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Chemical Characterization of Industrial Hemp (*Cannabis sativa*) Biomass as Biorefinery Feedstock

Soo-Jeong Shin, Gyu-Seong Han, In-Gyu Choi[1] and Sim-Hee Han[2]
Wood & Paper Science, Chungbuk National University, Cheongju 361-763, Korea
[1]Program in Environmental Material Science, College of Agricultural & Life Science, Seoul National University, Seoul 151-921, Korea
[2]Forest Seed Research Center, Korea Forest Research Institute, Chungju 380-941, Korea

Abstract - Chemical composition and enzymatic saccharification characteristics of hemp woody core were investigated by their chemical composition analysis and enzymatic saccharification with commercially available cellulases (Celluclast 1.5L and Novozym 342). Hemp woody core have higher xylan and lower lignin contents than its bast fiber. Based on hemicelluloses and lignin composition, hemp woody core is similar with hardwood biomass. However, cellulose was more easily converted to glucose than xylan to xylose and this trend was confirmed both hemp woody core and yellow poplar. Hemp woody core biomass shows higher saccharification than yellow poplar (hardwood biomass) based on cellulose and xylan hydrolysis. With easier enzymatic saccharification in cellulose and xylan, and similar chemical composition, hemp woody core have better biorefinery feedstock characteristics than hardwood biomass.

Key words - Carbohydrate composition, Bast fiber, Woody core, Lignin, Cellulose, Enzymatic saccharification

Introduction

With increasing global warming and depleting of fossil fuel resources, concerning about renewable energy resources is widely spread out all over the world (Demirbas, 2007). One of the promising sustainable energy could be the fuel ethanol (Berndes *et al.*, 2003). Plant biomass resources are produced by photosynthesis pathway using carbon dioxide, water and sunlight. Using biomass generates carbon dioxide, water and energy stored in biomass, which results in cyclic structure in energy utilization.

Lignocellulosic biomass consists of cellulose, hemicelluloses, and lignin as major structure components. Other minor components are non-polar solvent extracts and hot-water soluble extracts (polar extracts). Cellulose and hemicelluloses are polymeric form of carbohydrate which can be broken down to monosaccharides, such as glucose, mannose, galactose, and xylose. In annual plants and hardwood, main structural carbohydrates are cellulose and xylan. Cellulose is consisted by β-glucose with 1, 4-glucosidic ether bond. Xylan is main hemicelluloses in annual plant and hardwood biomass, which consisted by β-xylose with 1, 4-glycosidic ether bond. These plant biomass resources can replace the fossil fuels by biorefinery processes as conversion of polysasscharides in biomass to monosaccharide and fermentation of the monosaccharide to useful fermentation product such as bioethanol (Hamelinck *et al.*, 2005). Raw material secure supply is the one of the major part in biorefinery or bioenergy using biomass as replacement of fossil fuels.

Energy crops are biomass cultivated for energy generations which have higher biomass production per unit area. In normal forest, biomass production is 4∼5 dry tones yr^{-1} hr^{-1}. Energy crops have higher biomass productivity than normal forest as 20∼30 dry tones yr^{-1} hr^{-1}. Well-known energy crop candidates are switchgrass, industrial hemp, and short-rotation willow coppice (van der Werf *et al.*, 1996).

Industrial hemp is especially breeded for lower narcotic compound, Δ^9-tetrahydrocannabinol (THC) content less than 0.3%, compared to 3∼20% in normal hemp.

Since the hemp bast fibers have good characteristics as a cotton fiber alternative, many intensive studies have been conducted for characterizing the hemp bast fibers and the applications (Keller *et al.*, 2001; Crônier *et al.*, 2005; Gutiērrez *et al.*, 2006).

Hardwood and softwood biomass have a difficulty toward enzymatic saccharification due to their physical and chemical structure such as high degree of polymerization, crystalline structure in cellulose, complex structure in cellulose, hemicelluloses, and

*Corresponding author. E-mail : simhee02@forest.go.kr

lignin. However, annual plants have less restriction toward enzymatic saccharification than wood biomass.

In this work, chemical characterization of the bast fiber and woody core of industrial hemp biomass were investigated. Also, we compared the response to enzymatic saccharification with commercial cellulases complex to evaluate monosaccharide formation ability of biomass. And we evaluate industrial hemp biomass as biorefinery feedstock.

Materials and Methods

Industrial hemp

Industrial hemp was kindly supplied by Dangin Agricultural Technology Center (Dangjin, Chungnam, Korea) as agricultural residuals. This hemp was harvested at November, 2006, cultivated for hemp seed production. Supplied hemp was debarked by hand to separate bast fiber and woody core and these separated components was milled to less than 40 mesh by Wiley mill for chemical analysis.

Chemical characterization

Solvent extraction (TAPPI T 204 om-88), hot water extraction (TAPPI T 207 om-88), and lignin contents (TAPPI T 221 om-88) were measured for basic composition analysis both bast fiber and woody core. For carbohydrate analysis, the same procedure was done for lignin contents determination. The difference was that soluble fraction was collected for carbohydrate compositional analysis and solid fraction was collected by glass filter for lignin content determination. Collected liquid fractions were analyzed by High Performance Anion-Exchange Chromatography (HP-AEC) as described by Lee (1996). For further chemical analysis, hot-water soluble extracts fraction were freeze-dried and collected the dried solids, and carbohydrate composition in hot-water soluble were carried out the same procedure for carbohydrate analysis in polysaccharides fraction with freeze-dried solids.

Enzymatic saccharification

Enzymatic saccharification was carried out to investigate the hemp biomass as sugar generation ability. For comparing with other woody biomass, yellow poplar and spruce were carried out enzymatic saccharification with thsame reaction condition. The hemp powder were hydrolyzed using a commercial cellulase mixture, the Celluclast 1.5L (loading of 20 FPU/g biomass) with supplemented with the β-glucosidase preparation Novozym 342 (25.0% of the volumetric Celluclast addition). All saccharification were performed at 50℃ for 72 h in shaking incubator (120 rpm).

Results and Discussion

Hemp residual biomass consisted of 33% of the bast fiber and 67% of the woody core based on the hand separation. The chemical composition of residual biomass was significantly different as hot-water soluble extracts and Klason lignin content (Table 1). Higher hot-water soluble extracts and lower lignin content were the characteristic of bast fiber from other origin (Neto *et al.,* 1996).

Carbohydrate composition in hot-water soluble extracts and structural carbohydrate was analyzed by HP-AEC shown in Fig. 1. In hot-water soluble extracts, lower molecular weight carbohydrate and other polar extractives were extracted. Most of hot-water soluble was not carbohydrate origin but carbohydrates fractions come from starch or arabinogalactan based on the arabinose, galactose, and glucose content (Table 2). Arabinogalactan was hydrolyzed as arabinose and galactan, and starch was hydrolyzed as glucose.

In structural carbohydrate analysis, bast fiber has higher cellulose and lower xylan content than woody core based on monomeric composition of hemp biomass (Table 3). Mannose has only detected in bast fiber, which meant there is galactoglucomannan in bast fiber but not in woody core.

Based on enzymatic saccharification with commercial cellulose mixtures, hemp woody core show 3.5 times higher glucose conversion from cellulose than yellow poplar even though both biomass have similar chemical compositions (Fig. 2). This trend was less clear in xylan saccharification. Hemp woody core xylan showed 1.5 times more saccharification than yellow poplar xylan (Fig. 3).

Based on both chemical composition analysis and enzymatic saccharification, industrial hemp woody core have better monosaccharides conversion than yellow poplar, which means better characteristics for biorefinery feedstock than hardwood as yellow poplar.

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Table 1. Chemical composition of the bast fiber and woody core from industrial hemp

Chemical composition	Bast fiber	Woody core
Ethanol-benzene extracts (%)	2.6	2.1
Hot water-soluble extracts (%)	20.5	9.1
Klason lignin (%)	8.0	17.2
Polysaccharides (%)	68.9	71.6

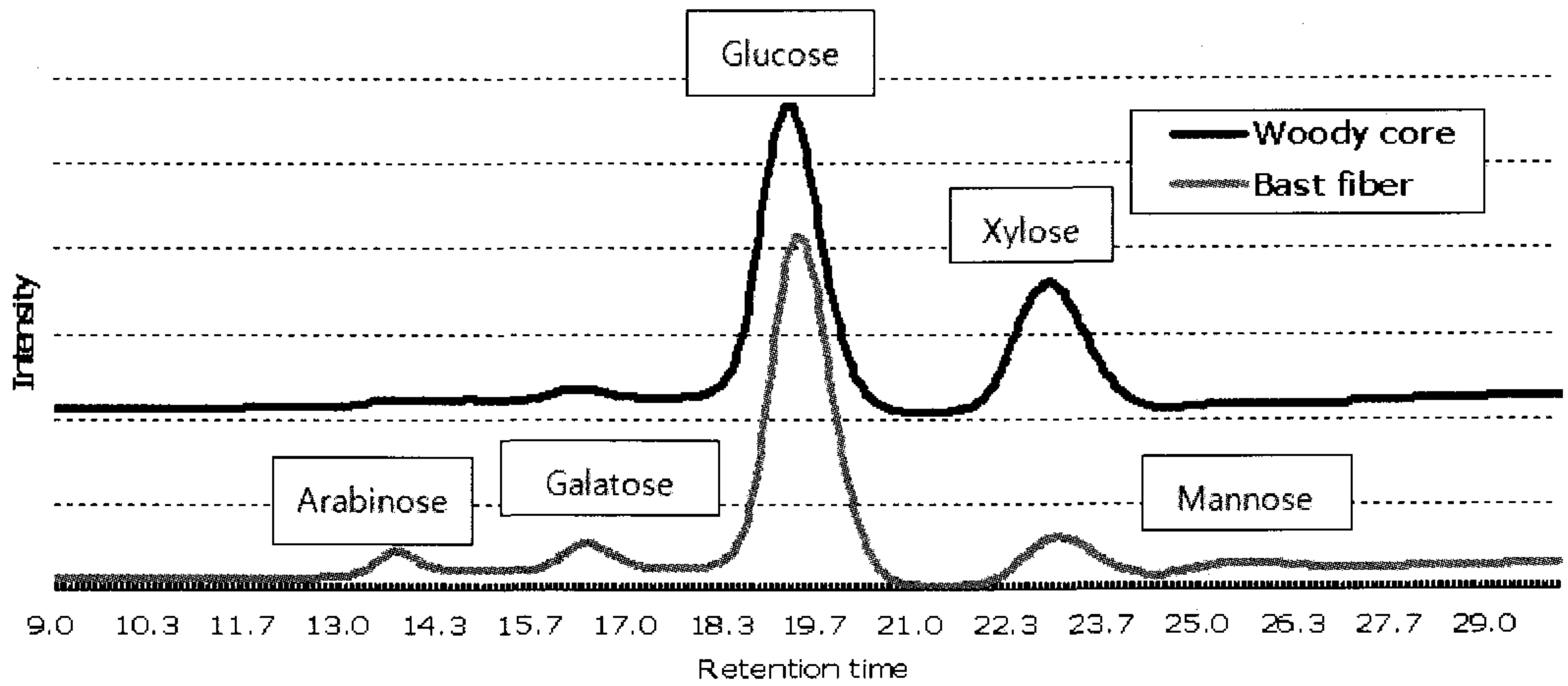

Fig. 1. Monosaccharide chromatogram of hemp by HP-AEC.

Table 2. Monomeric composition of oligosaccharides and monosaccharides from hot-water soluble extracts

Hemp parts	Total	Arabinose	Galactose	Glucose	Non-carbohydrate
Bast fiber (%)	20.5	0.5	0.7	3.7	15.7
Woody core (%)	9.1	0.1	0.3	1.7	7.0

Table 3. Monomeric composition of polysaccharides

Hemp parts	Total	Arabinose	Galactose	Glucose	Xylose	Mannose
Bast fiber (%)	68.9	2.7	3.5	52.0	7.7	3.0
Woody core (%)	71.6	0.4	1.5	44.5	25.2	n.d

n.d: not-detected.

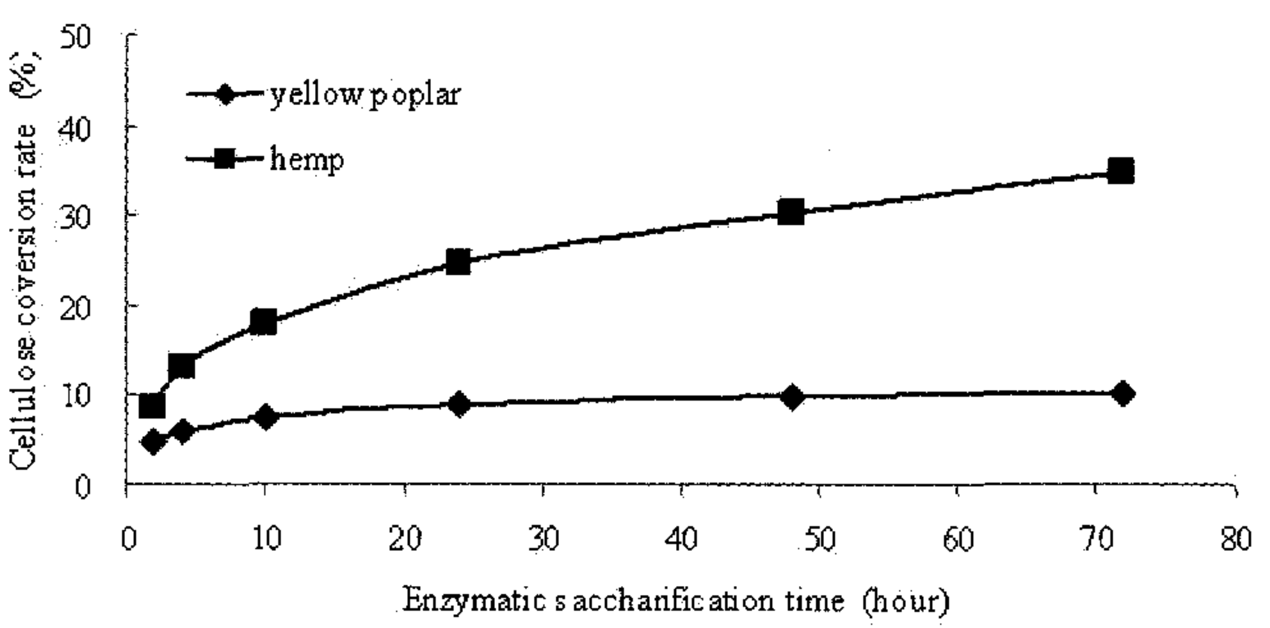

Fig. 2. Enzymatic saccharification of cellulose in hemp and yellow poplar.

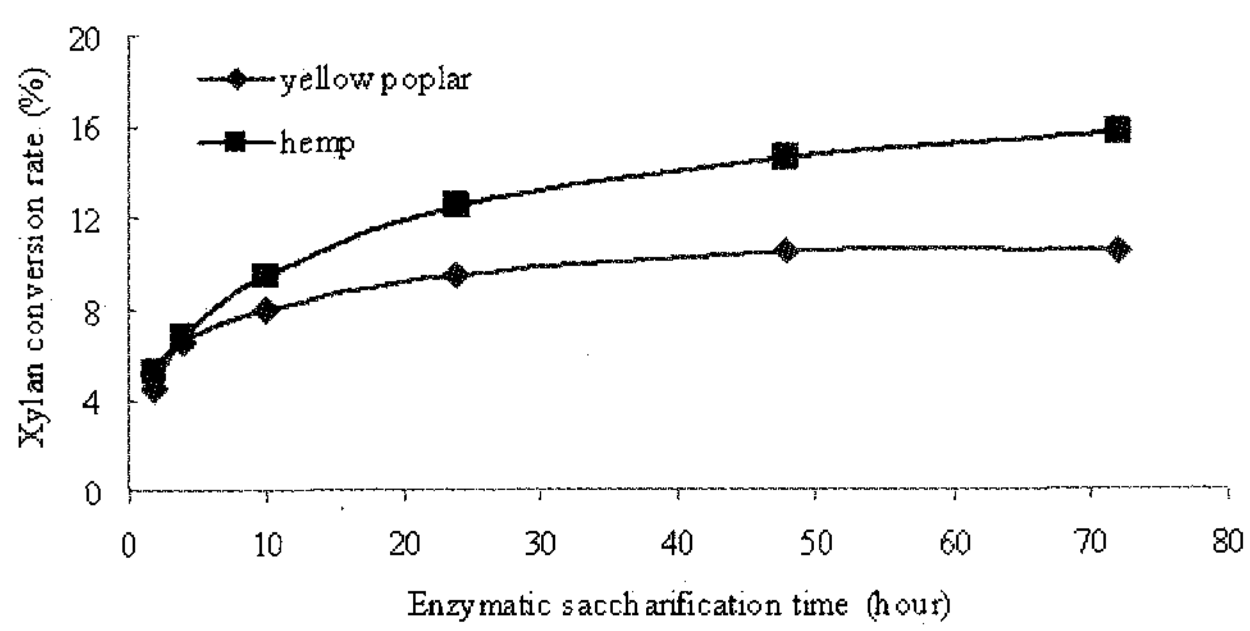

Fig. 3. Enzymatic saccharification of xylan in hemp and yellow poplar.

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