SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF SOUTHERN PINE AND PONDEROSA PINE[1]

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ABSTRACT

Pine wood and bark were extracted with supercritical (SC) carbon dioxide under various experimental conditions. The extractive yields ranged from 20–60% relative to the total diethyl ether extractive content. The yields were dependent on temperature, pressure, particle size, and fluid to wood ratio. The addition of ethanol to bark particles prior to SC CO_2 extraction produced higher yields of extracts relative to extractions without the addition of ethanol. Gas chromatographic (GC) analysis of selected SC carbon dioxide extracts revealed that the concentration of resin acids, as well as the yield of pure abietic acid, increased with temperature at constant pressure. Fatty acids were more soluble in SC carbon dioxide relative to diethyl ether. The concentration of fatty acids in SC carbon dioxide extracts did not appear to follow definite trends. In addition, observation of the wood particles with scanning electron microscope (SEM) revealed that the supercritical extraction process did not appear to significantly alter the wood surface structure.

Keywords: Southern pine, ponderosa pine, supercritical, carbon dioxide, extraction, scanning electron microscopy.

INTRODUCTION

Supercritical fluid (SCF) extraction is a rapidly developing technology that has great potential for separating and purifying high value products (Hoyer 1985; Williams 1981; Schneider 1978). Carbon dioxide (CO_2) is probably the most studied supercritical fluid since it is nonflammable, noncorrosive, nontoxic, and inexpensive (Brogle 1982). Carbon dioxide's critical pressure is 7.29 MPa (1,073 psi), its critical temperature is 31.3 C, and its heat of vaporization at 21 C is only 65 Btu/lb.

The concept of supercritical fluid (SCF) extraction first emerged over a hundred

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years ago when potassium iodide was dissolved in supercritical ethanol (Williams 1981). Later, it was discovered that supercritical steam deposited silica on the blades of steam turbines (Williams 1981). Deasphalting of petroleum was one of the first practical applications of the supercritical fluid extraction process. Examples of pilot plant or commercial applications include decaffeination of coffee, removal of nicotine from tobacco, deasphalting of petroleum, extraction of oil from oilseeds, and extraction of essential oils for flavorings and perfumes (Hoyer 1985; Williams 1981; Schneider 1978; Brogle 1982).

SCF extraction is effective for the isolation of relatively low polarity and medium molecular weight substances. Supercritical extraction with SC carbon dioxide potentially could be used to remove resinous extractives from wood chips prior to pulping or other commercial wood conversion processes. The advantages of removing valuable turpentine and tall oil precursors from wood prior to pulping are numerous. Wood extractives can hinder the pulping process and lower the final product quality (Casey 1960; Hillis 1980; Dorek and Allen 1978; Worster et al. 1986; Hrutfiord et al. 1975). Resinous extractives can consume pulping chemicals, decrease penetration of pulping liquors, increase organic loads on recovery furnaces and evaporators, and reduce fiber to fiber bonding, causing a reduction in paper strength. In addition, extractives contribute to significant air and water pollution problems in the pulp and paper industry. During the pulping process, potential tall oil yields are reduced as the result of thermal degradation (Holmbom and Eckerman 1983; Foster et al. 1986) and the conversion to oxygen or oxygen-aided pulping (Rao et al. 1981; Mittet and Thompson 1979; Pearl and Dickey 1977; Erickson and Dence 1975).

Fremont (1981) indicated in a patent that supercritical carbon dioxide at a 1.5:1 fluid to wood ratio (weight basis) could be used to quantitatively extract and separate resin acids, fatty acids, and volatile terpenes from southern pine pulp chips at 40 C and 7.98 MPa (1,175 psi). In a later study, McDonald et al. (1982, 1983) found that only 30% of the petroleum ether soluble resin acids in southern pine were extracted with supercritical CO_2 at 62 MPa and an 8.0:1 fluid to wood ratio (weight basis).

The same studies by McDonald et al. (1982, 1983) also showed that southern pine particles extracted first with SC carbon dioxide and then followed with a petroleum ether extraction produced a higher extract yield than a petroleum ether extraction alone. These results suggest that the SC carbon dioxide extraction may open the structure of the wood particles and allow greater penetration of the petroleum ether. This is supported by the fact that SC carbon dioxide extraction of tobacco leaves results in expanded leaf volume (Williams 1981). In addition, studies by Puri and Mamers (1983) also revealed that high pressure, noncritical point carbon dioxide could be used to explosively open lignocellulosic residues.

Because of the contradictory evidence presented by Fremont (1981) and McDonald et al. (1982, 1983), the primary objective of this study was to investigate and evaluate the extraction conditions required to remove resin and fatty acids from wood with supercritical carbon dioxide. A second objective was to ascertain, by means of scanning electron microscopy, if the rapid pressure reduction at the end of the extraction cycle would open or alter the surface of the wood structure and thus serve as an effective pretreatment prior to chemical or biological processing.

MATERIALS AND METHODS

Wood from an old southern pine stump was obtained from the United States Forest Service Southeastern Forest Experiment Station in Florida. Identification of the exact southern pine species, on the basis of anatomical characteristics, was not possible. Ponderosa pine (*Pinus ponderosa* Laws.) wood was obtained from the University of Idaho Experimental Forest. The wood samples had moisture contents of 8% and 75% (oven-dry basis), respectively. The wood samples were debarked if necessary, flaked, air-dried in the case of ponderosa pine, Wiley-milled, screened, and stored in double polyethylene bags. The bark from the ponderosa pine was processed in a manner similar to the wood. Because of a high extractive content that caused clumping of the particles in the Wiley mill, the southern pine flakes were reduced in size with a household blender rather than a Wiley mill. The 20–40 mesh fraction was used in all extraction experiments with the exception of the particle size study.

The southern pine and ponderosa pine wood particles, as well as the ponderosa pine bark particles, were extracted according to ASTM Standard Test Method D1108—Ether Solubility of Wood (ASTM 1979a) with the exception that the extractions were conducted for 24 hours. The ether extract yields were used as a means of relative comparison with the yields from the SC CO_2 extraction even though the extract components likely varied depending on the extraction technique.

The extracted and unextracted specific gravities of the southern and ponderosa pine particles were determined according to ASTM Standard Test Method D143—Small Clear Specimens of Wood (ASTM 1979b).

For each SC extraction, six grams of southern pine or twelve grams of ponderosa pine (wood or bark) were placed in a 75-ml stainless steel extraction vessel. A larger sample of ponderosa pine was extracted because of its lower extractive content. At the time of extraction, the wood particles averaged 6% moisture content (oven-dry basis). To test the effect of moisture content on extraction yield, several extractions were conducted with water-saturated southern pine (110% moisture content, oven-dry basis).

The supercritical extractions were conducted in an Autoclave Engineers Super-critical Extraction Screening System (Autoclave Engineers, Inc. 1983). The supercritical system had a high pressure pump with a maximum flow rate of 460 ml per hour, and temperature and pressure maximums of 240 C and 36.7 MPa (5,400 psi), respectively. The extraction process was considered a semi-batch process in that the wood and bark particles were placed in the extraction vessel prior to extraction, and then subjected to a continuous flow of carbon dioxide.

In addition to the extractions performed with carbon dioxide, ponderosa pine bark was extracted with carbon dioxide in the presence of ethanol. Prior to sealing the extraction vessel, 5 ml of ethanol were added directly to the bark particles after they had been placed in the extraction vessel.

A layer of glass wool was placed on both ends of the unsealed extraction vessel in order to prevent the movement of wood particles out of the vessel during the extraction process. The vessel was sealed, pressurized, and heated to the desired temperature; and the wood or bark particles were subjected to a continuous flow of supercritical carbon dioxide. The mass of carbon dioxide used in each extraction was calculated from a volumetric measurement of the gas at room temperature and pressure and then converted to standard temperature and pressure.

Because the extract material often condensed in the tubing leading to the separation vessel, the mass of extract removed in the supercritical extraction was calculated from the difference in oven-dry weight between the extracted and unextracted wood. In order to collect as much of the extract as possible, the tubing leading from the extraction vessel was flushed with ether. The extract from the tubing was added to the extract collected in the separation vessel.

Extractions were performed in duplicate or triplicate with the exception of the particle size experiments. These experiments exhibited such an obvious trend that only one observation per particle size was necessary. The supercritical extract yield was expressed as mg of extract per gram of carbon dioxide with all yields expressed on the basis of one gram of oven-dry wood. The data were plotted, and distinct trends relative to the extraction variable were noted. The data were not statistically analyzed in that the intent of this study was only to note the distinct trends associated with the SC CO_2 extraction of wood particles.

The extracts were stored in glass vials and refrigerated at approximately 4 C. A limited number of extract samples were analyzed by BC Research (Vancouver, British Columbia) in order to ascertain their chemical composition. For analysis, the samples were diluted in a 9:1 ether/methanol mixture and made up to either 10.0 ml or 25.0 ml, depending upon sample quantity. An aliquot then was methylated with diazomethane and analyzed by gas chromatography (GC).

Supercritical carbon dioxide extractions were also conducted to determine if the extraction process or subsequent pressure decrease opened or altered the surface of the wood particles. Scanning electron microscopy (SEM) was utilized to compare the wood surfaces before and after several types of ether and SC carbon dioxide extractions. As preparation for the SEM study, the wood particles were critical point dried, mounted with silver alloy paste or double stick tape on aluminum specimen stubs, and then coated with silver or gold-palladium alloy using a sputter coater. The particles were examined with either an ISI 60 or an ETEC Autoscan scanning electron microscope.

RESULTS AND DISCUSSION

Extraction of wood

The southern pine and the ponderosa pine samples had average ether soluble extractive contents, of 28.6% and 6.4%, respectively (based on oven-dry weight). The ponderosa pine bark had an ether soluble content of 9.0%. The average extracted and unextracted specific gravities for the southern pine were 0.50 and 0.77 and 0.49 and 0.58 for the ponderosa pine.

Southern pine wood particles were extracted with supercritical carbon dioxide over a range of particle sizes at 20.7 MPa (3,000 psi), 40 C, and a fluid-wood ratio of 8.00:1. The extraction process was dependent on particle size (Table 1) and appeared to be diffusion controlled because the extract yield decreased as the particle size increased. Extracting smaller relative particle sizes resulted in greater particle surface area exposure at a given level of solvent. In order to expose larger particle sizes to the same level of solvent per unit surface area, a larger quantity of total solvent would be required. Although the smallest particle size (40–60 mesh) produced the highest yields, later experiments utilized larger particles (20–40 mesh) because of the difficulty in handling the smallest particles.

These results are in contrast to the patent of Fremont (1981), which indicated

TABLE 1. *The effect of wood particle size on extract yield at 40 C, 20.7 MPa, and 9.25:1 fluid to wood ratio.*

Particle size (mesh size)	Extract yield (mg extract/g carbon dioxide)
>8	3.3
8–16	3.4
16–20	3.9
20–40	4.4
<40	5.2

that SC CO_2 extraction resulted in the almost complete removal of resin and fatty acids from pulp chips. In all cases, SC CO_2 yields were substantially less than the total ether extract yields. For example, a 24-hour ether extraction of southern pine yielded 286 mg of extract per gram of wood particles, while the largest SC carbon dioxide yield in this portion of the study produced only 48 mg of extract per gram of wood.

To determine the effect of pressure on extraction yield, southern pine particles were extracted at 40 C and a fluid to wood ratio of 9.25:1 (g of CO_2 : g of oven-dry wood) over a pressure range of 6.8 to 34.2 MPa (1,000–5,000 psi). Figure 1 shows that as extraction pressure increased and thus carbon dioxide solvent density, the extract solubility increased almost linearly from 13.8 MPa at a rate of 1.5 mg per 10 MPa. At 34.2 MPa, approximately 7.0 mg of extract per gram of CO_2 were removed. For comparison, a 24-hour diethyl ether extraction of southern pine yielded 286 mg of extract per gram of oven-dry wood, while the SC carbon dioxide extractions at 34.2 MPa yielded only 65 mg of extract per gram of oven-dry wood or approximately 22% relative to the ether extractions.

Ponderosa pine particles were also extracted over a range of 6.8–27.6 MPa (1,000–4,000 psi), at 40 C, and a fluid to wood ratio of 18.5:1. A maximum of 1.6 mg of extract per gram of carbon dioxide was removed at 27.6 MPa (4,000 psi) (Fig. 1). Relative yields likely were higher from southern pine because of a higher initial extractive content with southern pine and a possible difference in extract composition. For comparison, a 24-hour diethyl ether extraction produced an extract yield of 64.4 mg of extract per gram of oven-dry wood, while the maximum SC carbon dioxide yield was 29.6 mg per gram of oven-dry ponderosa pine wood or approximately 45% relative to the ether extractions. Although extract yield increased with SC extraction pressure, the results clearly indicated that under the conditions examined, extraction yields were not as high as ether extract levels.

Supercritical carbon dioxide extractions of the southern pine were conducted over a fluid to wood ratio range of 18–110:1 at 100 C and 27.6 MPa (4,000 psi). The yield of extract per gram of carbon dioxide decreased as the fluid to wood ratio increased (Fig. 2). At a fluid to wood ratio of 18.5:1, the yields of southern pine and ponderosa pine extracts were approximately 5.0 mg and 1.2 mg per gram of carbon dioxide, respectively. As the solvent ratio increased, the extract yield per gram of carbon dioxide decreased and then leveled off, suggesting that the accessible extractives had been removed from the surface of the wood particles.

Differences in extraction yields between southern pine and ponderosa pine likely were due to different extraction temperatures, as well as extraction pressure.
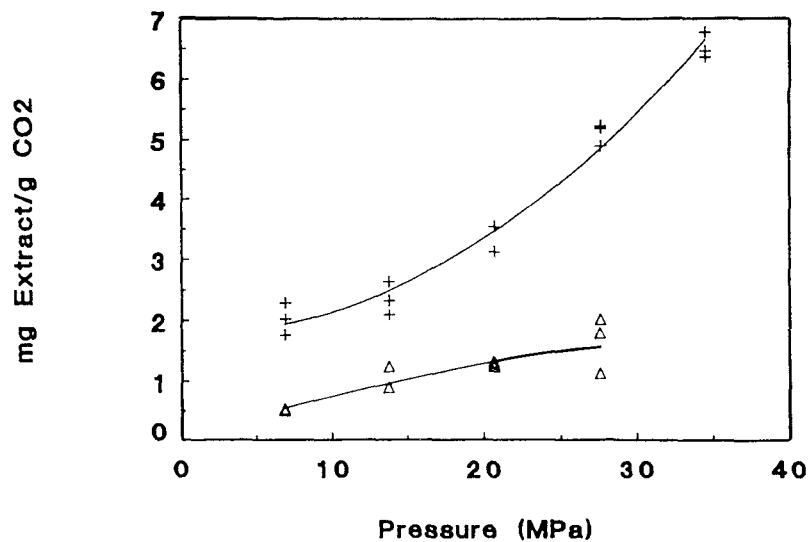
FIG. 1. The effect of pressure on extraction yields. Southern pine (+) extracted at 40 C and 9.25 g CO_2 per gram of wood. Ponderosa pine ($\triangle$) extracted at 40 C and 18.5 g CO_2 per gram of wood.

Southern pine and ponderosa pine were extracted at 100 and 40 C, respectively. A higher extraction temperature would result in a lower solvent density, while an increased pressure would result in a higher solvent density and, therefore, higher solubility. In addition, a higher extraction temperature would result in increased vapor pressure, which could lead to elevated solubility (Hoyer 1985).

The largest extract yields were obtained at the greatest fluid to wood ratios (Fig.
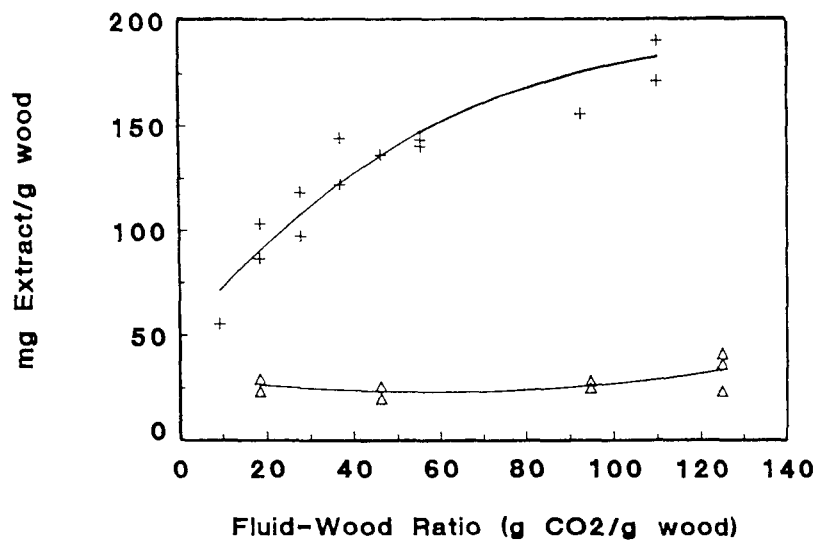

FIG. 2. The effect of fluid to wood ratio on extract yields. Southern pine (+) extracted at 100 C and 27.6 MPa. Ponderosa pine ($\triangle$) extracted at 40 C and 20.7 MPa.
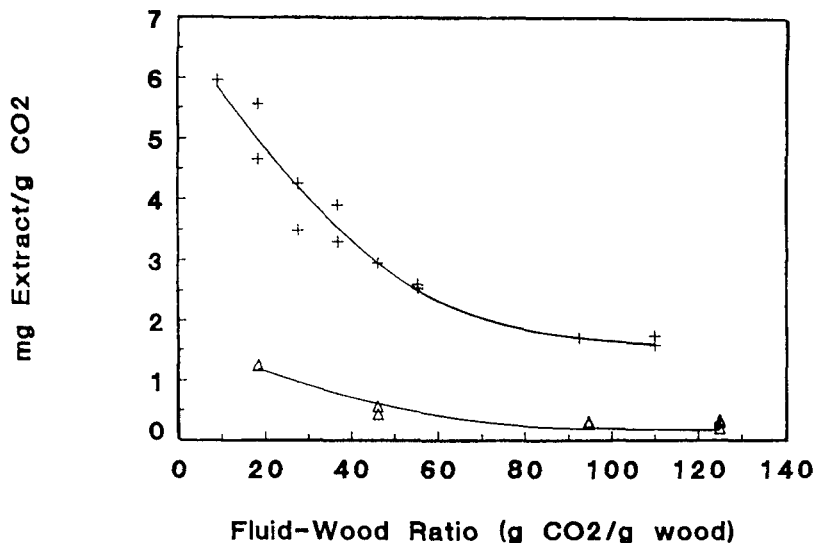
FIG. 3. The effect of fluid to wood ratio on mg of extract per gram of wood. Southern pine (+) extracted at 100 C and 27.6 MPa. Ponderosa pine (△) extracted at 40 C and 20.7 MPa.

3), but the yields are not as large as in ether extractions. The maximum fluid to wood ratios utilized in this study are significantly greater than those indicated by Fremont (1981), and yet the total SC CO_2 extract yields do not approach the levels of ether extractions.

Moisture content did not appear to play a significant role in the extraction process. Supercritical carbon dioxide extractions of southern pine were conducted at a 27.5:1 fluid to wood ratio, 20.7 MPa (3,000 psi), 100 C, and 6% and 110% moisture content (oven-dry basis). Yields from extractions at both moisture contents averaged 2.4 mg of extract per gram of carbon dioxide. Although moisture content is critical for the optimum extraction yields of nicotine from tobacco and caffeine from coffee (Zosel 1978), moisture content did not appear to play a significant role in the removal of extracts from wood particles.

Supercritical carbon dioxide extractions of southern pine also were conducted over a temperature range of 40 to 180 C, at 27.6 MPa (4,000 psi), and a fluid to wood ratio of 18.5:1. The extract solubility more than doubled from 2.6 mg per gram of carbon dioxide at 40 C to 6.2 mg per gram of carbon dioxide at 180 C (Fig. 4). The volatility of the resinous extract likely increased with higher temperature, resulting in higher extract yields. At temperatures of 180 C, hydrolysis of the hemicelluloses may have taken place, and therefore the measured mass difference may in fact have been a combination of extractive removal and loss of hemicelluloses through hydrolysis. An opposite trend was observed with ponderosa pine in which a slightly lower extract yield was obtained at the highest extraction temperature (Fig. 4). If extract yield is plotted as a function of solvent density (Fig. 5), with density decreasing as extraction temperature is elevated, the extract yields from southern pine were higher with decreased densities, while extraction of ponderosa pine exhibited an opposite trend. The difference is likely due to compositional differences which will be discussed in a later section.
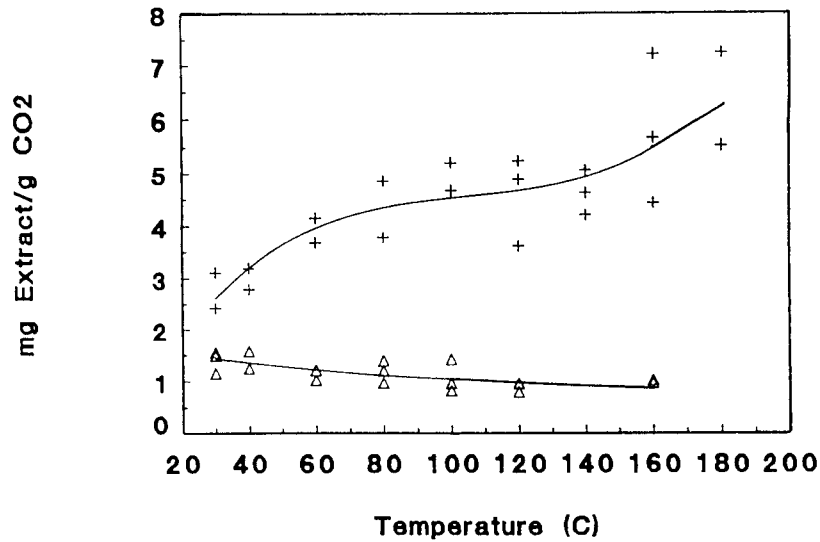
FIG. 4. The effect of extraction temperature on the solubility of extracts. Southern pine (+) extracted at 27.6 MPa and 18.5 g CO_2 per gram of wood. Ponderosa pine ($\triangle$) extracted at 20.7 MPa and 18.5 g of CO_2 per gram of wood.

Extraction of bark

Ponderosa pine bark was extracted with supercritical carbon dioxide at 20.7 MPa, 27.75 grams of carbon dioxide per gram of oven-dry bark, and at three temperatures (40, 100, and 160 C). Although the data were somewhat inconsistent, extraction yields appeared to increase from 40 to 160 C (Fig. 6).
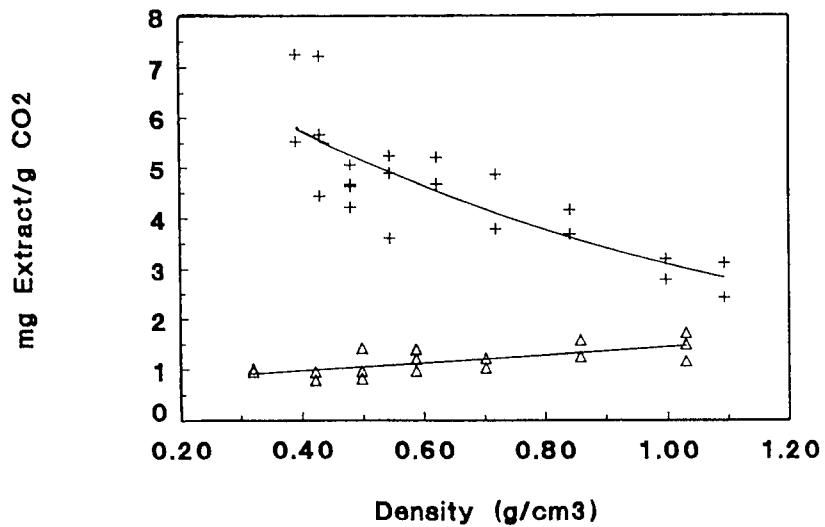

FIG. 5. The effect of solvent density on the solubility of extracts. Southern pine (+) extracted at 27.6 MPa and 18.5 g CO_2 per gram of wood. Ponderosa pine ($\triangle$) extracted at 20.7 MPa and 18.5 g of CO_2 per gram of wood.
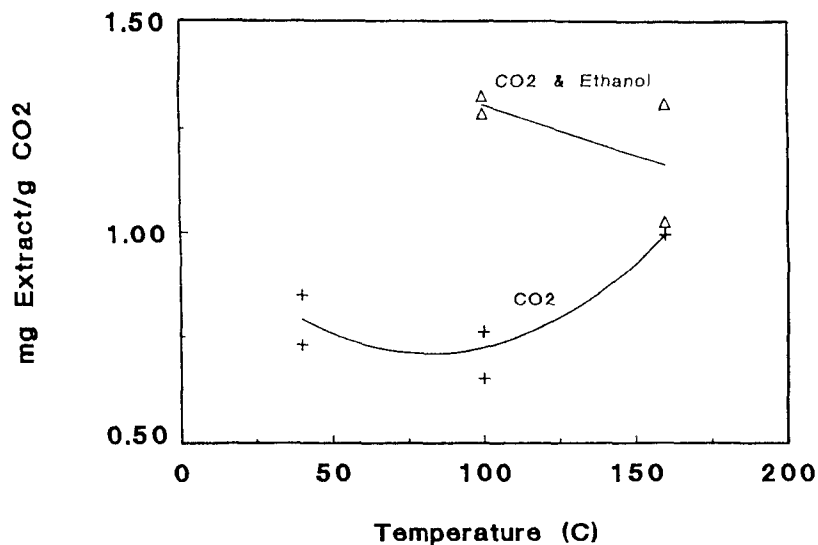
FIG. 6. The effect of temperature and a co-solvent (ethanol) on the extraction yields from ponderosa pine bark. Bark extracted at 27.8 g CO_2 per gram of bark and 20.7 MPa.

In addition, bark was also extracted with SC carbon dioxide in the presence of ethanol at 100 and 160 C. Ethanol was added as a co-solvent to enhance extractive solubility. The batch addition of ethanol doubled the yield at 100 C relative to the pure carbon dioxide extractions (Fig. 6). The effects of ethanol addition at 160 C were inconsistent. The addition of ethanol at 100 C may have had a three-fold effect. Ethanol, which has a critical temperature and pressure of 243.4 C and 6.4 MPa, may have produced a solvent that had a critical pressure slightly lower than that of pure carbon dioxide, and a critical temperature that was greater than that of carbon dioxide. The end result may have been a solvent system that reached a higher density at a lower pressure. The use of ethanol as a co-solvent may have increased solubility due to hydrogen bonding between the ethanol and the extract material. In addition, extraction in the presence of ethanol at high temperatures may have resulted in delignification products. Thus, the extractive yield, based on the mass of the wood prior to and after extraction, may have contained both extractives and limited quantities of delignification products.

Composition and solubility of extracts

Abietic acid and linseed oil were extracted with supercritical carbon dioxide in order to measure their solubility as compared to extract mixtures and to determine the effect of temperature on extract solubility. Abietic acid was selected as a model compound because it is a relatively common resin acid in pines. Linseed oil was selected because it contains glycerides of fatty acids commonly found in wood (linoleic, linolenic, oleic, and stearic acids).

Extractions were conducted at 20.7 MPa (3,000 psi) and at 40, 100, and 160 C. At 40 C the solubility of linseed oil was approximately 2.5 mg per gram of carbon dioxide, while the solubility of abietic acid was 0.8 mg per gram (Fig. 7). In comparison, the solubilities of southern pine and ponderosa pine extracts at
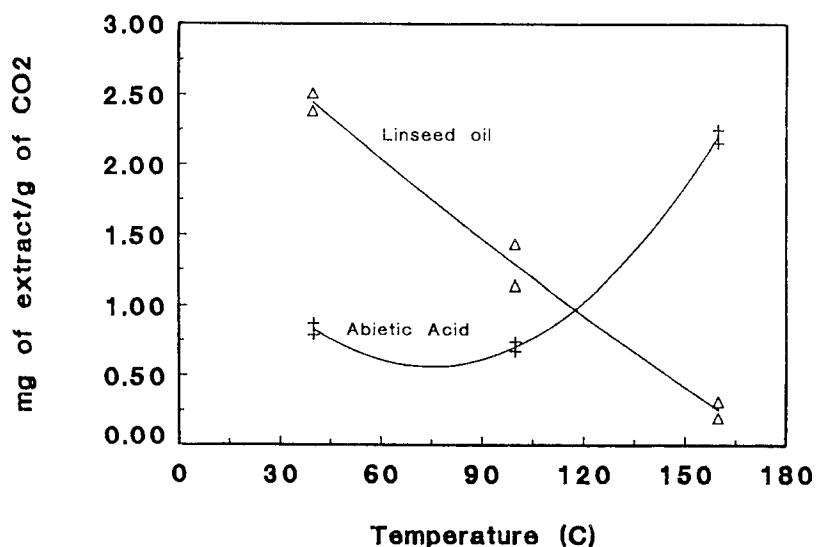
FIG. 7. The effect of extraction temperature on the solubility of abietic acid and linseed oil in supercritical CO_2 at 20.7 MPa.

20.7 MPa and 40 C were approximately 3.5 mg and 1.0 mg per gram of carbon dioxide, respectively. The linseed oil extraction yield decreased linearly as a function of temperature (Fig. 7), while the abietic acid extraction yield generally increased as a function of temperature. At pressures below approximately 47 MPa, Moses and DeFilippi (1983) also demonstrated that soybean oil yield decreased as the SC carbon dioxide extraction temperature increased.

Linseed oil yields, relative to abietic acid, may have been higher at lower temperatures for several reasons. At lower extraction temperatures, the polarity of the CO_2 may have been better matched to that of the fats present in the wood. At a lower relative temperature, the density of the CO_2 was higher, making it a more efficient solvent. In addition, because the fats that make up linseed oil have a higher vapor pressure relative to the resin acids (Drew and Propst 1981), they may be more soluble at lower temperatures.

The outcome of the SCF extraction of linseed oil and abietic acid helps to explain the results obtained in the temperature study. The literature indicates that ponderosa pine sapwood, which made up approximately 90% of this particular sample, contains a much higher proportion of fats than the heartwood of the common southern pines (Conner et al. 1980; Zinkel and Foster 1980; Zinkel 1975). Therefore, extraction of fat-rich ponderosa pine sapwood at increasingly higher temperatures could have resulted in a decreased extraction yield as observed with linseed oil. Likewise, the extraction of resin-rich southern pine at higher temperatures may have resulted in an increase in yield as observed with abietic acid.

Selected extracts from the SCF and diethyl ether extractions were analyzed by gas chromatography (GC) (Tables 2 and 3). In every case listed in Tables 2 and 3, the components that are listed account for only a relatively small percentage of the sample. The remaining portion of the sample may have consisted of un-

TABLE 2. *Composition of ponderosa pine extracts.*

	Extract concentration (mg/g extract)			
	Ether	13.8 MPa 40 C	27.6 MPa 40 C	20.7 MPa 160 C
Resin acids				
Pimaric	31.16	26.45	17.19	44.97
Sandaraco-pimaric	5.81	4.84	3.13	9.04
Isopimaric	42.39	35.16	21.56	66.45
Levopimaric/palustric	33.10	16.45	6.25	21.92
Dehydro-abietic	66.26	76.13	46.86	70.29
Abietic	120.45	59.03	29.06	127.94
Neoabietic	5.81	1.52	nd[1]	6.33
Total resin acids	304.97	219.58	124.06	346.94
Fatty acids				
Oleic/linolenic	0.32	13.55	29.38	5.43
Linoleic	nd	1.61	nd	3.38
Total fatty acids	0.32	15.07	29.38	8.81

[1] Not detected.

hydrolyzed fats or high temperature hydrolysis products from hemicellulose. Although only single samples were analyzed, general observations relative to solubility were made. The diethyl ether extracts obtained from Soxhlet extractions of southern pine contained higher concentrations of resin and fatty acids than any of the SC carbon dioxide extracts. SC carbon dioxide extracts of ponderosa pine at 160 C and 20.7 MPa contained the highest levels of resin and fatty acids as compared to other SC carbon dioxide and ether extractions.

With few exceptions, the resin acid proportion of the extract for both ponderosa pine and southern pine was highest at 160 C. The resin acid levels decreased when extraction pressure was elevated from 13.8 MPa to 27.6 MPa, with temperature

TABLE 3. *Composition of southern pine extracts.*

	Extract concentration (mg/g extract)			
	Ether	13.8 MPa 40 C	27.6 MPa 40 C	27.6 MPa 160 C
Resin acid				
Pimaric	40.70	57.43	36.58	53.96
Sandaraco-pimaric	8.07	10.76	6.58	10.21
Isopimaric	61.93	75.67	46.33	74.80
Levopimaric/palustric	103.48	59.24	5.58	45.62
Dehydro-abietic	59.30	70.35	70.92	109.16
Abietic	253.69	128.83	27.83	135.83
Neoabietic	39.30	14.09	1.62	4.73
Total resin acids	566.45	358.95	195.44	434.31
Fatty acids				
Oleic/linolenic	0.04	7.66	3.92	0.17
Linoleic	0.04	5.09	0.92	0.07
Total fatty acids	0.08	12.75	4.84	0.24

[1] Not detected.

constant at 40 C. When the extraction temperature was elevated from 40 to 160 C and pressure was maintained at 27.6 MPa (20.7 MPa for ponderosa pine), the concentration of resin acids increased substantially.

These results, which showed the effect of temperature and pressure on resin acid composition, were not in general agreement with the findings of McDonald et al. (1982, 1983). McDonald et al. (1982, 1983) indicated that the resin acid content increased with pressure at constant temperature, and decreased with elevated temperature at constant pressure. The temperature range utilized by McDonald et al. (1982, 1983) was 30 to 60 C. The decrease in extract yield from 35 to 60 C was approximately 30%, based on extract yield at 35 C, and may have been a nonsignificant difference.

Hoyer (1985) indicated that a higher extraction temperature at constant pressure may result in higher solute vapor pressure and elevated solubility. This suggests that resin acid solubility may be controlled to a greater degree by vapor pressure than solvent density. Figure 5, which shows extraction yields as a function of density, supports this idea. The results indicating that resin acid levels increase with elevated extraction pressure are in agreement with the extraction of abietic acid. Increasing the extraction temperature from 100 to 160 C resulted in an increased solubility of abietic acid (Fig. 5).

The concentration of fatty acids did not follow a regular trend as was observed with the resin acid data. In the case of ponderosa pine, total fatty acid levels are greatest at 40 C and 27.6 MPa. For southern pine, total mg of fatty acids per gram of extract was highest at 40 C and 13.8 MPa. Tables 2 and 3 also reveal that the fatty acids appear to be more soluble in SC carbon dioxide than in diethyl ether. In all cases, SC carbon dioxide extractions produced greater concentrations of fatty acids than diethyl ether extractions.

Microscopic analysis of SCF extracted wood

Preliminary observations in our laboratory suggested that a high pressure extraction could potentially serve as a pretreatment to open the wood structure. Wood particles were observed to move slightly, and a crackling sound emanated from the particles immediately after SC carbon dioxide extraction and removal from the extraction vessel. This suggested that the wood fiber structure or pit areas could be opened or mechanically damaged by escaping gases during the rapid pressure reduction following the extraction. McDonald et al. (1982) observed that supercritical extraction increased extractive yield from a subsequent petroleum ether extraction suggesting that changes in the wood surface structure had occurred. In addition, supercritical extraction of nicotine from tobacco has been shown to expand the leaf volume (Zosel 1978; Hubert and Vitzthum 1978). The magnitude of the volume expansion was dependent on temperature, moisture content, and other extraction variables.

The objective of this portion of the project was to ascertain if supercritical carbon dioxide extraction altered or opened the structure of the wood surface. If so, this process could be an important benefit in wood processing technologies. Scanning electron microscopy (SEM) was used to observe the effect of temperature, pressure, moisture content, extractive content, and rate of pressure release on the wood structure during supercritical extraction.

SEM micrographs of both untreated and ether-extracted wood were compared

FIG. 8.   Scanning electron micrograph of southern pine wood extracted at 40 C and 10.4 MPa.

with wood extracted with supercritical carbon dioxide. Micrographs of the resinous southern pine wood taken after supercritical extraction at a low temperature and pressure (40 C and 10.4 MPa) revealed small bubbles or nodules of the extractives on the wood surface (Fig. 8). The extractives likely softened and flowed in the cell lumens and then exited through the pits and solidified as the carbon dioxide escaped at the end of the extraction. With the exception of extractive flow, SEM micrographs of wood taken after an extraction at a higher temperature and pressure (100 C and 27.6 MPa) also revealed a lack of wood surface alteration (Fig. 9).

Micrographs of southern pine wood extracted at 100 C and 27.6 MPa in the water-saturated condition did not reveal any openings or alterations of the wood surface. The extractives appeared to have flowed freely over the wood surface during the extraction process, and then formed many small ruptured bubbles in the extractive layer as steam escaped during depressurization (Fig. 10).

Ponderosa pine samples of 6.4% extractive content also were extracted at 40 and 100 C and 10.3 and 27.6 MPa. Because of the lower extractive content, there was no apparent flow of extractives through the pits and onto the cell surfaces.

Micrographs of wood extracted with diethyl ether and then with supercritical carbon dioxide were virtually identical to those of the untreated wood. The lack of visible extractives on the surface of the ponderosa pine samples also supported the conclusion that SC carbon dioxide yields from southern pine were likely higher due to the presence of extracts on the particle surface. No major changes in wood cell surface structure were observed with any of the wood samples at the temperatures, pressures, and moisture contents investigated.

FIG. 9. Scanning electron micrograph of southern pine wood extracted at 100 C and 27.6 MPa.
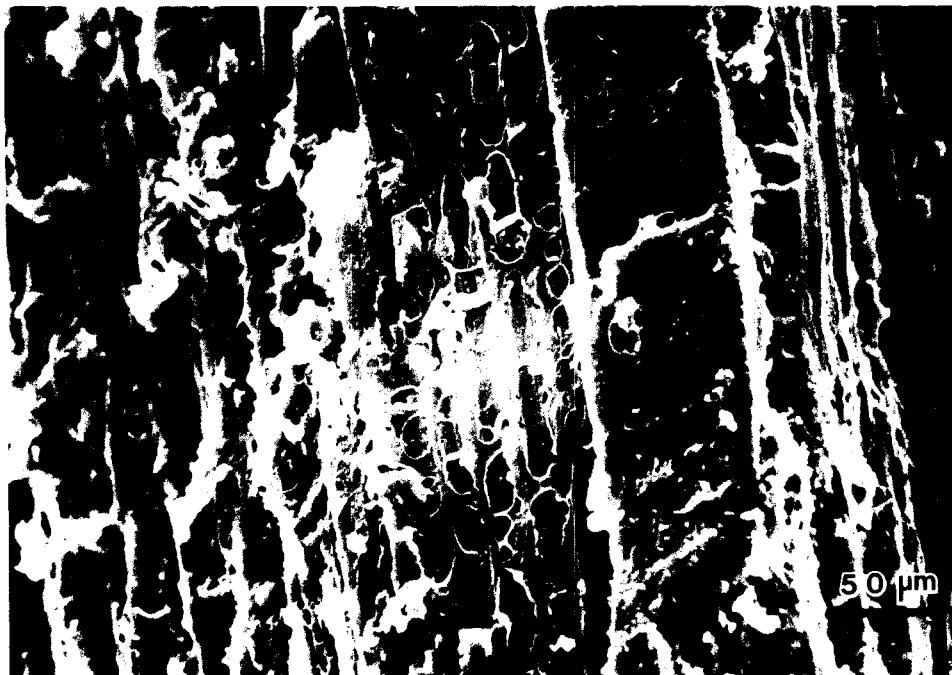

FIG. 10. Scanning electron micrograph of southern pine wood extracted while water-saturated at 100 C and 27.6 MPa.

SUMMARY

Supercritical carbon dioxide extraction yields were dependent on particle size, substantially lower than ether extractions, and appeared to be diffusion controlled. Yields approaching 60% of the diethyl ether extractions were achieved only at high pressures and high fluid to wood ratios. In the case of the southern pine samples, extract yield increased as a function of extraction temperature, while in the case of ponderosa pine extract yield appeared to decrease slightly as a function of temperature.

GC analysis of the extracts revealed that the concentration of resin acids, as well as the "model" compound abietic acid, increased with temperature. In most cases, resin acid concentration decreased as pressure increased at constant temperature. Resin acid concentration increased as temperature was elevated at constant pressure. Levels of fatty acids per gram of extract did not produce clearly defined trends. Ether extractions usually produced greater levels of resin acids, while SC carbon dioxide extractions resulted in higher levels of fatty acids.

The physical changes observed on the wood particle surface in the SEM study were due primarily to the extractive material which softened, flowed, and formed bubbles as gas escaped from the cell lumens when the pressure and temperature were reduced at the end of the extraction. Supercritical carbon dioxide extraction of wet or dry pine wood at 100 C and 27.6 MPa did not appear to mechanically alter or open the wood structure, and thus supercritical fluid extraction did not appear to be an effective wood pretreatment.

Future research on the removal of the tall oil precursors from extractive-rich wood should concentrate on utilizing other supercritical solvents such as halo- and hydrocarbons. These solvents have been shown to effectively remove oil from oilseeds (Moses and DeFilippi 1983) and may have potential in wood extraction. As shown in the extractions of ponderosa pine bark, the addition of ethanol or other co-solvents to carbon dioxide may result in increased yields of resinous extracts from wood. In addition, future studies should investigate the economic aspects of employing this process to remove extractives from wood prior to pulping.

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