

## Original Paper

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## Pyrolysis of Barks from Three Japanese Softwoods

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Along with Japanese cedar bark, fir bark and Japanese larch bark were pyrolyzed to estimate the possibility of utilizing these softwood barks as resources for fine chemicals by comparing the pyrolysis product compositions. The three softwood barks contained higher ash content and yielded lower amount of volatiles when compared with cedar heartwood. The major pyrolysis products from their barks were similar to those previously reported from softwood trunks. Levoglucosan was a major pyrolysis product formed from the three softwood barks, despite being a minor product from wood trunk pyrolysis. Therefore, softwood barks can be expected as a feedstock for production of levoglucosan. An increase in the moisture content in the cedar bark generated more pyrolysis products. This result indicates that softwood barks do not require drying prior to pyrolysis, which simplifies the pyrolysis system.

化成品供給原料としての針葉樹皮の可能性を評価するために、日本の代表的な人工林樹種であるスギ、トドマツ、カラマツの樹皮を熱分解し、その生成物の解析を行った。工業分析の結果は、杉心材部と比較して、それら3樹種からの樹皮は灰分を多く含み、揮発成分も少ないことが示された。樹皮熱分解生成物の構成は針葉樹材部からの熱分解生成物と比較して大きな差異は認めず、熱分解による化成品供給源として有用であることが明らかになった。levoglucosanについては、材部からの熱分解生成物では微量構成成分であったが、3樹皮からの熱分解では主要な生成物であった。このことは生化学的に有用な levoglucosan の供給源としても針葉樹皮が有用な資源となることを示唆している。熱分解における原料の含水率の影響は少なく、熱分解処理前の樹皮の乾燥工程は重要ではないことが示された。

## Key Words

Softwood, Japanese cedar, Fir, Japanese larch, Bark pyrolysis, Levoglucosan

## 1. Introduction

Pyrolysis, as a promising thermo-chemical conversion route, plays a vital role in the conversion of biomass to new green energy, which results in solid, gas, and liquid fuel. A liquid pyrolysate termed bio-oil is a complex mixture of numerous organic molecules with diverse molar masses and structures, and is derived from the condensation of vapors released during biomass pyrolysis. It is the cheapest biofuel currently produced from lignocellulosic materials<sup>1)</sup>. The chemical compounds found in bio-oil are derived from the breakdown of cellulose, lignin, hemicellulose, and biomass extractives, which make it entirely different from petroleum-derived fuel.

Bio-oil consists of various organic compounds such as low-molecular acids and aldehydes, phenols, furans, and sugar derivatives. Many of its poor fuel characteristics, such as acidity, low thermal stability, low calorific value, and high viscosity, are generally associated with the low-molecular-weight organic compounds, water, and the oligomers. The furans and phenols, as well as sugars, diphenols, and extractive derivatives, are the fractions with more promising fuel properties<sup>2)</sup>.

Most of the wood barks are left behind as residues and not utilized. Therefore, finding good end applications for them is a worldwide industry concern. A few studies have reported on bio-oil production from bark. For example, Boucher *et al.*<sup>3)</sup> investigated that the properties of bio-oil from softwood bark are advantageous for a gas turbine.

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This study evaluated the possibility of softwood barks as resources for the production of bio-oil, which can be used as a potential fuel and a value-added chemical. For this purpose, three softwood barks were selected, and the compositions of their pyrolysates were analyzed and compared. Furthermore, the major components, *i.e.*, cellulose, hemicellulose, and lignin, were prepared from Japanese cedar bark and pyrolyzed individually. The cedar barks with moisture content 0%-50% were subjected to pyrolysis to estimate the effects of moisture content on the composition and yield of the pyrolysates.

## 2. Materials and Methods

### 2.1 Materials

Japanese cedar (*Cryptomeria japonica*) bark was provided by Azuma-Sansho Co, Ltd, Akita, Japan. Fir (*Abies sachalinensis*) bark and Japanese larch (*Larix leptolepis*) bark were provided by the Forest Product Research Institute of the Hokkaido Research Organization in Asahikawa, Hokkaido, Japan. These barks were individually milled and sieved to 0.36 - 0.42 mm. The samples were subsequently oven-dried at 105 °C overnight. Chemical and proximate analyses of these barks were performed according to the Japanese Industrial Standards methods.

### 2.2 Identification with Py-GC-TOFMS

The Py-GC-TOFMS system used was a combination of a JCI-22 model Curie-point pyrolyzer (JAI) and a JMS T-100GCV GC-TOFMS instrument (JEOL). The oven-dried samples of ca. 0.5 mg were pyrolyzed at 590 °C. GC-TOFMS analyses employed an Rtx-Wax capillary column (60 m × 0.25 mm *i.d.*; 0.25 µm film thickness). The National Institute of Standards and Technology mass spectral library was employed for the identification of each peak.

### 2.3 Py-GC-FID analysis

Pyrolysis of oven-dried samples was performed with a Py-GC-FID: EGA/PY-3030D pyrolyzer (FRONTIER LAB) and Shimadzu GC-2010 Plus. Samples of ca. 0.5 mg were pyrolyzed at 500 °C, 550 °C, and 600 °C. The GC condition was similar to the Py-GC-TOFMS condition. Peaks of Py-GC-FID chromatogram were identified and compared with the results of Py-GC-TOFMS. To estimate the effects of bark moisture content on the bio-oil composition and yield, the cedar bark sample was adjusted to 50% moisture content by adding the same amount of water to the oven-dried sample. The adjusted sample was pyrolyzed at 550 °C.

## 3. Results and Discussion

### 3.1 Characteristics of the three softwood barks

The chemical analysis results of the three softwood barks are presented in Table 1. The fir bark contained less Klason lignin and more  $\alpha$ -cellulose than other barks. Lignin pyrolysis produced more char than cellulose pyrolysis; however, the latter produced more bio-oil than the former<sup>4)</sup>. Therefore, the different contents of Klason lignin and  $\alpha$ -cellulose among the three softwood barks are expected to influence the production of fixed carbon and volatile from their barks.

The proximate analysis results are shown in Table 2. Compared with Japanese cedar heartwood, the barks contained more ash and less volatiles; this result fits to a well-known fact that the barks had higher ash content. Among the three softwood barks, in fir, the contents of ash and volatiles were the highest and that of fixed carbon was the least. Volatile and fixed carbon would reflect bio-oil and char, respectively. Thus, the fir bark is expected to be the most suitable feedstock for bio-oil production.

### 3.2 Major pyrolysis products from lignin, holocellulose, and $\alpha$ -cellulose prepared from the cedar bark

Klason lignin, holocellulose, and  $\alpha$ -cellulose prepared from Japanese cedar bark were pyrolyzed at 550 °C for identification of major pyrolysis products from each component of the cedar bark. GC-FID chromatograms of pyrolysates of lignin, holocellulose, and  $\alpha$ -cellulose from the cedar bark are shown in Figs. 1 - 3, respectively. The major pyrolysis products are listed in Table 3. The pyrolysis products from lignin were guaiacol, 4MG, 4VG, IE, and vanillin (Fig. 1). Softwoods contained guaiacyl lignin predominantly, which resulted from the polymerization of a higher fraction of coniferyl propane units. Therefore, these compounds involved the guaiacyl group. Typical pyrolysis products produced from holocellulose and  $\alpha$ -cellulose were acetol, GA, FF, HMF, and

Table 1 Chemical analysis of softwood barks (%)

	EtOH-benzene extract	Klason Lignin	Holocellulose	$\alpha$ -Cellulose
Cedar	2.6	53.4	34.9	21.8
Fir	11.1	31.1	55.9	34.3
Larch	7.6	43.9	43.9	22.4

Table 2 Proximate analysis of softwood barks (%)

	Ash	Volatile	Fixed Carbon
Cedar heartwood	0.7	81.3	18.0
Cedar	3.0	73.2	23.8
Fir	9.5	78.0	12.5
Larch	4.3	67.6	28.1

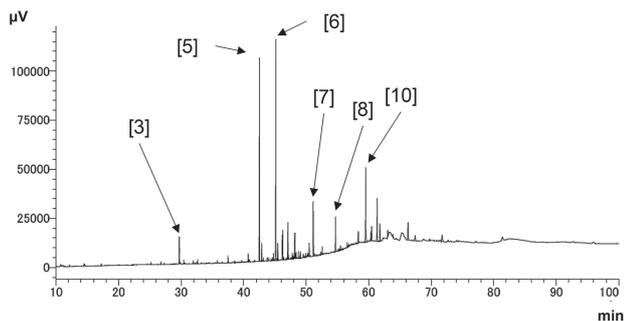


Fig. 1 Py-GC-FID chromatogram of lignin from Japanese cedar bark

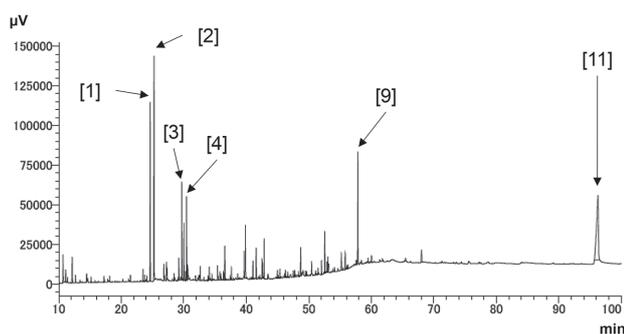


Fig. 2 Py-GC-FID chromatogram of holocellulose from Japanese cedar bark

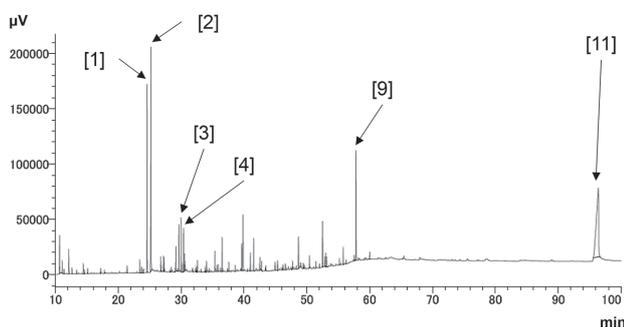


Fig. 3 Py-GC-FID-chromatogram of  $\alpha$ -cellulose from Japanese cedar bark

Table 3 List of pyrolysis products on GC-FID

Peak number on GC	Compound name
[1]	Acetol
[2]	Glycolaldehyde (GA)
[3]	Acetic Acid (AA)
[4]	Furfural (FF)
[5]	Guaiacol
[6]	4-Methylguaiacol (4MG)
[7]	4-Vinylguaiacol (4VG)
[8]	E-Isoeugenol (IE)
[9]	Hydroxymethylfurfural (HMF)
[10]	Vanillin
[11]	Levogluconan (LG)

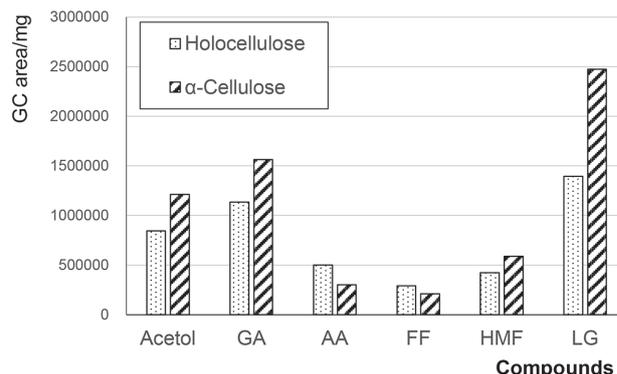


Fig. 4 Comparison in yield of major pyrolysis products from holocellulose and  $\alpha$ -cellulose

levoglucosan (LG) (Figs. 2 and 3). The contents of AA and FF were higher in the volatile fraction from holocellulose than  $\alpha$ -cellulose, while the contents of acetol, GA, HMF, and LG were higher in the latter than in the former (Fig. 4). The holocellulose of the cedar bark comprised 26.8% hemicellulose and 73.2%  $\alpha$ -cellulose. These results indicated that the AA and FF obtained from pyrolyzed holocellulose could be produced from hemicellulose, and the other compounds could be produced from cellulose predominantly. Acetic acid, commonly found in pyrolyzed products from holocellulose and hemicellulose, was detected in pyrolysis products of lignin, as shown in Fig. 1. Dong *et al.*<sup>5)</sup> reported that a part of acetic acid is produced from the lignin fraction.

### 3.3 Comparison of bio-oil composition in the three different barks

The major pyrolysis products identified among the three softwood barks in this study were acetol, GA, AA, FF, guaiacol, 4MG, 4VG, IE, HMF, vanillin, and LG, as shown in Figs. 5 - 7. Their bark pyrolysis products were similar to the products previously reported from softwood trunk<sup>6)</sup>. The concentration of acetol, GA, and AA in the products from the cedar bark was the lowest compared with the other barks (Table 4). In general, carbohydrates decomposed to lower molecular products such as acetol, GA, and AA

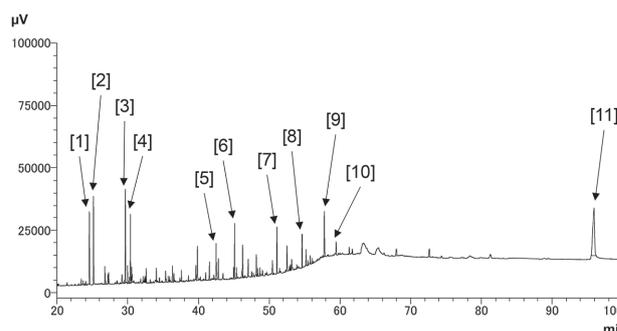


Fig. 5 Py-GC-FID chromatogram of Japanese cedar bark

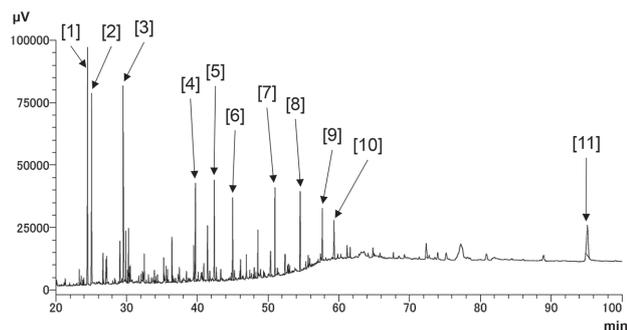


Fig. 6 Py-GC-FID chromatogram of fir bark

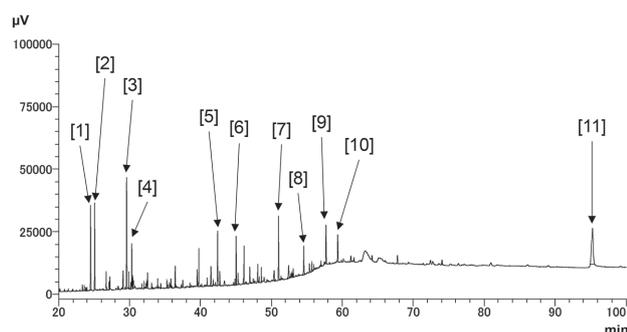


Fig. 7 GC-FID chromatogram of Japanese larch bark

Table 4 Area percent of pyrolysis products from softwood barks at 550 °C

	Cedar	Fir	Larch
[1] Acetol	3.92	8.21	5.23
[2] GA	4.59	7.69	5.60
[3] AA	6.07	8.68	7.67
[4] FF	4.42	2.03	2.93
[5] Guaiacol	2.69	3.52	3.99
[6] 4MG	3.32	2.79	3.59
[7] 4VG	3.10	3.21	4.51
[8] IE	2.14	2.81	2.33
[9] HMF	3.01	2.22	2.81
[10] Vanillin	1.04	2.12	2.29
[11] LG	15.04	6.73	11.45

Table 5 Yields of char from softwood barks at 550 °C

	Char (%)
Cedar	43.8
Fir	34.6
Larch	43.6

by pyrolysis. Barks of the fir and the larch contained much more holocellulose than the cedar bark (Table 1); therefore, these barks yielded low-molecular-weight products than the cedar bark (Table 4). LG was a major pyrolysis product from softwood barks, despite previous reports of being a minor product from wood trunk pyrolysis<sup>6)</sup>. As shown by the chemical analysis results, the fir bark had higher lignin content (Table 1). Lignin pyrolysis produced more char than cellulose pyrolysis. However, the average yield of char at 550 °C was lowest in the fir bark, as shown in

Table 6 Comparison of peak area and char from Japanese cedar bark with different moisture content

Moisture content(%)	Bio-oil (Peak Area)	Char (%)
0	2174374	45
50	2752405	28

Table 5, which was similar to the yield of fixed carbon in the proximate analysis (Table 2). The fir bark contained higher ash content than the other barks (Table 2). It was previously reported that mineral matter in ash influenced the production of char, gas, and liquid by biomass pyrolysis<sup>7)</sup>. Therefore, the ash in the fir bark is likely to influence its pyrolytic behavior.

### 3.4 Influence of moisture content

Because raw bark contains up to 50% moisture content, the effect of bark moisture on bio-oil composition needs to be estimated in order to determine whether feedstock should be dried prior to pyrolysis. The yields of bio-oil and char from Japanese cedar bark with varying moisture content are presented in Table 6. The total area of pyrolysis products was used to estimate the yield of bio-oil. The area increased with increasing moisture content. However, there was no significant increase in a specific product. In other words, each product contributed to increasing the yield of bio-oil. This high bio-oil yield would be an effect of hydrolysis, which could promote the depolymerization of cellulose and hemicellulose. As a result, the yield of char from high-moisture-content bark was low. These results indicate that the moisture content in softwood barks can contribute to an acceleration of their thermal degradation. Therefore, softwood barks do not require drying prior to pyrolysis, thus simplifying the pyrolysis system.

### 3.5 Possibility of softwood barks as resources for bio-oil production

Pyrolysates of the three softwood barks contained major compounds such as furans (FF, HMF), LG, and guaiacols (guaiacol, 4MG, 4VG, IE, vanillin). These compounds are value-added chemicals; for example, FF is widely used as an organic solvent or an organic reagent for the production of medicines, resins, and other special chemicals, LG can be used as a chiral synthon for the synthesis of stereoregular polysaccharides possessing biological activities, and guaiacols can be used as phenol replacements in the production of phenol-formaldehyde resins<sup>8)</sup>. In particular, LG was a major pyrolysis product from softwood barks, despite being a minor product from wood trunk pyrolysis. Therefore, softwood barks can be

potential resources for the production of bio-oil containing value-added chemicals.

#### 4. Conclusions

Three softwood barks that were investigated in this study contained higher ash content and yielded a lower volatile fraction than Japanese cedar heartwood. The major pyrolysis products from these barks were similar to the products previously reported for softwood pyrolysis. Pyrolysis product distributions from softwood barks were similar to those from softwood trunks, and indicated that these barks could be utilized as a biofuel resource as well as wood. Furthermore, pyrolysis products contained high value-added compounds such as FF, VG, and LG. In particular, LG was a major product from the barks, despite being a minor product from wood trunk. These compounds can be utilized as fine chemicals, raw materials of polymer, and bioactive compounds.

An increase in moisture content in the cedar bark generated more pyrolysis products. This result indicates that softwood barks do not require drying prior to pyrolysis, thus simplifying the pyrolysis system.

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