

CHARACTERIZATIONS AND PROPERTIES OF TORREFIED *QUERCUS VARIABILIS* CORK

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ABSTRACT

The energy properties and physicochemical structure of torrefied *Quercus variabilis* cork were investigated with torrefaction between 150°C and 300°C in a tubular furnace. The mass yield, energy yield, and physicochemical properties of torrefied cork were characterized via proximate analysis, elemental analysis, colour analysis, and scanning electron microscope. The results showed that volatiles, moisture content, and the ratios of oxygen to carbon and hydrogen to carbon decreased with increasing torrefaction temperature. Ash content and fixed carbon content increased with increasing temperature, and the enhanced fixed carbon content resulted in the increase of high heating value (HHV) of cork. The HHV compared to untreated cork increased by around 16% after torrefaction at 300°C for 1h. With increasing torrefaction temperature, the cell cavity increased in size, the corrugation was less deformed, and less sediment appeared on cell walls. In conclusion, torrefaction improved both the energy and physicochemical properties of cork. In addition, FTIR and CP/MAS ¹³C NMR spectra analysis showed that polysaccharide degraded at 200°C, and lignin degraded between 250 and 300°C. Although suberin had better thermal resistance, its NMR signal intensity decreased after torrefaction at 300°C.

KEYWORDS: Cork, *Quercus variabilis*, torrefaction, FTIR, CP/MAS ¹³C NMR.

INTRODUCTION

Cork, the phellem layer of the bark, is a secondary protection organization of oak trees and anatomically, part of the periderm (Bai et al. 2014). It has many excellent properties including low specific gravity, high hydrophobicity, high resilience, and good thermal and sound insulation

(Lagorce-Tachon et al. 2015, Ferreira et al. 2016). Cork is primarily composed of suberin, lignin, holocellulose, and extractives; the cells are dead at maturity and do not contain cytoplasm. There are also no gaps among cells. The cell wall structure and chemical composition results in the excellent performances of cork (Pereira 2007, 2015).

Cork distributed throughout the west coast of the Mediterranean are mainly from *Quercus suber* (Surový et al. 2009, Gil 2014). In China however, the major species is *Quercus variabilis* and it is distributed in the northwest of China, north and south China, central China and southwest of China (Song et al. 2011, Qiu et al. 2011). Cork is used for a variety of products, including seal and gasket material, heat insulation materials, constructive and decorative materials, and all types of ornaments (Silva et al. 2005).

Biomass torrefaction is a slow pyrolysis process under low temperature (200-300°C), normal pressure and inert gases protected atmosphere. Torrefaction can remove moisture and part of volatiles in biomass, initiate chemical reactions of polymers in cell walls, improve substance energy density and grindability, homogenize the chemical structure, and thus, improve the overall material properties and facilitate biomass combustion and gasification (Van der Stelt et al. 2011, Wannapeera and Worasuwanarak 2012, Shang et al. 2012).

Many publications address on the anatomical structure, chemical composition, mechanical properties, utilization, and composite materials of cork (Jové et al. 2011, Şen et al. 2014). The thermal treatment process of cork under oxygen environment has also been reported. Rosa et al. (1994) heated cork to 100-150°C and reported mass loss, composition analysis, and changes of compression curves. They also investigated the effect of compositional changes on compression strength. The change of CIE-Lab parameters with mass loss of cork after thermal treatment at 150-400°C for different time was investigated by Şen et al. (2012a). Although the kinetics of pyrolysis was investigated by Wei (2010), the reports on cork torrefaction are still insufficient.

In this paper, cork of *Quercus variabilis* was torrefied in a tubular furnace at different temperatures under nitrogen protection. The impact of torrefaction on energy properties and physicochemical structures was analyzed. This study aims to improve the cork processing efficiency by optimizing cork torrefaction procedures and utilizing of the cork by-product as energy feedstock.

MATERIALS AND METHODS

Cork materials selection

The reproduction cork was obtained from Qinba mountain area, Shaanxi Province. Cork was stored in natural conditions for six months (with equilibrium moisture content (EMC) around 6%). After peeling off the defects of bark, including black parts and inside parts, cork panels were ground into particles via FW-100D mill (Xinbode, China), and sorted to a size between 20 to 40 meshes. Some torrefied cork blocks in the size of 30 × 30 × > 6 mm (transverses × radial × tangential) were only prepared for the scanning electron microscope (SEM) experiment.

Cork torrefaction

Cork samples, including cork particles and cork blocks were arranged in crucibles, respectively. With the protection of a nitrogen flow of 0.5 L·min⁻¹, they were heated in a tubular furnace (Furnace 1200C, Tianjin, China) to respective temperatures 150°C, 200°C, 250°C, and 300°C at a rate of 5°C·min⁻¹, and then held for 1 h. The torrefied samples were picked out when cooled down to 80°C. Then, they were weighted and sealed after cooling down to room temperature. All torrefied experiments were conducted in triplicate.

Properties analysis of the torrefied cork

The moisture content (M), volatile matter content (VM), ash content (A), and fixed carbon content (FC) of cork particle samples were performed according to the standard method of ASTM D1762-84. Each experiment was conducted in triplicate, and the average value was calculated. The high heating value (HHV) was characterized via Calorimeter (ZDHW-9000, Hongke, China) according to the standard GB/T 30727-2014. The mass yield and energy yield were calculated on the following formulas:

$$\text{Mass yield (\%)} = m_1 / m_0 \times 100\%$$

$$\text{Energy yield (\%)} = \text{mass yield} \times \text{HHV}_1 / \text{HHV}_0 \times 100\%$$

In the above formulas, m refers to mass of the cork samples, and the subscript 1 refers to samples torrefied at different temperatures, while 0 refers to untreated samples.

The carbon, hydrogen, and nitrogen contents were analyzed via Vario EL elemental analyser (Elementar, Hanau, Germany) and the oxygen content was then calculated by deducting C, H, and N contents.

CIE-LAB colour system analysis

Samples of 1.5 g with different torrefaction temperatures were evenly distributed in Petri dishes. L^* (lightness index), a^* (red-green index), and b^* (yellow-blue index) were all tested via spectrophotometer (CM-5, Konica minolta, Japan). Each measurement was conducted in triplicate and the average value was calculated. The difference in the colour parameters ΔL^* , Δa^* , Δb^* , and ΔE (total colour difference) was determined based on the following formulas:

$$\Delta L^* = L_1^* - L_0^*$$

$$\Delta a^* = a_1^* - a_0^*$$

$$\Delta b^* = b_1^* - b_0^*$$

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

In the above formulas, the subscript 1 refers to samples torrefied at different temperatures, while 0 refers to untreated samples.

FTIR

FTIR spectrometer was obtained on a spectrophotometer (Vetex70, Bruker, Germany) in attenuated total reflectance infrared (ATR-IR) mode, to obtain the spectrum from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans per sample.

SEM

Cell morphology was imaged on a SEM (TM-3030, Hitachi, Japan). Torrefied blocks samples were cut into small blocks with smooth surface and regular thickness. The dried samples were attached to the sample holder via conductive tape, and spray-coated by gold. Images were taken on each section at proper magnifications, based on which, the impact of torrefaction on cork cell structure and arrangement was analyzed.

CP/MAS ^{13}C NMR spectra

100 mg cork samples before and after torrefaction were milled and filled into a 4 mm zirconia (ZrO) rotor, following analysis via AV-III 400 M spectrometer (Bruker, Germany) with the following parameters: 100.6 MHz, transitions delay 2 s, contact time 1 ms, and spinning rate 5 KHz.

RESULTS AND DISCUSSION

Impact of torrefaction on cork properties

Torrefaction is a process of thermochemistry, during which, moisture content and low molecular weight volatiles are removed, and the material energy density is improved (Melkior et al. 2012). The mass yield, energy yield, and HHV are listed in Tab. 1. Tab. 2 lists the proximate analysis both before and after torrefaction, and Tab. 3 shows the elemental analysis.

Tab. 1: Mass yield, energy yield, and high heating value at different torrefaction temperatures.

Torrefaction temperature (°C)	Mass yield (%)	Energy yield (%)	HHV (MJ·kg ⁻¹)
0	100±0.00	100±0.00	27.86±0.25
150	96.33±0.38	99.52±1.20	28.78±0.23
200	95.33±0.09	99.70±1.01	29.14±0.32
250	90.47±0.57	97.96±1.68	30.17±0.33
300	81.97±0.33	94.79±0.04	32.22±0.12

Tab. 2: Proximate analysis of *Q. variabilis* cork at different torrefaction temperatures.

Torrefaction temperature (°C)	Moisture content (wt %)	Volatile matter content (wt %)	Ash content (wt %)	Fixed carbon content (wt %)
0	2.20±0.01	84.02±0.85	0.82±0.06	12.96±0.13
150	1.77±0.01	83.00±1.02	0.94±0.05	14.23±0.15
200	1.53±0.01	81.99±0.68	0.95±0.02	15.53±0.10
250	0.55±0.03	79.85±0.70	0.98±0.04	18.62±0.11
300	0.30±0.01	71.96±1.14	1.22±0.01	26.52±0.15

Tab. 3: Elemental analysis of *Q. variabilis* cork at different torrefaction temperatures.

Torrefaction temperature (°C)	C (wt%)	N (wt%)	H (wt%)	O (wt%)	O/C ^a	H/C ^a
0	63.90±0.18	0.40±0.02	7.41±0.16	28.21±0.35	0.33	1.39
150	64.59±0.09	0.31±0.02	7.32±0.21	27.77±0.32	0.32	1.36
200	64.89±0.06	0.28±0.01	7.26±0.23	27.56±0.30	0.32	1.34
250	67.26±0.11	0.29±0.01	7.12±0.16	25.33±0.28	0.28	1.27
300	70.59±0.09	0.23±0.01	7.04±0.24	22.12±0.34	0.24	1.20

^a Atomic ratio

Tab. 1 shows decreasing mass yield and energy yield of the cork of *Q. variabilis* with increasing torrefaction temperatures. However, the energy yield was consistently better than the mass yield at all different temperatures. When cork sample was treated at 300°C, the mass and energy yield were 81.97% and 94.79%, respectively. Cork lost 18.03% of its initial weight and only 5.21% of its initial energy. In this study, more than 90% energy still retained in the substance at different torrefaction temperatures. The HHV of cork also had a strong correlation with the torrefaction temperatures. Untreated cork had a HHV of 27.86 MJ·kg⁻¹, which increased by 16% to 32.22 MJ·kg⁻¹ after torrefaction at 300°C. Cork after torrefaction had higher HHV when compared with other torrefied biomass (e.g. 23.4 MJ·kg⁻¹ for torrefied bagasse and 25.4 MJ·kg⁻¹ for torrefied pine at 300°C) (Chen et al. 2015).

Tab. 2 indicates that volatile matter and moisture content decreased with increasing temperatures. This mainly resulted from the removal of volatile hydrocarbons from cork during torrefaction. Moisture content is an important property of biomass fuels. The reduction of moisture content increased the energy efficiency of torrefied cork, improved the energy product quality and reduced the emissions in the thermochemical energy conversion process (Chen et al. 2015). The volatile matter content was 84.02% for untreated cork and 71.96% for torrefied cork at 300°C. During the torrefaction process, the volatile matter continuously evaporated while the ash remained in the solid product, so that the ash content increased as the torrefaction temperature increase. Because of the removal of water and oxygen-containing volatiles during torrefaction, the fixed carbon content increased with increasing temperatures, giving rise to higher HHV of torrefied cork. At the same time, the removal of volatile matter decreased the energy yield of torrefied cork.

Tab. 3 shows the results of elemental analysis. Compared to untreated cork, when temperature increased to 300°C, carbon content increased from 63.90% to 70.59%, while oxygen content decreased from 28.21% to 22.12%. The ratio of oxygen to carbon decreased from 0.33 to 0.24, and the ratio of hydrogen to carbon decreased from 1.39 to 1.20. The decrease in oxygen to carbon ratio was caused by the loss of oxygen content, which was removed through the formation of H₂O, CO, and CO₂.

Cork is a low density material and its chemical composition includes volatile matter, which leads to some technical and safety difficulties in terms of energy use (Nunes et al. 2013). In this study, the experiment showed that torrefaction could improve the cork energy properties. The cork torrefied at 300°C for 1h had higher fixed carbon content and HHV, lower O/C and H/C atomic ratios and moisture content, which was the optimal condition within the investigated ranges. An optimal balance of mass and energy for cork torrefaction still need to be deeply studied.

Impact of torrefaction on colour differences

Fig. 1 shows the images of cork samples before and after torrefaction. The colour of untreated cork was tawny. As the torrefaction temperature increased, the colour of cork gradually became darker. At 300°C, the colour of torrefied cork changed into brownish-black.

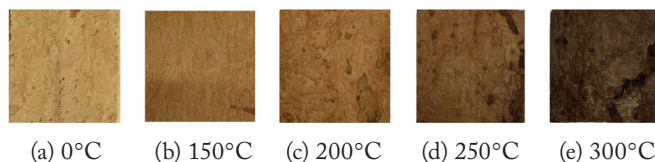


Fig. 1: Images of cork at different torrefaction temperatures.

The CIE-Lab parameter test results are shown in Tab. 4. Compared to untreated cork, with increasing torrefaction temperature, the lightness value L*, red-green value a*, and yellow-blue value b* decreased significantly, while comprehensive colour difference ΔE gradually increased. In the experiment, the L*, a*, and b* values of untreated cork were 52.13, 14.19, and 27.32 respectively, and the corresponding values after torrefaction at 300°C were 24.47, 5.21, and 8.33, respectively, which decreased by 53.06%, 63.28%, and 69.51%, respectively. This demonstrates a reduction of red and yellow light reflection from the cork surface with increasing temperature.

The reason for the discoloration of cork could be that the moisture in the sample was shifted outwards, and the water-soluble flavonoids and phenols contained in the material also

moved to the surface during the torrefaction. In addition, colored substances formed by phenol compounds in cork and dark substances formed by hydrolysis of hemicellulose were oxidized at high temperatures, which also resulted in the colour change of cork (Wei 2012).

Tab. 4: Colour differences at different torrefaction temperatures.

Torrefaction temperature (°C)	L*	a*	b*	ΔE
0	52.13±0.04	14.19±0.02	27.32±0.02	---
150	50.59±0.14	14.57±0.08	25.91±0.14	2.12±0.18
200	43.81±0.18	12.68±0.02	20.31±0.07	10.98±0.18
250	32.07±0.30	8.33±0.17	12.82±0.22	25.44±0.40
300	24.47±0.12	5.21±0.06	8.33±0.10	34.74±0.14

According to the relationship between ΔE and the ability of human visual perception to colour difference: human cannot differentiate colour differences if ΔE is 0-0.5 NBS; human eyes will be able to perceive colour differences if ΔE is 1.5-3.0 NBS; and humans can distinctly perceive colour differences if ΔE is 6.0-12.0 NBS. When the value of ΔE was more than 12.0, the colour totally changed to the other color (Wei 2012). After torrefaction at 150°C for 1 h, the colour difference could be visually perceived. After torrefaction at 250°C and 300°C for 1 h, ΔE was 25.44 and 34.74, respectively, and the cork surface turned to brownish-black due to significant drops in L^* , a^* , and b^* values.

FTIR spectra of cork

Q. variabilis is primarily composed of suberin, lignin, polysaccharide, and extractives. Furthermore, its cell wall mostly consists of suberin, a complex biopolymer cross-linked by aromatic and aliphatic molecules (Ranathunge et al. 2011, Vishwanath et al. 2015). The FTIR results of untreated and torrefied corks at different temperatures are shown in Fig. 2.

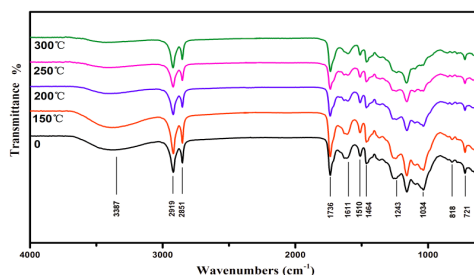


Fig. 2: FTIR spectrum at different torrefaction temperatures.

The band at 3387 cm^{-1} was attributed to OH stretching of absorbed water and polysaccharides in cork. The bands at 2919 cm^{-1} and 2851 cm^{-1} were attributed to asymmetric and symmetric C-H stretching vibrations on aliphatic chains in suberin. The band at 1736 cm^{-1} from carbonyl C=O stretching was attributed to esters in suberin, and the band at 721 cm^{-1} originated from the $R_1\text{CH}=\text{CHR}_2$ structure in suberin. Bands at 1464 cm^{-1} and 1243 cm^{-1} also related to groups in suberin, however, these signals usually overlapped with cellulose and lignin signals. Bands at 1611 cm^{-1} and 1510 cm^{-1} had been associated with aromatic C=C group in lignin, and the band at 818 cm^{-1} also related to typical lignin structures. The band at 1034 cm^{-1} should be the C-O

stretching vibration of polysaccharides in cork (Şen et al. 2012b, Ferreira et al. 2013).

Untreated cork contains many oxygenated organic functional groups and high oxygen content is the main reason for the low HHV of the cork raw materials. As shown in Fig. 2, the absorption peak of the organic functional groups of the cork had changed greatly after the torrefaction treatments. The intensity of bands at 3387 cm^{-1} and 1034 cm^{-1} strongly weakened for samples treated at 200°C , and almost disappeared at 300°C . This implies that polysaccharides started decomposing at these temperatures. The cork component especially hemicelluloses, occurred dehydration, dehydroxylation and carbonylation reactions under torrefaction treatment, which led to simplified structures of organic functional groups and the decrease of oxygen content. The bands at 1510 cm^{-1} and 818 cm^{-1} also became weaker mainly due to lignin degradation between 250°C and 300°C . During this experiment, the typical suberin structure bands had no obvious change, suggesting high thermal resistance of suberin.

Impact of torrefaction on cell structures

Many studies reported cell structures via SEM. Each individual cork cell has a prismatic shape and cells are arranged in honeycomb-type structure on the tangential section. On non-tangential sections, cells are arranged in brick wall-type structure without intercellular voids (Miranda et al. 2013, Song et al. 2016). SEM images of the transverses section of cork cells that were torrefied at different temperatures are shown in Fig. 3. It worth noting that cork cells started swelling when treatment temperatures increased from 150°C to 300°C , with larger cells lumen, smoother cell wall, less corrugation and distortion, and less sediments on cell wall.

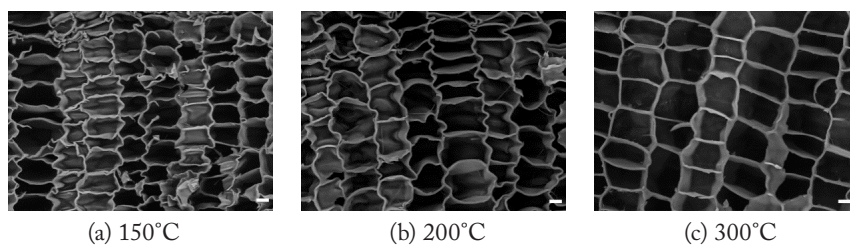


Fig. 3: SEM images after torrefaction at 150°C (a), 200°C (b), and 300°C (c) on cross section, scale bar: $10\ \mu\text{m}$.

Thermogravimetric analysis from Shangguan et al. (2017) illustrated that the major components in cork of *Q. variabilis*, namely suberin, lignin, and polysaccharides, had peak temperatures of thermal decomposition at 414.41°C , 366.25°C , and 323.03°C , respectively. Therefore, although the cork had partially degraded in this study, the major compositional components and cell wall structures maintained. The phenomena that cork cell would swell at increasing temperatures was also observed and confirmed in the experiment of water boiling and steam treatment of cork (Rosa and Fortes 1989, Rosa et al. 1990). However, more precise measurements on SEM images are required to quantify the decrease in cell wall thickness.

CP/MAS ^{13}C NMR spectra of cork

CP-MAS ^{13}C NMR spectra are a powerful technique for characterizing biopolymer chemical structure and physical properties. Generally, 22-40 ppm in the NMR spectra of cork attributes to the methylene (CH_2) groups in aliphatic structure of suberin, and wax in cork extractives also has signals in this region. 65-105 ppm belongs to the carbons of cellulose and hemicellulose.

112–156 ppm attributes to the aromatic carbon groups from lignin and a small amount aromatic component of suberin. In some regions of the spectrum there is significant overlap of signals from the different cork component (Gil et al. 1997, Lopes et al. 2000, Neto et al. 1995).

Fig. 4 shows the CP-MAS ^{13}C NMR spectra of untreated, 200°C, and 300°C torrefied cork. The weak peak at 17.9 ppm was attributed to the CH_3COOR groups of hemicellulose. The strong peak around 30 ppm originated from the C-H bond in methylene groups of suberin. The peak around 54 ppm was assigned to the methoxy groups of lignin or suberin, but it could also contain a small amount of methoxy groups in the hemicellulose. The peak at about 72 ppm originated from cellulose and hemicellulose. The peak at about 171 ppm was assigned to carbonyl groups from the ester groups in suberin and hemicellulose (Fig. 4a).

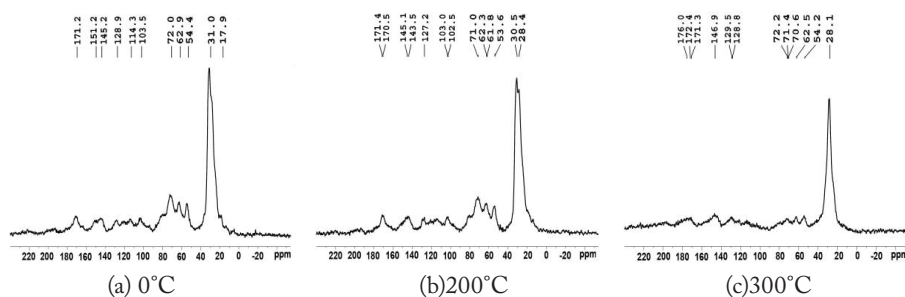


Fig. 4. CP-MAS ^{13}C NMR spectra at different torrefaction temperatures.

For CP-MAS ^{13}C NMR spectra of torrefied and untreated cork, the reduction of peak about 72 ppm and the disappearances of 17.9 ppm indicated decomposition of polysaccharides at 200°C (Fig. 4b). At 300°C, a great reduction in peak intensity from 65 to 105 ppm regions showed an obvious degradation of polysaccharides (Fig. 4c). These results corroborated the data of cork FTIR. The decrease in the peak intensity at about 54 ppm originated from a degradation of lignin. The decrease in peak intensity at about 171 ppm may be due to the degradation of carbohydrates or the breakage of ester bonds in suberin.

Previous studies showed two strong peaks at 30 ppm and 33 ppm in the cork from *Quercus suber*, which differed from the results in this study where only one peak was found in this region (Lopes et al. 2001). Further investigation is required in future.

CONCLUSIONS

This paper presents an experimental investigation for the torrefaction of *Quercus variabilis* cork. The specific conclusions can be drawn as follows:

1. In this study, torrefaction was proved to have numerous merits in improving the energy properties of cork. With increasing torrefied temperature, the carbon content of torrefied cork increased, oxygen and hydrogen content decreased, and the HHV increased. Compared to untreated cork, the HHV of cork increased by 16% after torrefaction at 300°C for 1 h. Torrefied cork possessed a great potential for industrial applications.
2. Compared to untreated cork, the lightness L^* , red-green index a^* , and yellow-blue index b^* of torrefied cork decreased significantly, and total colour difference ΔE gradually increased with increasing torrefied temperatures. After torrefaction, cork cells swelled with enlarged cell lumen, smoother cell walls with less corrugation, and less sediments on the cell wall.

3. Torrefaction of cork at 200°C resulted in degradation of carbohydrates, and lignin started degrading at 250-300°C; suberin had high thermal resistance, but also commenced degrading at 300°C.

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