Thermochemical Treatment of Radiata Pine (*Pinus radiata*) Bark with Hydrogen Peroxide Solutions at Temperatures Higher than 100 °C

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Radiata pine bark was treated with 0—15% hydrogen peroxide (H_2O_2) solutions at temperatures higher than 100 °C, and fractionated into water soluble, insoluble, and gas fractions. The distribution of these fractions was calculated on the basis of weight and carbon content, and compared with the aim of finding the optimum conditions for efficiently obtaining water-soluble materials for producing wood adhesives. The yield of water-soluble materials was significantly dependent on the temperature and the concentration of H_2O_2 solution. The highest yields of water-soluble materials (47.4 and 47.9% on the basis of weight and carbon content, respectively) were obtained with 15% H_2O_2 solution at 120 °C. The yield increased with increasing temperature up to 120 °C and then decreased at higher temperatures. Under the latter conditions, gases such as CO_2 and CO were generated. When the bark was treated with 15% H_2O_2 solution at 140 °C, an exothermic reaction took place and 47.4% of the carbon of the bark was converted into gases. At the same time, most of the H_2O_2 was decomposed. The water-soluble fraction mainly consisted of low molecular weight acidic components, which are degaradated and oxygenated products of lignin and polyflavanoids. This bark solubilization process consists of very complicated combinations of various reactions. Many organic compounds, other than acids, might be present in the water-soluble fraction. The water-insoluble material is the oxygenated cellulose compound.

Radiata pine bark contains large amounts of polyphenols called "polyflavanoids" (radiata tannin) (Chart 1) that react with formaldehyde. These compounds have attracted great interest because they might allow radiata pine bark extracts to be used in the formulation of waterproof wood adhesives.

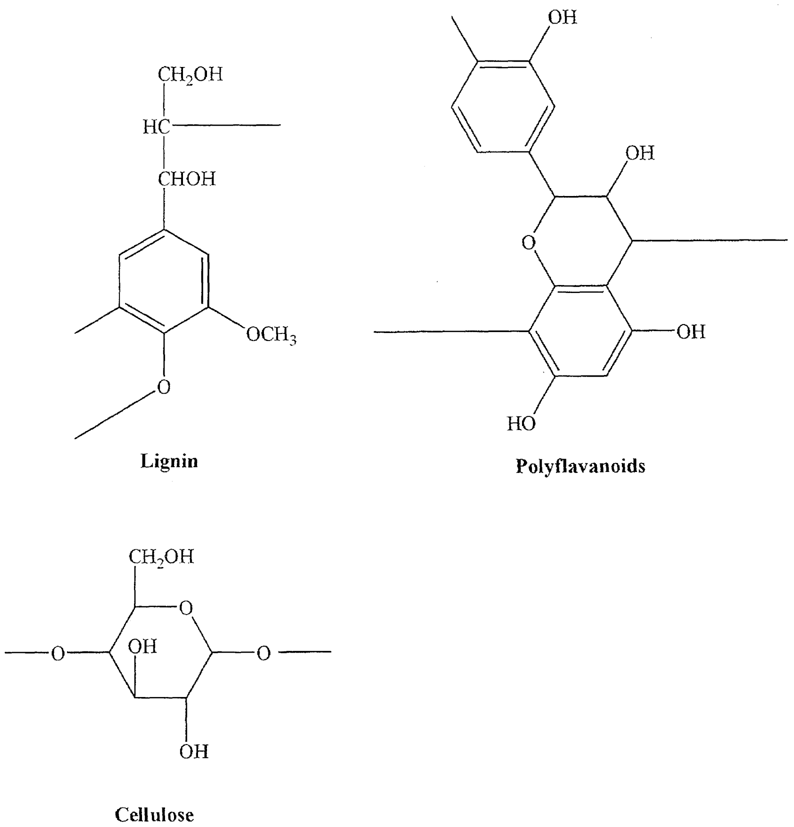
In radiata bark extraction, it is known that the extractive yield increases with increasing water temperature, up to 100 °C. The addition of sodium hydroxide (NaOH) to the water used for the extraction also increases the yield[1] but the amount of NaOH added to the bark needs to be carefully monitored. Highly alkaline conditions cause the rearrangement of the A-ring structure of the polyflavanoids resulting in the loss of reactivity of the polyflavanoids with formaldehyde.[2]

Hydrogen peroxide (H_2O_2) yields only water and/or oxygen upon decomposition, so it is an ecologically and environmentally desirable pollution control agent. Alkaline H_2O_2 solutions are also used to chemimechanically bleach ground wood, and to chemically treat pulps. Peroxide is often used in the final stages of the chemical pulp bleaching sequences to obtain a very white product, in the deinking of wastepaper, and to bleach solid surfaces such as wood.[3] The use of H_2O_2 for pulping, bleaching, and deinking processes is based on the delignification and decomposition of wood and its components.

An efficient extraction of radiata pine bark was studied using a high-pressure reactor at temperatures higher than 100 °C and holding time for 0 or 30 min. The extractive yields from the radiata pine bark using hot compressed water as a solvent were lower than those from a conventional extraction method at 100 °C under ambient pressure. However, when 1% aqueous NaOH (based on the weight of dried bark) was added to the hot compressed water, the extractive yields significantly increased. The highest extractive yield (31.3%) was obtained from the extraction with 1% aqueous NaOH at 140 °C and 10 atm with no holding time. These tannin extracts were still reactive with formaldehyde.[4] Since these high extractives yields would probably be due to softening of the lignin, and H_2O_2 is used in the pulp and paper industry to delignify wood, the results of this study prompted an investigation of the effects of H_2O_2 at temperatures higher than 100 °C on the yield of water-soluble materials from radiata pine bark.

A preliminary experiment showed that when the bark was treated with 30% H_2O_2 at 140 °C, the temperature increased so rapidly that its exotherm could not be controlled. At the same time, the solids of the bark almost completely disappeared and the pressure of the reaction vessel increased greatly. These results indicated that the bark was converted into water soluble and insoluble components and gases.

The objectives of this study were first to examine the effects of H_2O_2 on the yield of water-soluble materials when bark was treated under different conditions with H_2O_2; and second to analyze the distribution of the products between water-soluble and insoluble materials and gases on the basis of the weight and carbon content of each fraction. Furthermore, the water-soluble and water-insoluble compounds were analyzed by GC-MS and IR, respectively.



Lignin

Polyflavanoids

Cellulose

Chart 1.

Materials and Methods

Radiata Pine Bark. The bark samples were collected from the debarker of a plywood and laminated veneer lumber mill that was using logs from 35-year-old radiata pine trees at Mt. Gambier in South Australia. The bark samples were air-dried and ground to pass through a 2-mm screen in a Wiley mill. The resulting particle size distribution was: 2 mm to 1.25 mm (3.7%), 1.25 mm to 0.6 mm (57.5%), 0.6 mm to 0.25 mm (25.3%), 0.25 mm to 0.15 mm (1.5%), and less than 0.125 mm (12.0%).

The moisture content was calculated by weighing the bark after drying at 105 °C for 16 h. The ash content was found by weighing the residue after heating at 600 °C for 1 h, and the organic content was obtained by difference. The results of these analyses are summarized in Table 1. Details of the chemical composition of the radiata pine bark were reported in a previous work.[4]

Treatment of Radiata Pine Bark Using H_2O_2 at Temperatures Higher than 100 °C. On the basis of the preliminary experiment and previous work,[4] the treatment of the ground bark was as follows. The ground bark (particle size 1.25 mm to 0.65 mm, 3.0 g) and 0, 5, 10, or 15% H_2O_2 solution (30 mL) were added to an electrically heated 100 mL stainless steel pressure vessel. After this was purged with nitrogen gas, a pressure of 10 atm nitrogen gas was applied and then the vessel was heated. The temperature was increased to 100, 110, 120, 130, or 140 °C, maintained at the designated temperature for 30 min, and then reduced to room temperature.

Treatments of Radiata Pine Bark with H_2O_2 at 100 °C under Ambient Pressure. The bark sample (3 g) was added to 0, 5, 10, or 15% H_2O_2 solution (30 mL) in a round-bottom flask. The mixture was heated under reflux for 30 min and then filtered through a No.3 glass filter.

Table 1. Composition of Radiata Pine Bark

	Radiata pine bark
Moisture (wt%)	9.3
Organics (wt%)	89.9
Ash (wt%)	0.8
Elemental composition (wt%)	
C	51.9
H	5.7
O[a)]	42.1
Lignin (Polyflavanoids)	56.6 (29.8)
Cellulose	12.4
Hemicellulose	17.8

a) By difference.

Fractionation and Analyses of Products from Radiata Pine Bark after Treatment with H_2O_2. Figure 1 is a schematic diagram showing the procedures for the fractionation of products after the bark was treated with H_2O_2. The evolved gas was collected in a sample bag and then analyzed using gas chromatography (GC). The GC analysis was done using a WG-100 column (Shimadzu GC-8A). The temperatures of the oven, injector and detector were 50 °C, 50 °C, and 70 °C, respectively. The TCD current was 120 mA. The carrier gas was helium at a flow rate of 33 $\mathrm{mL\,min^{-1}}$. The products obtained from the treatment of the bark with H_2O_2 were separated into water-soluble and insoluble fractions by filtering and washing with water (60 mL) on a No.3 glass filter. The water-soluble fraction was diluted with water exactly to 200 mL and was measured for Total Organic Carbon (TOC), pH (using Duotest pH indicator paper), and residual H_2O_2 (titrimetric permanganate

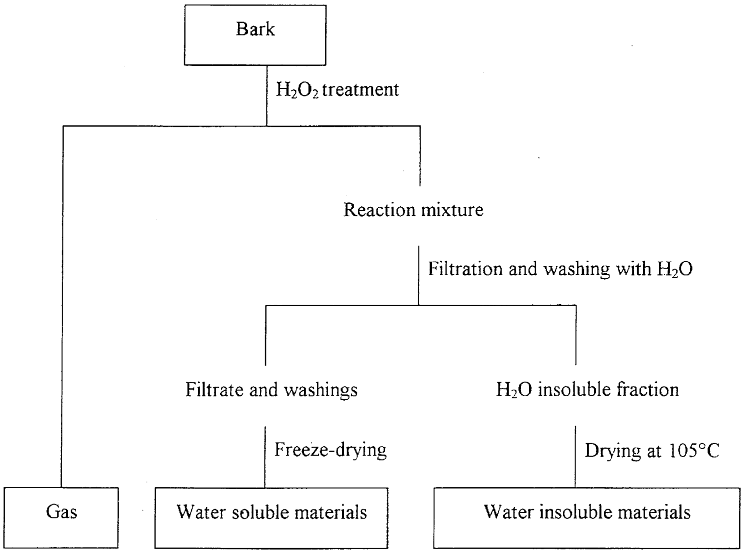


Fig. 1. Procedures for the fractionation of products from radiata pine bark treated with H_2O_2 at temperatures higher than 100 °C.

method), then freeze-dried. The TOC was measured using a TOC meter (Shimadzu TOC-5000A). Elemental composition was analyzed by an NA-1500 Elemental Analyzer (Carlo Erba NA-1500). GC-MS analysis was done using a Hewlett-Packard 5890 Series 2 GC with HP 5971 MS Detector. GC was done on a DB-5 column using He carrier gas at 0.9 mL min^{-1}. Injector and detector temperatures were 320 and 280 °C, respectively. The sample was injected into the GC column at 40 °C, left for 3 min, and then heated to 320 °C at 5 °C min^{-1}. The water-insoluble fraction was dried at 105 °C for 16 h. After drying, the water-insolubles were analyzed elemental composition and IR. IR spectra were recorded as KBr discs scanning from 400—4500 cm^{-1} (Perkin–Elmer 1600 FT-IR).

Results and Discussion

Decomposition of Radiata Pine Bark Treated with H_2O_2. The yields of the water-soluble and insoluble materials obtained from radiata pine bark after treatment with H_2O_2 solutions at temperatures higher than 100 °C are summarized in Fig. 2.

At temperatures higher than 100 °C, the yield of water-soluble materials increased with increasing H_2O_2 concentration from 0 to 15%. The highest yield of water-soluble material (47.4%) was obtained when the bark was treated with 15% H_2O_2 solution at 120 °C for 30 min. Very similar yields were obtained with the same H_2O_2 charge at 100 °C and 110 °C. Over 130 °C, the yield of water-insoluble materials was similar to that of at 120 °C but the yield of the water-soluble materials decreased due to the production of gases such as CO_2 and CO.

Various amounts of H_2O_2 remained in the aqueous phase after the bark treatments (Table 2). The highest concentration of residual H_2O_2 was obtained when the bark was treated with 15% H_2O_2 under reflux conditions. As the decomposition of H_2O_2 was dependent on the temperature applied for the treatments, there was no residual H_2O_2 after treatments at 140 °C. Residual H_2O_2 limits the use of the water-soluble materials, so it is important to find conditions in which there is no residual H_2O_2 in the aqueous phase.

Table 2. Residual H_2O_2 and pH in the Aqueous Phase Obtained from Radiata Pine Bark Treated with H_2O_2 at Temperatures Higher than 100 °C

Run	H_2O_2	Temp	H_2O_2 (g)		pH
	%	°C	Initial	Residual	
1	0	Reflux		—	5.0
2	5	Reflux	1.5	1.4	3.1
3	10	Reflux	3.0	2.8	2.8
4	15	Reflux	4.5	4.0	2.8
5	0	100		—	5.0
6	5	100	1.5	1.2	3.1
7	10	100	3.0	2.7	2.8
8	15	100	4.5	3.8	2.8
9	0	110		—	4.4
10	5	110	1.5	1.0	3.1
11	10	110	3.0	2.1	3.1
12	15	110	4.5	3.0	2.8
13	0	120		—	4.1
14	5	120	1.5	0.4	3.1
15	10	120	3.0	1.1	2.8
16	15	120	4.5	2.4	2.8
17	0	130		—	4.4
18	5	130	1.5	<0.1	2.8
19	10	130	3.0	0.5	2.8
20	15	130	4.5	0.5	2.8
21	0	140		—	4.1
22	5	140	1.5	<0.1	2.8
23	10	140	3.0	<0.1	2.8
24[a)]	15	233	4.5	<0.1	3.1

a) Exothermic reaction, holding time: 0 min.

When the bark was heated with a H_2O_2 solution, an exothermic reaction took place. This exothermic reaction was vigorous, particularly at 140 °C where both temperature and pressure increased so abruptly that they could not be controlled. In this instance, the temperature reached 233 °C instead of 140 °C and at the same time (holding time 0 min) the concentration of residual H_2O_2 in the aqueous phase was extremely low. As the exothermic reaction began after only a few minutes at 140 °C, the holding time became immaterial.

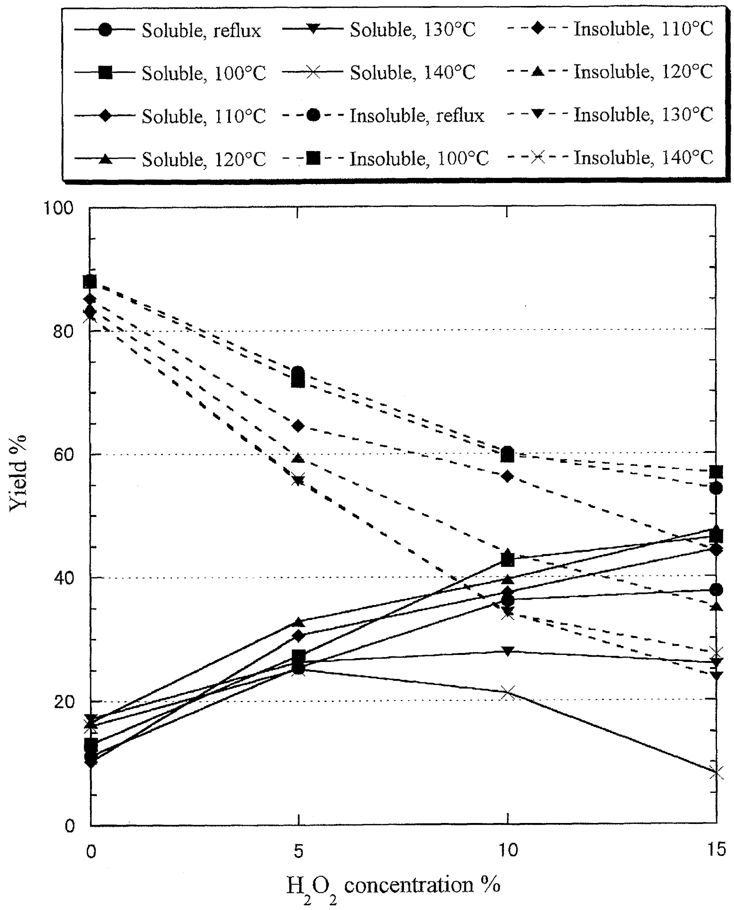


Fig. 2. The yields of water-soluble and -insoluble materials under reflux at ambient pressure and under high pressure at temperatures higher than 100 °C.

Products. The elemental compositions of the water-soluble and insoluble materials are shown in Table 3. Since the elemental analysis was measured after drying, some low molecular weight compounds might be vaporized. The oxygen concentration of the water-soluble materials increased with increasing temperature and H_2O_2 concentration. This means that the solubilization and oxygenation of the bark solids was promoted. On the other hand, the ratio of the carbon content of the water-soluble to that of the insoluble materials increased with increasing temperature and H_2O_2 concentration. When the bark was treated with 15% H_2O_2 solution at 140 °C, a strong exothermic reaction took place and the temperature reached 233 °C, resulting in a carbon distribution in the insoluble material of 61.4%. This indicates that carbonization occurred with the uncontrolled high temperature.

The results of the GC-MS for water-soluble materials showed the presence of many low molecular weight organic acidic compounds (Table 4). Furthermore, the pHs of water layers after treatments were between 2.8 and 5.0 as shown in Table 2. Kadla et al. studied the reactions of lignin model compounds treated with H_2O_2 at a high temperature (90 °C). In addition to the reactions of the phenolic representatives, proceeding via the well known Dakin and Dakin-like mechanisms, the non-phenolic compounds are shown to react at these higher temperatures via an S_N2 mechanism to ultimately give the corresponding benzoic acids and dimeric ether compound.[5] Krochta et al. reported the thermochemical degradation of cellulose into organic acids.[6] Consequently, it is expected that lignin and/or cellulose contained in the bark react to give acids during the treatments with H_2O_2 solutions at temperatures higher than 100 °C.

Radiata pine bark mainly consists of cellulose, hemicellulose, and lignin (polyflavanoids) (shown to Table 1). It is a complex feedstock so that many organic compounds, other than acids, might be contained in the water-soluble materials. Russell et al. recognized the formation of aromatic compounds, when cellulose was converted by a thermochemical treatment.[7] The results of GC-MS analysis also showed phenolic and non-phenolic compounds contained in the water-soluble materials, which maintain the structure of lignin and polyflavanoids after the treatments. The main compounds in the water-soluble are succinic acid and malonic acid. It is presumed that their compounds are obtained by degradation and oxidation of lignin. The solubilization process of the bark consists of a very complicated combination of various reactions such as oxidation, dehydration, and cyclization. Therefore, the water-soluble materials may contain many unidentifiable organic compounds.

Many organic acidic compounds were contained in the water-soluble materials. They can be used in isocyanate adhesives. It is widely known that compounds that contain

Table 3. Elemental Compositions of Water-Soluble and Water-Insoluble Materials

Run	Conditions		Water-soluble materials			Water-insoluble materials		
	H_2O_2	Temp	Carbon	Hydrogen	Oxygen	Carbon	Hydrogen	Oxygen
	%	°C	%	%	%[a]	%	%	%[a]
1	0	Reflux	52.3	5.3	42.2	50.9	5.6	43.3
2	5	Reflux	45.3	5.2	49.2	53.9	5.6	40.1
3	10	Reflux	45.2	5.0	49.7	53.8	6.0	40.0
4	15	Reflux	43.5	4.7	51.6	53.7	6.1	40.0
5	0	100	49.9	5.4	44.5	53.3	5.6	40.9
6	5	100	42.9	5.0	51.9	53.6	6.1	40.2
7	10	100	40.4	5.2	54.3	53.4	5.9	40.6
8	15	100	41.8	5.3	52.7	53.0	6.1	40.7
9	0	110	49.3	5.5	45.1	53.7	5.8	40.3
10	5	110	44.0	5.1	50.6	53.3	5.7	40.9
11	10	110	38.0	5.0	56.9	54.6	6.0	39.4
12	15	110	37.7	5.1	57.0	53.9	6.6	39.3
13	0	120	50.5	5.7	43.8	54.5	5.5	39.9
14	5	120	42.9	4.6	52.4	59.1	6.5	34.1
15	10	120	40.7	4.8	54.3	54.9	6.1	38.8
16	15	120	38.5	4.7	56.6	56.5	6.8	36.6
17	0	130	47.8	5.3	46.7	52.8	5.3	41.7
18	5	130	44.3	4.9	50.5	56.6	5.9	37.4
19	10	130	42.5	4.8	52.4	58.5	6.7	34.7
20	15	130	39.1	4.7	55.8	56.2	7.0	35.9
21	0	140	44.8	5.7	49.3	55.2	5.5	39.2
22	5	140	43.5	5.0	51.3	57.5	5.8	36.5
23	10	140	42.5	4.8	52.3	59.3	6.1	34.5
24[b]	15	233	44.1	5.0	49.9	61.4	5.9	32.6

a) By difference. b) Exothermic reaction, holding time 0 min.

Table 4. GC-MS Analysis of Water Solubles

Compounds
Glycolic acid
Levulinic acid
3-Hydroxy propanoic acid
Malonic acid
Maleic acid
Succinic acid
Methyl succinic acid
2,3-Dihydroxy propanoic acid
Fumaric acid
Pentanedioic acid
2-Pentenedioic acid
DL-malic acid
2-Hydroxypentanedioic acid
meso-Tartaric acid
Xylonic acid
2,3-Dihydroxy succinic acid
Aconitic acid
Vanillic acid
3,4-Dihydroxy benzoic acid

hydroxyl groups such as alcoholic hydroxyl groups, phenolic hydroxyl groups, and carboxyl groups, react easily with isocyanate to produce the adhesive.[8,9]

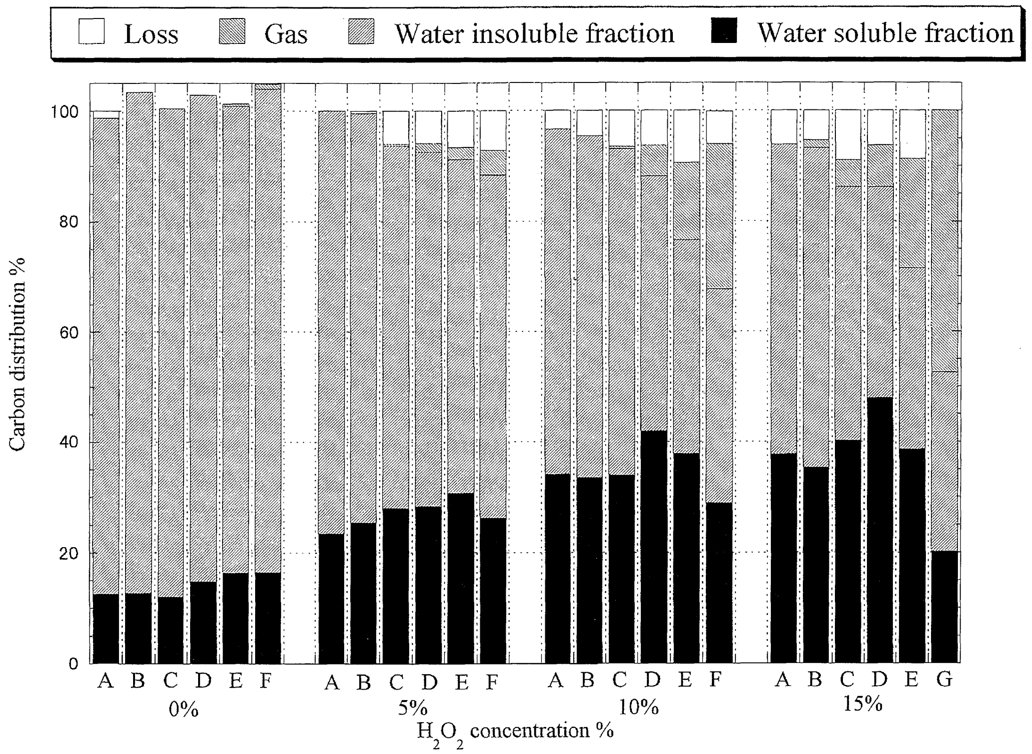
The water-insoluble material was analyzed using IR. The spectra contained a distinctive peak at 1738 cm^{-1}, which is due to –C=O. Except for this peak, the spectra of water-insoluble material coincided with that of cellulose. Gierer was reported that, in carbohydrates, the oxygenation of the carbon-centered radical and elimination of superoxide anion radical leads to the introduction of carbonyl groups.[10] It is interesting to find that the tendency is similar in hot compressed water.

Carbon Balance. The proportion of products (water-insoluble and soluble materials and gas) from radiata pine bark treated with H_2O_2 was described as a carbon distribution or carbon balance defined as follows:

C distribution (%) = [C (wt) in product/C (wt) in radiata pine bark] × 100.

The results are shown in Fig. 3. When radiata pine bark was treated with H_2O_2 at temperatures lower than 120 °C, the distribution of carbon in the gas phase was minimal. At temperatures higher than 120 °C, significant amounts of gas were generated, in which CO_2 was the major component together with small amounts of CO. On the other hand, when the bark was treated at various temperatures without H_2O_2 no gas was generated. The highest distribution of carbon in the water-soluble material (47.9%) was obtained by the treatment with a 15% H_2O_2 solution at 120 °C.

Whilst the carbon distribution of water-soluble material increased with increasing temperature up to 120 °C, that of the water-insoluble material decreased. However, the carbon distribution of the water-soluble fraction decreased at temperatures higher than 130 °C, while the amount of gases increased with the temperature. The carbon distribution of the water-insoluble material decreased with increasing tem-



Reaction condition: A; reflux, B; 100°C, C; 110°C, D; 120°C, E ;130°C, F; 140°C, G;233°C

Fig. 3. Carbon distribution of products obtained from radiata pine bark treated with H_2O_2.

perature and H_2O_2 concentration.

These results indicated that the bark was converted into water-soluble material at up to 120 °C, and with increasing temperature the water-soluble material was converted into gases. Minowa et al. proposed a gasification mechanism for cellulose with a nickel catalyst, in which cellulose was converted into water-soluble products by a hydrolysis reaction at the first step of decomposition, followed by conversion into gases.[11] It is interesting to find that the reaction mechanism of gasification shown in this study is similar to that of cellulose.

Radiata pine bark mainly consists of polyflavanoids, cellulose, and lignin. Polyflavanoids are major components of the water-soluble materials in radiata pine bark. When bark is treated with H_2O_2, an amount of water-soluble material greater than the polyflavanoid content of the bark might be obtained. It has been reported that cellulose decomposition starts at a reaction temperature lower than 180 °C.[12] Furthermore, lignin has been reported to soften at a temperature of 140 °C.[13] Since the yield of water-soluble materials from the bark was promoted by the treatment with H_2O_2 solution at temperatures higher than 100 °C, the treatment is an effective method for converting the bark into water-soluble material.

Conclusions

Radiata pine bark was treated with 0—15% hydrogen peroxide (H_2O_2) solution as a solvent at temperatures higher than 100 °C. The reaction mixture was separated into gas, water-soluble, and water-insoluble fractions. The distribution of products from the treated bark was analyzed. The following conclusions were obtained.

1. The highest yield (47.4%) of water-soluble materials was obtained when the bark was treated with 15% H_2O_2 at 120 °C.
2. The water-soluble materials contain many organic acidic components. Furthermore, many organic compounds may be contained in the water-soluble materials, because this process consists of a very complicated combination of various reactions. The obtained compounds could be used in wood adhesives, because they contain hydroxyl groups.
3. The water-insoluble materials contain oxygenated cellulose compounds.
4. On a carbon basis, the highest water-soluble yield (47.9%) was also obtained with the 15% H_2O_2 at 120 °C.
5. When the bark was converted into gas, it might form water-soluble materials as intermediates.

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