Variation of Chemical Constituents of Qinghai Spruce in Natural Decay Process, Including Furfural Production

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Chemical constituents of naturally decayed Qinghai spruce branches were analyzed in terms of holocellulose, lignin, and pentosan. The holocellulose content declined from 57.98% to 35.29% in one year. The rate of change may be related to weather conditions, *i.e.*, the rate of variation was higher when the temperature was high and rainfall was abundant. The changes in lignin and pentosan relative content were completely different from holocellulose; they increased first and then decreased during the decay period. Compared with fresh raw materials, pentosan content (from 14.44% to 25.9%) was increased by 79.4% after four months decay. The highest yield of furfural (10.2%) prepared by a two-stage method from decayed Qinghai spruce branches was similar to the reported yield from corncobs.

Keywords: Qinghai spruce; Decay; Pentosan; Furfural

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INTRODUCTION

Qinghai spruce (*Picea crassifolia* Kom.) is one of the endemic and widespread tree species on the northeast Qinghai-Tibetan Plateau, the highest plateau in the world. Qinghai spruce is an important tree species because of its unique characteristics, such as high longevity, sensitivity to climate change, and ability to grow at low latitudes and high elevation (Liang *et al.* 2006). Qinghai spruce is tolerant to cold as well as dry and poor soil environments, permitting it to grow across a large elevation range from 2350 to 3300 m (Gou *et al.* 2005). Qinghai spruce often coexists with Qilian juniper in vast areas. Various relevant studies of Qinghai spruce have focused on its ecology (Du *et al.* 2009; Xu *et al.* 2013; Zhang *et al.* 2011; Zhang *et al.* 2009; Meng *et al.* 2007; Chang *et al.* 2014; Tian *et al.* 2011; Liu *et al.* 2013), but there is little known about its chemical constitution.

The accumulation area of Qinghai spruce is 113,000 ha, and the stand volume is 14.4 million m^3 (Yao *et al.* 2016). An estimate for the Qinghai spruce branches would be more than one million tons. This forestry residue is either burned for energy production or discarded without any valuable application. Thus, improving the value of this residue is important for the economy and ecology of the local Qinghai-Tibetan area.

Wood decay is extremely important and indispensable in the forest ecosystem. Rot fungi degrade the chemical components in wood into nutrients that are used by organisms and plants. With regard to production and utilization of wood, decay is generally harmful and adverse, resulting in the decline of material properties. Decay is an inevitable process and it is not always disadvantageous to production; such as biopulping can be regarded as a decay under control for some microbial species only lead to lignin degradation in such a “decay” process (Badr El-Din *et al.* 2013). Natural decay always happens.

This study investigated changes in the lignin, holocellulose, and pentosan contents of Qinghai spruce branches after a natural decay process. The results show that the trend of these components is different during natural decay. The relative pentosan content increased from 14.44% to 25.9%. Furfural was prepared from the decayed residue. The objective of this work is to evaluate the potential use as a bio-resource for decayed Qinghai spruce branches.

EXPERIMENTAL

Preparation of Raw Materials

Qinghai spruce samples (fresh branches of 1 to 5 cm diameter with needles cut from trees) were provided by the Huzhu Beishan National Forest Park (36°6′ E; 101°8′ N) in Qinghai province in June 2015. Figure 1 shows a typical scene of Qinghai spruce in the field. Fresh samples were buried in the ground about 2 cm for natural decay. Every 2 months, samples were removed for analysis, which lasted for 12 months with a total of 6 batches (Jun 2015, Aug 2015, Oct 2015, Dec 2015, Apr 2016, and Jun 2016). Figure 2 shows the samples in the field. The samples were washed, dried (at 103 ± 2 ℃ 24 h), ground, and sieved to obtain a granulometry of 0.251 to 0.422 mm (40- to 60-mesh) and to remove impurities such as sand and dust. All raw material samples were stored in sealed plastic bags.

Fig. 1. Qinghai spruce forest of Huzhu Beishan National Forest Park

Characterization of the Raw Materials

The chemical composition of samples was determined in accordance with the GB/T 2677.10 (1995), GB/T 2677.9 (1994), and GB/T 2677.8 (1994) standards. The wood powder were extracted by benzene-ethanol (2:1) in a Soxhlet extractor for 9 h and air dried for 12 h. The content of holocellulose was by the sodium chlorite method and lignin was by the sulfuric acid method. The determination of pentosan was based on the hydrolysis of sample with 12% hydrochloric acid and the conversion of pentose from the sample into furfural. All experiments were taken at least three times in parallel, and the average values of the three replications were taken as the final result. Chemicals were used without further treatment. Hydrochloric acid, sulfuric acid, dihydroxytoluene, acetic acid, sodium chlorite, ferric chloride, sodium bromide, sodium bromide, sodium thiosulfate, acetic acid, aniline, phenolphthalein, potassium iodide, starch, alcohol, sodium chloride, barium chloride, and benzene were analytical reagents and purchased in Tianjin Damao chemical reagent factory. Deionized water was used for all experiments.

Furfural Preparation

Furfural was prepared by a two-stage process. In the first stage (pre-hydrolysis), 10 g of sample was mixed with 100 mL of 3% (w/w) sulphuric acid for a reflux time of 30 min. In the second step, the hydrolysate was adjusted to 250 mL with 15% sulphuric acid and heated to 125 ± 5 °C. Furfural was recovered with steam distillation during the boiling. Furfural was determined using a colorimetric method (Mansilla *et al.* 1998).

Fig. 2. Natural decay of Qinghai spruce branches. (a: fresh branches; b: 2-month decayed samples; c: 6-month decayed samples; d: 10-month decayed samples)

RESULTS AND DISCUSSION

There is no denying that the vast majority of decay processes occur in nature. Therefore, the changes in chemical composition during natural decay has practical significance, but there are few reports about it. Wood decay in nature is mainly caused by fungus (Curling *et al.* 2002). Considering the complexity of nature, the fungal environment was not examined in this work, although the activity of fungi is related to the weather. The weather conditions in the Xining area are shown in Table 1 (Qinghai Provincial Meteorological Bureau 2016). The compositional analysis for different natural decay stages of Qinghai spruce branches was conducted in one year (06/2015 – 06/2016).

Table 1. The Weather Conditions in Xining, Qinghai Province, China

Month	Jul 2015	Aug 2015	Sep 2015	Oct 2015	Nov 2015	Dec 2015	Jan 2016	Feb 2016	Mar 2016	Apr 2016	May 2016	Jun 2016
Mean maximum temperature (°C)	25	24	19	14	8	3	1	4	10	16	20	23
Mean minimum temperature (°C)	11	11	7	1	-6	-12	-14	-11	-4	2	6	9
Average precipitation (mm)	82	81	57	23	3	1	1	2	7	21	47	57

Holocellulose

The relative content of holocellulose decreased with the extension of decay time (Fig. 3). Within one year, the holocellulose content decreased from 55.0% to 35.3%. The rate of decline was different at different time periods. From June to August, the loss of holocellulose was the fastest (from 55.0% to 49.1%).

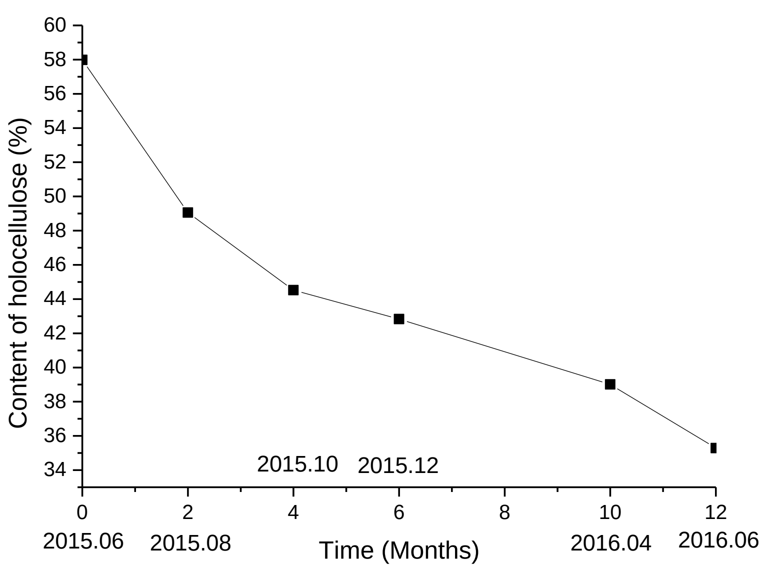

Fig. 3. Holocellulose content as a function of time in natural decay

During the period between August and October, the relative content of holocellulose decreased by 4.5%, which was noticeable slower than 8.9% (from June to August 2015). This rate seems to be related to the weather. June to August is the period of highest temperature and most abundant rainfall (Table 1). Accordingly, during the 4 months (from December 2015 to April 2016) of the coldest and driest period of the year, holocellulose decreased by only about 3.8%. The cellulose content in Qinghai spruce will continue to decline in the process of natural decay, which is disadvantageous for pulp and papermaking and alcohol production by hydrolysis, if decayed wood were to be used as raw material.

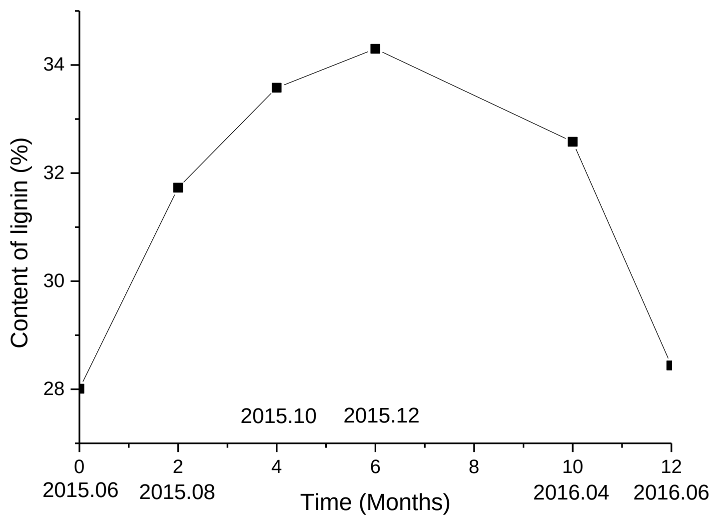

Fig. 4. Lignin content as a function of time in natural decay

Lignin

Lignin is a three-dimensional network of macromolecular structure, and it is one of the main components of wood. Lignin is not a polysaccharide, and it is composed of syringyl, guaiacyl, and p-hydroxyphenyl basic structural units. During natural decay, the relative change in lignin content is different from that of cellulose. The relative lignin content first increased and then decreased, with a peak value of 34.3% (Fig. 4). Fresh branches of Qinghai spruce contained 28.0% lignin. The increase in the relative content does not mean that the absolute amount was also increased. The reason for the increase in lignin content may be that microorganisms preferentially utilize other components such as hemicellulose and cellulose. Lignin is also used by microbes, but the rate is not high at the initial stage. The decrease in lignin content later may be the result of the expansion of lignin-consuming fungi. Overall, the relative lignin content increased by 6.3% over the first six months of decay.

Pentosan

The pentosan content in fresh branches was 14.4%. During decay, the relative content of pentosan and lignin was similar, gradually increasing in the early stage (Fig. 5). After 4 months (from June to October), the relative content of pentosan was approximately 25.9%. Relative to the initial content of fresh branches, pentosan content increased in amplitude (11.46:14.44), much greater than that of lignin (6.29:28.01). During natural decay, the relative content of pentosan first increased and then decreased, probably for reasons similar to those cause changes in lignin content.

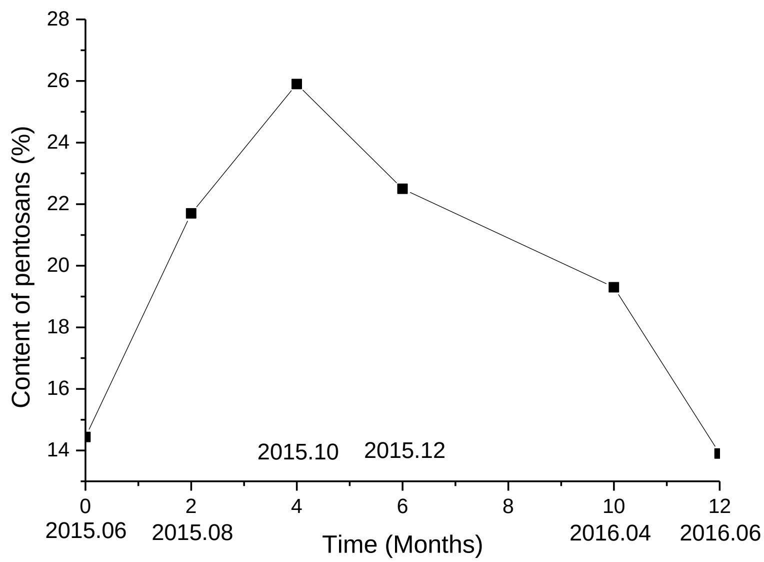

Fig. 5. Pentosan content as a function of time in natural decay

Furfural Production

In industry, the hydrolysis of the pentosan-rich plants is the only practical way to obtain furfural. Pentosan is one of the main components of almost all plants. The content of pentosan in raw material is above 18% to 20%, which has industrial value in furfural production (Mansilla *et al.* 1998; Nhien *et al.* 2017). At present, the main raw materials of furfural production are corncobs (pentosan content 30 to 40%), bagasse (pentosan content 25 to 27%), cotton husks (27%), and hardwoods (21 to 24%) (Jaeggle 1976). Furfural was prepared from decayed Qinghai spruce branches (Table 2).

Table 2. Yields of Furfural from Decayed Qinghai Spruce Branches

Decay Period (Date Harvested)	Pentosan Content (%)	Furfural Yield (%)
Fresh (06/2015)	14.4	2.9
2 months (08/2015)	21.7	8.2
4 months (10/2015)	25.9	10.2
6 months (12/2015)	22.5	8.9
10 months (04/2016)	19.3	6.2
12 months (06/2016)	13.9	2.4

As shown in Table 2, furfural yield change was consistent with the pentosan content of raw materials. The highest yield of furfural was 10.2%, which was similar to that of furfural production from corncobs (Jaeggle 1976). This result indicates that decayed Qinghai spruce branches can be used for furfural production.

CONCLUSIONS

1. During natural decay, the relative content of holocellulose in the branches of Qinghai spruce declined continuously. The relative content of lignin and pentosan reached the highest values with extended decay, indicating that during natural decay, the content variations of cellulose, lignin, and pentosan in Qinghai spruce branches are different.

2. The natural decay process increased the relative pentosan content of Qinghai spruce branches from 14.4% to 25.9% compared with fresh raw materials, which increased by 79.4%.
3. Based on these results, furfural was prepared from decayed Qinghai spruce branches. The highest yield was 10.2%, which was similar to that of corncobs. This result indicates that a certain degree decayed plant, not necessarily residue, is likely to have potential uses.

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