# 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 Supercritical 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.