSTRACT

Woody biomass is widely available around the world. Cellulose is the major structural component of woody biomass and is the most abundant polymer synthesized by nature, with hemicellulose and lignin being second and third. Despite this great abundance, woody biomass has seen limited application outside of the paper and lumber industries. Its use as a feedstock for fuels and chemicals has been limited because of its highly crystalline structure, inaccessible morphology, and limited solubility (recalcitrance). Any economic use of woody biomass for the production of fuels and chemicals requires a "pretreatment" process to enhance the accessibility of the biomass to enzymes and/or chemical reagents. Electron beams (EB), X-rays, and gamma rays produce ions in a material which can then initiate chemical reactions and cleavage of chemical bonds. Such ionizing radiation predominantly scissions and degrades or depolymerizes both cellulose and hemicelluloses, less is known about its effects on lignin. This paper discusses how ionizing radiation can be used to make a wood-based biorefinery more environmentally friendly and profitable for its operators.

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1. Macro composition of wood

The three major components of wood are cellulose, hemicellulose, and lignin. All three are biopolymers, with cellulose and hemicellulose being polysaccharides. Wood is about 38–50% cellulose, 23–32% hemicellulose, and 15–25% lignin. The exact composition is species-specific (Boerjan et al., 2003; Huber et al., 2006; Sjostrom, 1993;). Wood is an excellent example of a biocomposite.

Cellulose is a linear, high molecular-weight (MW) polymer of anhydro-D-glucopyranosyl units linked by β -(1 \rightarrow 4) glycosidic linkages. The degree of polymerization (DP) for glucosyl residues is between 500 and 14,000 for wood celluloses (Mohenen et al., 2008). The linear chains of cellulose are highly ordered due to hydrogen bonding and high crystallinity, making them insoluble in conventional solvents and resistant to hydrolysis. The cellulose in wood and other lignocellulosic

biomass acts as the "fibers" of the composite, giving the wood its stiffness (Panshin and de Zeeuw, 1980).

Hemicelluloses are irregular, complex polysaccharides which consist chiefly of heteroglucans (xyloglucans), heteroxylans, and heteromannans. For woody plants, glucomannans are the dominant components of hemicelluloses in softwood, while glucuronoxylans are the dominant components in hardwood (Harris and Stone, 2008). The principle sugar components of hemicelluloses include: D-xylose, D-mannose, D-glucose, D-galactose, L-arabinose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid and D-galactouronic acid. Hemicelluloses have considerably lower DPs than cellulose, ranging from less than 70 to about 200 units and have a high percentage of short-branch chains (Kuhad et al., 2007). Due to their short-chain lengths, branching, low hydrogen bonding, and crystallinity, hemicelluloses are much more easily hydrolyzed than cellulose. In wood, hemicelluloses act as a bonding agent between cellulose and lignin.

Lignin is an amorphous, highly-branched, three-dimensional, polyphenolic hetero-polymer synthesized by enzymatic dehydrogenative

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polymerization of 4-hydroxyphenyl propanoid units (Sasaki et al., 2004). The three general monomeric phenylpropane units are coniferyl, *p*-coumaryl, and sinapyl alcohol. The relative proportions of the three cinamyl alcohol precursors incorporated into lignin vary with plant species as well as the locations of the lignin within the plant cell wall. These phenolic monomers are linked together mainly by alkyl-aryl, alkyl-alkyl, and aryl-aryl ether bonds. The MW of lignins can be 100 kDa or more (Kuhad et al., 1997). Lignin acts as the cementing agent or resin in wood (Sjostrom, 1993).

2. Wood-based biorefinery

Wood-based biorefineries have the potential to reduce the world's reliance on nonrenewable fossil fuels and chemicals. These biorefineries convert the stored chemical energy of woody biomass to energy, chemicals, and materials (Amidon et al., 2011).

Woody biomass is the largest source of organic carbon on Earth, with a production of over 5.6×10^{13} kg of organic carbon per year (Field et al., 1998). Only about 5% of the annual woody biomass produced each year is utilized by humankind (Thoen and Busch, 2006). This leaves a large amount of untapped and renewable chemical energy that can be used. If one looks at natural forest woody biomass in terms of energy, forests produce about 1.1×10^{18} kJ per year (Klass, 1998). This is over two times the world's total annual energy consumption of 5.0×10^{17} kJ (Amidon et al., 2008). The above numbers are used to illustrate the potential of woody biomass as an energy source; most of the woody biomass for a wood-based biorefinery would come from managed energy crops, such as willow.

Any widespread use of woody biomass as a feedstock for a biorefinery would require the development of an economical way to separate the components of wood from the wood composite and to overcome the recalcitrance of cellulose (Agbor et al., 2011; Aita and Kim, 2010; Amidon et al., 2011; Hendriks and Zeeman, 2009; Himmel et al., 2007; Lynd et al., 2008).

3. Lignin separation and/or removal

Historically, lignin has been removed from wood by the pulping process that is used in the production of paper and paper products. The pulping process is energy intensive and requires a large amount of toxic chemicals (Sumathi and Hung, 2006; Thompson et al., 2001). The extracted lignin was considered as a waste product with little value other than burning for its heat; more recently, lignin is being considered as a possible valuable chemical (Amidon et al., 2011). The use of biopulping or biodelignification is now being used as an alternative to conventional chemical pulping. This method relies on natural white rot fungus to degrade the lignin in wood chips and uses less energy and fewer chemicals than traditional methods (Akhtar et al., 2000). Biopulping removes only about 25% of the lignin from the woody biomass.

Lignin, along with hemicelluloses, can also be extracted from wood chips by pressurized hot water extraction (PHWE) (Leppanen et al., 2011; Song et al., 2012; Stipanovic et al., 2006). For full extraction of both lignin and hemicellulose, temperatures as high as 280 °C are required. At these high temperatures, hemicellulose is depolymerized and furfural, a poison in fermentation, is produced. The temperature can be reduced to 140 °C if the wood chips are biodelignified before PHWE with good extraction efficiency (Stipanovic et al., 2006). PHWE also produces acidic acid as a byproduct of the extraction. Membrane separation methods can be used to isolate the individual components of the extract (Amidon et al., 2011).

4. Reducing the recalcitrance of cellulose

Wood chips, pulp, or pure cellulose require a pretreatment process to allow enzymes or acids to efficiently hydrolyze cellulose to sugars. The most common methods used include: steam explosion (Avellar and Glasser, 1998; Brownell and Saddler, 1987; Brownell et al., 1986; Glasser and Wright, 1998), liquid hot water (Mosier et al., 2005), dilute acid (Kim and Lee, 2002; Lau et al., 2009), and ammonia fiber explosion (Moniruzzaman et al., 1997; Teymouri et al., 2004). The pretreatment methods listed above enhance the accessibility of biomass to enzymatic or acid attack by a combination of surface area increases, cellulose decrystallization, and removal/modification of hemicelluloses and lignin. As a result, the sugar yields recovered from plant polysaccharides have been significantly increased. However, each pretreatment method has its disadvantages, with the overall effectiveness of the methods being dependent on the biomass composition and operating conditions. The three biggest disadvantages are high energy usage, fermentation poison production, and environmental concerns due to hazardous chemical use (Hendriks and Zeeman, 2009).

5. Ionizing radiation treatment

Maple wood chips irradiated with electron beam gave increased extraction by PHWE at 160 °C when compared to non-irradiated control chips in studies by Cheng (2010), Cheng et al. *in press* and Driscoll (unpublished data). It was shown that the amount of mass lost increased from 18.6% for controlled chips to 26.6% for 250 kGy irradiated chips and 40.1% for 1000 kGy irradiated chips, after 120 min of extraction (Cheng, 2010; Cheng et al., *in press*; Stipanovic unpublished data). This is a much greater loss in mass than what can be achieved using biodelignification methods (Cheng, 2010; Cheng et al., *in press*; Stipanovic unpublished data). In the irradiation of cellulose, the pH of the water extract decreased as the dose to the wood chips increased. After extraction for 1 h at 50 °C, the pH of the non-irradiated chips was about 5.8, but the pH of the irradiated wood chips that received a dose of 750 kGy was 3.8 (Cheng, 2010). This decrease in pH was attributed to an increase in the removal of the acetate groups on the hemicelluloses and an increase in the free acetic acid.

Many researchers have shown that the irradiation of cellulose can reduce its crystallinity (Cheng et al., *in press*; Driscoll et al., 2009; Kasprzyk et al., 2004; Khan et al., 2006; Toth et al., 2003). Khan et al. (2006) reported that the overall crystallinity of irradiated jute fibers decreased from 42% to 31% by a gamma irradiation at 100 kGy. Studies conducted on pure cellulose indicated that as the dose increased from 0 to 1000 kGy by electron beam, the crystallinity decreased from 87% to 45% (Driscoll et al., 2009). At very high doses of 9000 kGy, the crystallinity of pine cellulose was zero (Kasprzyk et al., 2004). While the total amount of crystallinity decreased after high doses of irradiation, lower doses may reduce the size of the crystallites (Kasprzyk et al., 2004).

Irradiation has been shown to reduce the DP and thus the MW of cellulose. Takacs et al. (1999) showed that the DP of cotton cellulose was reduced from about 1600 to 300 after 10 kGy of gamma irradiation. Toth et al. (2003), working with pre-swollen cotton cellulose, observed that the DP decreased from 1600 to 800 after 3 kGy and to 400 after 10 kGy. While these studies show a large decrease in the DP after a relatively low dose, other studies required higher doses (Cheng, 2010; Driscoll et al., 2009). Working with micro-crystalline cellulose (MCC), Driscoll et al. (2009) showed that the MW was reduced from 82,000 Da to 80,800 Da at 10 kGy, to 5389 Da at 100 kGy, and 2137 at 1000 kGy. Also working with MCC, Cheng (2010) showed that the MW was

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