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Analysis of Chemical Compositions and Energy Contents of Different Parts of Yellow Poplar for Development of Bioenergy Technology

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Abstract : Understanding of chemical composition and energy contents in tree is important to develope strategies of renewable energy policy to cope with climate change. Residual biomass as renewable energy source was evaluated and focused on the bark-containing branches. Chemical analysis studies were conducted for different part of yellow poplar (*Liriodendron tulipifera*), which were partitioned to inner bark, outer bark, small branches, medium branches, big branches and trunk. The variations in hydrophobic extractives, hydrophilic extractives, lignin, carbohydrate compositions, energy contents (higher heating value) and the ash content were determined. The inner and outer bark had higher ash content, hydrophobic and hydrophilic extractives content, and higher energy content than those of tree trunk. Polysaccharides content in inner and outer bark was quite lower than those of stem or branches. Based on the energy content of residual biomass, replacement of fossil fuel and greenhouse gas emission abatement were calculated.

Key words **:** *yellow poplar, bark, branch, elementary analysis, energy content, ash*

Introduction

Human-being has accumulated CO_2, the major greenhouse gas in the air since industrial revolution. These increased greenhouse gas brought climate change. It is estimated that the unprecedented natural disasters occurring over the world lately are to be the negative impact of climate change. IPCC (Intergovernmental Panel on Climate Change) also expressed their concern about the impact of climate change in their 4th climate change assessment report. Greenhouse gases such as CO_2 and CH_4 block thermal energy from radiating out into space and trap heat within Earth's atmosphere, which consequently brought global warming effect to the Earth. Climate Change is one of the main environmental issues that we are facing presently. Under the UNFCCC (Unite Nations Framework Convention of Climate Change), every country has the pressure to reduce greenhouse gas and Korea is also under the strong pressure of greenhouse gas emission reduction (IPCC, 2007).

To solve this global environmental problem, we should reduce greenhouse gas emission, and absorb greenhouse gas in the air as much as possible. One of the main solutions for this global environmental problem is to capture the atmospheric carbon into some kind of carbon storage. The most suitable types of carbon storage can be plants and soil. Especially trees can be good carbon storage as long as we maintain trees growing well. Another solution can be converting main energy source from fossil fuel into renewable energy. Developing renewable energy can be good solutions for climate change: wind energy, solar energy, and bioenergy are some examples. One of the best examples can be bio-energy. In Korea, it is known that there are lots of available tree residuals from forest thinning activities. Wood became the main source of renewable energy in many countries such as United States, because generating bioenergy from waste wood can be a good substitute for burning fossil fuels such as coal, oil, and gas. Korea forest is 65% of land. It is reported that forest absorbs about 6.3% of greenhouse gas emissions in Korea. If we manage forest and waste wood more efficiently, we can reduce greenhouse gas emission. Therefore, it is necessary to develop technologies that can convert trees into bioenergy.

In addition, the increase of world population and the

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improvement of living standard require more amount of woody biomass as energy sources or wood products forms. The wood processing industries use the raw material selectively. In forest harvesting, most of top unmerchantable stem, branches, stump and roots are neither harvested nor collected due to less economically attractive (Hakkila, 1989). Those less attractive biomass can be defined as residual biomass. Residual biomass has lower commercial values as wood product industry, but it can be used as bioenergy resources. Compared to wood trunk, bark has different anantomical and chemical characteristics (Usia and Kara, 1997). The most of residual biomass has difficulty in debarking, because the process that can control bark containing biomass are essential. Effective uses of residual biomass can overcome the shortage of biomass in renewable energy resources. Chemical compositional analysis and elementary analysis can estimate the biomass as a potential feedstock for biofuel production (Hallac *et al*., 2009; Hu *et al*., 2010; Madakadze *et al*., 1999; Yan *et al*., 2010)

In this study, we investigated the chemical composition of tree trunk, inner and outer bark and different size of branches. With chemical compositional analysis and elementary composition analysis, we evaluated the residual biomass values as biosolid fuels and their impact of carbon dioxide emission abatement.

Material and Methods

1. Wood materials

Twenty-year old yellow poplar grown at Chungbuk National University campus (Cheongju, South Korea) was cut, debarked, chipped and air-dried for one week. Air-dried chip were milled to less than 20 meshes for chemical analyses. Inner bark and outer bark were separated by debarking process. Branches were collected and grouped to small branches (diameter less than 1.0 cm), medium branches (diameter 1-3 cm), and big branches (diameter bigger than 3 cm). Collected barks and branches were cut and milled to less than 20 meshes.

2. Extractives content

Extractives content was measured according to TAPPI procedure T 204-om 82 for hydrophobic extractives (TAPPI, 1989a) and T 207-om 88 for hydrophilic extractives (TAPPI, 1989b). Due to high carcinogenic property of benzene, ethanol-benzene solvent extraction was replaced by acetone. Extractives content was calculated based on the difference between oven-dried weight of un-extracted and extracted samples. Air-dried samples were extracted by acetone (for hydrophobic extractives) followed by hot-water (for hydrophilic extractives) as successive extraction.

Table 1. Operating conditions of ^{1}H-NMR Spectroscopy for monosaccharide composition.

	^{1}H-NMR
Model	Bruker, AVACE NMR Spectrometer (500 MHZ)
Solvent	D2O
Pulse	11 μsec
Delay between pulse	10 s
Acquistiton time	2.73 sec
Sweep width	10 ppm
Center of spectrum	4.5 ppm
Temperature	295.6 K

3. Monosaccharides and lignin content analysis:

Extractives-free samples (200 mg) were hydrolyzed with 72% sulfuric acid (1.5 mL) for 2 hours at 20°C. The hydrolyzate was diluted to 4.0% sulfuric acid with distilled water and boiled for 3 hours. The boiled hydrolyzate solution was cooled to room temperature for overnight and filtered through 1G4 porcelain crucible filter and the residue was calculated as Klason lignin content. For monosaccharide compositional analysis, experiment was run as 1/10 scale down and 2nd stage hydrolysis was diluted by deuterium oxide instead of distilled water for ^{1}H-nuclear magnetic resource spectroscopic analysis (Shin and Cho, 2008). Operating conditions are listed in Table 1.

4. Ash analysis

The ash content of unextracted samples was analyzed according to TAPPI method T211 om-85 (TAPPI, 1989c).

5. Energy content

The higher heating value (HHV) for the yellow poplar was analyzed according to TAPPI method T684 pm-84 in an adiabatic oxygen bomb calorimeter (TAPPI, 1989).

Results and Discussion

Tree crowns, unmerchantable tops, stumps, and roots form a huge reserve of renewable raw material. Compared with merchantable stems, some additional biomass is potentially available from these unutilized tree components in silviculturally managed forests, and undersized trees and defected stem parts include a considerably higher percentage in overmature, unmanaged forests.

Utilization of the residual biomass is constrained and frequently totally prevented by many economic, technical, and ecological barriers (Hakkila, 1989). A critical factor is the high cost of recovery due to the small unit size, low areal yield, low bulk density and need for special equipment. In conventional use of raw material, high content and irregular variation of bark and foliage are serious drawbacks as well. This problematic situation is reflected in the perspective of wood technology research, which is traditionally aimed at improved utilization of stem wood. Only a very small fraction of the efforts is directed toward the utilization of other components of the tree.

In branch, softwood forms compression wood as eccentric growth rings, which appears on the lower side of branch. However, hardwood branch forms tension wood as eccentric growth rings, which appear on the upper side of branch. These tension wood and compression wood have different anantomical and chemical composition compared with stem (Okuyama *et al*., 1994). Compression wood has less cellulose and galactoglucomannan but more lignin and galactan than those in normal wood. Tension wood has more cellulose and less lignin than those in normal wood.

From the utilization point of view, in some tree species juvenile and mature woods may be considered as two different materials in the same stem. The duration of the juvenile period, usually from 5 to 20 years, is quite variable among species (Hakkila, 1989).

The bark locates external to vascular cambium, which is composed of phloem, cortex, periderm and remnants of the epidermis. This complex structure and composition allows the multiple functions, such as photosynthesis, sap conduction, tissue aeration and protection from external stresses (Niklas, 1999). The outer bark forms a protective barrier between plant axis and the abiotic and biotic environment. The inner bark (phloem) serves as sugar transport and defend against herbivores or cells and tubes filled with bitter or toxic chemicals. Due to these characteristics, bark has different chemical composition with stem.

Extractives (both hydrophobic and hydrophilic) and ash content in bark were higher than those in trunk (Table 2). Due to higher extractives and ash contents in bark, bark containing branches also had higher extractives and ash content than those in trunk. Within barks, there was different chemical composition between inner and outer bark, and inner bark had more hydrophilic extractives but outer bark had more lignin content.

In carbohydrate compositional analysis and polysaccharide contents in overall compositional analysis, bark had less polysaccharide than trunk, which resulted in less cellulose and xylan content (Table 3). However, glucomannan content was similar between bark and trunk. Holocellulose and cellulose content in bark were lower than those in sapwood and heartwood (Usia and Kara, 1997). Due to higher bark portion, carbohydrate content in small branch was lower than that in middle, larger branch or stem. Due to lower cellulose and xylose content in bark and small branch, this fraction can produce less monosaccharides than bigger branch or stem by acid or enzymatic saccharification with theoretical yield.

In elementary analysis, bark had higher hydrogen and nitrogen and lower oxygen content than trunk (Table 4). In branch, small or medium branches had similar elementary composition with bark but big branch had similar composition with trunk. Higher amount of nitrogen in bark means higher physiological activity in bark area.

Table 2. Chemical composition of different part of yellow poplar (unit: %).

Part	Inorganic	Acetone soluble	Hot water Soluble	Lignin	Polysaccharides
Trunk	0.4	2.5	13.9	17.4	65.8
Outer bark	4.4	6.2	24.0	18.6	46.8
Inner bark	4.6	8.8	28.5	9.2	48.9
Small branch	3.1	4.7	20.9	21.1	50.2
Medium branch	2.1	2.7	11.3	17.8	65.4
Big branch	1.6	1.9	12.8	17.1	66.6

Small: less than 1 cm diameter, medium: 1-3 cm diameter, big: more than 3 cm diameter

Table 3. Carbohydrate composition of different part of yellow poplar.

Part	Polysaccharides	Cellulose	Xylan	Glucomannan
Trunk	65.8	46.2	17.5	2.1
Outer bark	46.8	35.5	9	2.3
Inner bark	48.9	37.8	8.7	2.4
Small branch	50.2	35.7	14.4	0.1
Medium branch	65.4	44.6	18.5	2.3
Big branch	66.6	49.4	16.3	0.9

Table 4. Elementary analysis of different part of yellow poplar.

Part	C	H	O	N
Trunk	49.45	6.66	43.76	0.13
Outer bark	50.37	6.9	42.04	0.7
Inner bark	49.25	7.04	43.02	0.7
Small branch	50.97	6.88	41.22	0.93
Medium branch	50.79	6.83	41.92	0.46
Big branch	49.51	6.66	43.54	0.29

Table 5. Energy contents in different part of yellow poplar based on oven-dried biomass (HHV: higher heating values, Unit: MJ/kg)

Part	HHV	MODEL1)	MODEL2)
Trunk	18.8	18.44	19.14
Outer bark	19	19.39	20.05
Inner bark	19.1	19.05	19.72
Small branch	19.4	19.72	20.36
Medium branch	18.7	19.47	20.13
Big branch	18.5	18.49	19.19

1)Based on Dulong's model

2)Based on Ruyter's model

Table 6. Replaceme.nt of fossil fuel by residual biomass and net carbon dioxide emission.

	Residual biomass	Natural gas	Petroleum	Coal
Energy value (MJ)	19	18.8	19.1	19.1
Unit Energy value (MJ/kg)	19	49.4	43.5	29
Net weight (kg)	1	0.38	0.44	0.66
Net carbon dioxide emission (kg)	0.12	1.02	1.51	1.55

In energy content and elementary composition analysis, energy content was measured by bomb calorimeter and compared with theoretical energy content based on the elementary compositional analysis with Dulong's model and Ruyter model. The equations of two different models are listed in below. In Dulong's model, calorie unit value was converted to Joule unit value (Table 5).

1) Dulong model (Sivapalan *et al.*, 2003)

$$CV\ (\text{Calorimetric value}) = 80.80\%C + 344.60(\%H - \%O/8) + 22.50\%S\ (\text{kcal/kg})$$

2) Ruyter model (Ruyter, 1982)

$$CV = 0.34\%C + 1.40\%H - 0.16\%O\ (\text{MJ/kg})$$

With elementary analysis and energy content model calculation, Ruyter's model gave higher energy content than Dulong's one (Table 4). In yellow poplar biomass, Dulong's model gave closer energy content value to bomb calorimetric energy content value than Ruyter's one. Even though bark had higher ash content, it had higher energy content than trunk, which meant higher energy in hydrophic and hydrophilic extractives than polysaccharides or lignin. Due to different elementary composition, lignin and extractives has higher heating value than other wood component (White, 1986). With appropriate design in ash removal part, bark and bark-containing branch should be superior bio-solid fuels than trunk.

1. Comparison with fossil fuels

In secondary metabolism, main wood structural components are biosynthesized from glucose. Due to high oxygen content in woody biomass, residual biomass has less energy content than natural gas, petroleum and coal (Table 6). However, effective usages of residual biomass can extract the energy, otherwise, there will be decomposed to carbon dioxide and water. Net carbon dioxide emission for 19 MJ was compared in Table 6. Residual biomass had far less carbon dioxide emission than fossil fuels.

Conclusions

This study showed the potential to use residual wood for generating bioenergy. Residual wood showed the different chemical composition compared with those of trunk in yellow poplar. Inner and outer bark had higher extractives content than those in trunk, which led to higher energy content than main woody trunk. Branches which contain the bark showed very similar chemical composition and energy content compared with trunk in yellow poplar. Therefore, residual biomass in yellow poplar can replace the trunk in the point of bioenergy generation based on the combustion.

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