

Change of Heating Value, pH and FT-IR Spectra of Charcoal at Different Carbonization Temperatures*¹

Sung-Min Kwon*², Jae-Hyuk Jang*², Seung-Hwan Lee*², Sang-Bum Park*³,
and Nam-Hun Kim*^{2†}

ABSTRACT

To understand transition characteristics from wood to charcoal, *Quercus variabilis* wood was carbonized at 200, 250, 300, 340, 540 and 740°C, respectively. Heating value, pH and surface property by FT-IR spectroscopy of the carbonized charcoal were investigated. Heating value and pH increased with increasing carbonization temperature from 4500 cal/g and 4.3 of the control wood to 8,000 cal/g and 9 of the charcoal carbonized at 740°C, respectively. From FT-IR spectroscopy, the peaks from O-H, C-H and C-O stretching disappeared during carbonization at 540 and 740°C. Aromatic skeletal vibration at near 1,506~1,593 cm⁻¹ was rapidly increased until 540°C. These results suggest that the chemical and physical characteristics of wood components in cell wall can be easily changed by increasing carbonization temperature and the carbonization seem to be incomplete at temperature below 540°C.

Keywords : carbonization, charcoal, heating value, pH, FT-IR

1. INTRODUCTION

Charcoal can be generally produced when wood is heated in the absence of oxygen. In this process, the water contained in the wood is first driven off before the wood constituents (cellulose, hemicellulose and lignin) begin to be thermally decomposed. Wood pyrolysis is a complex combination with the individual pyrolysis of cellulose, hemicellulose, lignin and extractives, each of which has its own characteristics (Kwon *et al.*, 2009).

Zerriouh and Belkbir (1995) reported that, in the pyrolysis process of wood constituents with heating rate of 5°C min⁻¹, hemicellulose is decomposed at the temperatures ranging 170~240°C, cellulose 240~310°C and lignin 320~400°C. Between 260°C and 400°C, almost 80% of the total weight loss occurs, which may vary between 40% (lignin) to about 80 (cellulose) due to the evolution of H₂O, CO₂, and volatile hydrocarbon (Qian *et al.*, 2004). Wood constituents are complexly bonded each other, so that they release various different compounds as

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*² Department of Forest Biomaterials Engineering, College of Forest & Environmental Sciences, Kangwon National University, Chuncheon 200-701, Korea

*³ Korea Forest Research Institute, Seoul 130-172, Korea

[†] Corresponding author : Nam-Hun Kim (e-mail: kimnh@kangwon.ac.kr)

pyrolysis proceeds. After the wood compounds are evaporated by metathesis, only charcoal is left over.

The mechanisms involved in the transition from wood to charcoal are known as follows; (1) evaporation of adsorbed water up to 150°C, (2) splitting off of water in wood structure between 150°C and 260°C, (3) chain scissions or depolymerization and breaking of C-O and C-C bonds within ring units evolving water, CO and CO₂ between 260°C and 400°C, and (4) formation of graphitic layers above 400°C (Greil, 2001). It has been also known that thermally induced decomposition and rearrangement reaction above 800°C are almost terminated leaving a carbon structure (Mopoung, 2008).

However, the mechanisms for wood carbonization are not fully understood because of the complexity caused by the varying physical and chemical properties of wood. In the previous researches (Kim and Hanna, 2006; Kwon and Kim, 2006; 2007; Kwon *et al.*, 2009), we reported the anatomical characteristics of the carbonized woods at different temperatures and the transition temperature from wood to charcoal. From our results, we understood the morphological change of wood cell wall layers from multilayered to amorphous structure and decomposition of cellulose crystal by increasing carbonization temperature.

In this study, we examined the change of calorific value, pH and FT-IR spectra in different temperatures in order to understand the transformation characteristics from wood to charcoal.

2. MATERIAL and METHODS

2.1. Material

Quercus variabilis woods obtained from the research forest of Kangwon National University in Chuncheon, Korea were used for this study.

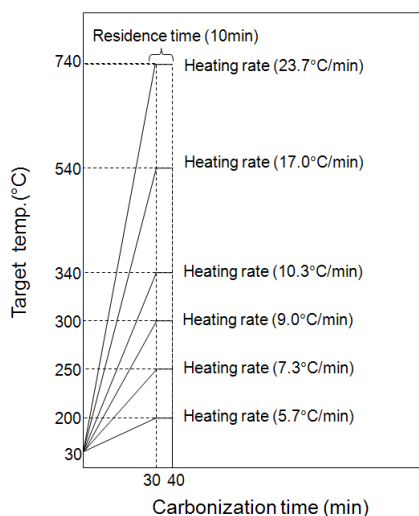


Fig. 1. Time-temperature profiles for wood carbonization with different heating rate.

Air-dried wood samples were cut into small blocks with the dimensions of 20 mm in thickness and width and 40 mm in length. The detail characteristics of sample tree has been described in previous work (Kwon and Kim, 2006).

2.2. Methods

2.2.1. Carbonization Process

Wood blocks were carbonized in an electric furnace under the nitrogen gas atmosphere (1 kg cm⁻²) at 200, 250, 300, 340, 540, and 740°C, respectively. The carbonization was carried out by heating the wood samples from room temperature to the final carbonization temperature. The samples were set to be heated for 30 minutes to reach each targeted temperature. After reaching the final carbonization temperature, the samples were scheduled to keep for 10 minutes at constant temperature and then rapidly soaked into the sand for cooling. Heating rate of each target temperature are shown in Fig. 1.

2.2.2. Measurement of Heating Value

The heating value of charcoal samples (0.5 g, 60 mesh) was measured by oxygen bomb calorimeter (Parr, 6300) in accordance with the KS E 3707 standard test method.

2.2.3. Measurement of pH Value

Oven-dried charcoal samples (1 g, 60 mesh) and 100 ml of distilled water were shaken together and boiled for 10 minutes. The samples left to settle for 10 minutes, and then pH was determined with a pH meter (inoLab, pH Level 2).

2.2.4. FT-IR Spectroscopy

To investigate the changes in the surface chemical properties during carbonization, FT-IR spectroscopy was used. The spectra were recorded on a BIO-RAD Cambridge, EXCALIBER Series FT-IR spectrometer in the range of 500-4,000 cm^{-1} wavenumber. In the preparation of pellets, wood chips were powdered and then mixed with KBr at an approximate ratio of 1/500. Each pellet's mass was about 400 mg.

3. RESULTS and DISCUSSION

3.1. Change of Heating Value

Fig. 2 shows the change of the heating value of *Quercus variabilis* wood during carbonization at different temperatures. The heating value was gradually increased from 4,530 cal/g at 200°C to 8,030 cal/g at 740°C. In our recent work (Kwon *et al.*, 2012) we reported that heating value increased with increasing carbonization temperature from 6,800 cal/g at 400°C to 7,250 cal/g at 600°C. Rhee and Cho (2008) reported that with increasing carbonization temperature, fuel ratio (fixed carbon/volatile combustible), carbon content, and heating value of

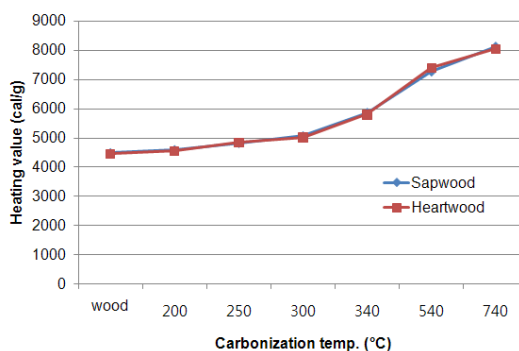


Fig. 2. The heating value of *Quercus variabilis* wood during carbonization at different temperatures.

carbonization residue increased but the yield of the residue decreased. Phan *et al.* (2008) examined the fuel properties of the slow pyrolysis products from three segregated waste materials (waste wood, cardboard and textile) heated at 350, 400, 500, 600, and 700°C. They reported that the heating value was increased with increasing the charring temperature. Encinar *et al.* (1996, 2000) carried out the detailed study on the conventional pyrolysis of *Cynara cardunculus*, in order to determine the quality of the charcoal obtained in the process. They reported that the heating value increased with increasing carbonization temperature as the fixed carbon content increased. They also concluded that the most favourable pyrolysis temperature of residue from an energy point of view should be ranged between 600 and 700°C, at which thus obtained charcoal would have a higher heating value and a suitable percentage of fixed carbon.

3.2. Change of pH Value During Carbonization

The pH values of the wood and carbonized wood from 250 to 740°C are presented in Fig. 3. The pH value increased with increasing the carbonization temperatures. In this study, pH

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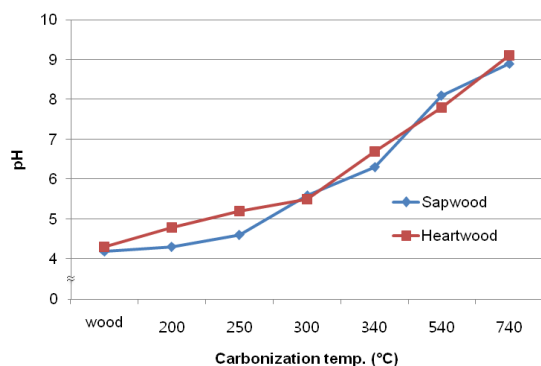


Fig. 3. The pH value of *Quercus variabilis* wood during carbonization at different temperatures.

value were low acidic until 340°C, and changed to basic at over 540°C. Recently, Kwon *et al.* (2012) also reported that pH value increased with increasing carbonization temperature from 7.6 at 400°C to 9.7 at 1200°C. Yatagai *et al.* (1995) examined the pH of five kinds of charcoal prepared at 600 to 800°C by traditional black charcoal kiln. They found that pH values of most charcoal were ranged from 6.48 to 8.35. Jo *et al.* (2009) examined the properties and chemical bonding of wood charcoal carbonized at different temperatures. They reported that the pH become acidic to weakly basic for carbonized wood at about 300°C, whereas it turned to basic at carbonization temperature higher than 600°C.

3.3. Change of Surface Chemical Property

Fig. 4 shows FT-IR spectra from 500~4,000 cm^{-1} for *Quercus variabilis* wood. A strong hydrogen bonded O-H stretching absorption was seen at 3,338 cm^{-1} and a prominent C-H stretching absorption around 2,904 cm^{-1} . In addition, there were many well-defined peaks in the region between 1,800 and 600 cm^{-1} (Table 1). The peaks in 1,734 cm^{-1} for non-conjugated C = O

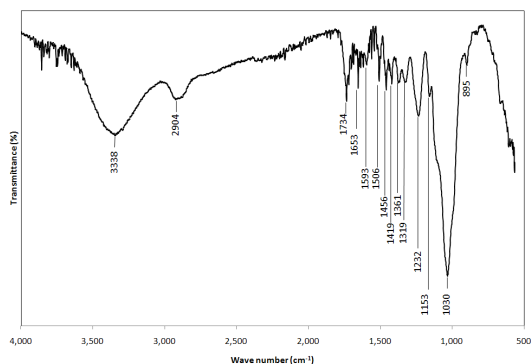


Fig. 4. FT-IR spectra of *Quercus variabilis* wood.

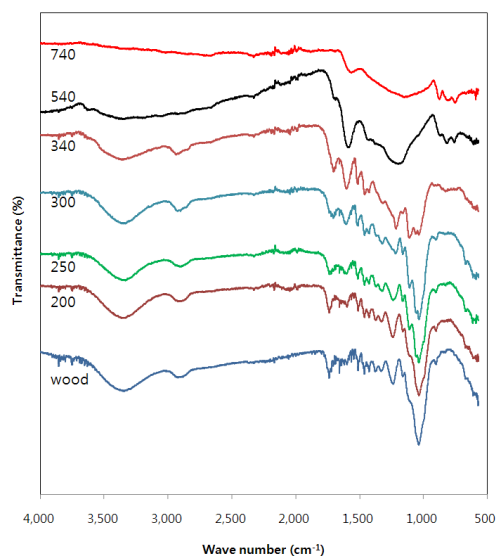


Fig. 5. FT-IR spectra of *Quercus variabilis* woods charred at different temperatures.

in xylans (hemicellulose), 1,653 cm^{-1} for conjugated C = O in lignin, 1,593 and 1,506 cm^{-1} for aromatic skeletal in lignin, 1,456 and 1,419 cm^{-1} for C-H deformation in lignin and carbohydrates, 1,361 cm^{-1} for C-H deformation in cellulose and hemicellulose, 1,319 cm^{-1} for C-H vibration in cellulose and C-O vibration in syringyl derivatives, 1,232 cm^{-1} for syringyl ring

Table 1. Peak assignment of FT-IR spectra peaks in *Quercus variabilis* wood

Wave number (cm ⁻¹)	Peak assignment (Schwanninger <i>et al.</i> , 2004)
3338	O-H stretching
2904	C-H stretching
1734	Non-conjugated C=O in hemicellulose
1653	Conjugated C=O in lignin
1593	Aromatic skeletal vibration in lignin
1506	Aromatic skeletal vibration in lignin
1456	C-H deformation in lignin and carbohydrates
1419	C-H deformation in lignin and carbohydrates
1361	C-H deformation in cellulose and hemicellulose
1319	C-H vibration in cellulose and
"	C-O vibration in syringyl derivatives
1232	Syringyl ring and C-O stretch in lignin and xylan
1153	C-O-C vibration in cellulose and hemicellulose
1030	C-O stretch in cellulose and hemicellulose
895	C-H deformation in cellulose

and C-O stretch in lignin and xylan, 1,153 cm⁻¹ for C-O-C vibration in cellulose and hemicellulose, 1,030 cm⁻¹ for C-O stretch in cellulose and hemicellulose and 895 cm⁻¹ for C-H deformation in cellulose.

Fig. 5 displays the FT-IR spectra of the wood sample and its chars obtained at different temperatures. At the temperature lower than 300°C, the shape of the spectra was little changed, indicating almost no change in the chemical structure of the material. Wang *et al.* (2009) found that the charcoal of Chinese white pine prepared at 300°C showed the similar IR spectrum with complex transmittance bands with the raw sample. When the temperature was higher than 340°C, however, the chemical structure of the samples started to change drastically, in good agreement with the result on X-ray diffraction analysis and trend in weight loss (Kwon and Kim, 2006). A broad band at 3,338 cm⁻¹ was probably due to the hydrogen bonded O-H stretching. In the temperature range of 200~300°C, the intensity of O-H band did not decrease noticeably. However, its intensity disappeared significantly at the temperature higher

than 540°C, implying the dehydration of wood. Sharma *et al.* (2004) characterized the functional change of lignin by heating with temperatures between 150 and 550°C. They reported that the peak of the bonded OH stretch disappeared at 550°C. The intensity of (C-H) band attributed to aliphatic CH₂ and aromatic CH₃ (2904 cm⁻¹) decreased significantly between 340 and 540°C. The bands arising from the stretching of the 1,734 (C = O), 1,361 (C-H), 1,153 (C-O-C), 1,030 (C-O) and 895 cm⁻¹ (C-H) in cellulose and hemicellulose showed an evident decrease in intensity from wood to chars obtained at between 340 and 540°C. Wang *et al.* (2009) reported that the striking evolution of CO₂ and CO occurred at an onset temperature of 250°C, with a peak temperature of around 350°C. For the intensities of lignin, associated bands at 1,456, 1,419, 1,319 (C-H) and 1,232 cm⁻¹ (C-O) decreased with increasing the carbonization temperature. These bands nearly disappeared between 340 and 540°C. Aromatic skeletal vibration (1,593 and 1,506 cm⁻¹) showed maximum intensities at 540°C. This result indicated the concomitant aromatization of a por-

tion of residue upon the degradation of hemicellulose and lignin. A decrease of these bands at higher temperature reflected the carbonization by pyrolysis and the rebuilding of aromatic rings.

4. CONCLUSION

Quercus variabilis woods carbonized at 200, 250, 300, 340, 540 and 740°C were characterized. Heating value and pH increased with increasing carbonization temperature. From FT-IR spectroscopy, some chemical shifts were confirmed with increasing temperature.

The detailed characteristics are summarized as follows;

At the temperature range of 200 to 300°C, pH and heating value were 4.6~5.65 and 4,538~5,020 cal/g, respectively. The FT-IR spectra was not significantly changed in this temperature range. At 340°C, pH and heating value were found to be ca. 6.5 and 5,800 cal/g, respectively. The intensities of absorption bands from cellulose and hemicellulose in FT-IR spectra almost disappeared and the aromatization process started at this temperature. At 540°C, pH and heating value were found to be ca. 8 and 7,400 cal/g, respectively. The intensities of FT-IR absorption bands from cellulose, hemicellulose and lignin were almost absent and only a small amount of ether typed structures were retained. At 740°C, pH and heating value were ca. 9 and 8,000 cal/g, respectively. The intensities of FT-IR absorption bands from cellulose, hemicellulose and lignin almost disappeared.

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