

Chemicals and biofuels from pine oleoresin

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Coniferous trees are rich in chemical compounds such as terpenes, fats/fatty acids, waxes, tannins and phenolics, which function to protect the tree against insect pests and diseases, and as energy reserves. Compounds extractable with organic solvents typically comprise about 3 to 5 percent of total biomass on a whole tree dry basis, and may represent up to 25 percent in certain tree parts, such as heartwood in the inner basal portion of the stem and roots. Trees may develop higher levels or altered profiles of extractives when subjected to stressors, including mechanical injury, water-deficit, pest attack, or atmospheric pollutants. Terpenes are a large group of compounds having molecular formulas that are multiples of C_5H_8 . Oleoresin is an important natural product that is a mixture of resins (diterpene acids) that are normally a solid material at room temperature, and volatile essential oils (mono- and sesquiterpenes) that serve as a solvent to maintain the oleoresin in a fluid state. Oleoresin is synthesized by the thin-walled epithelial cells within the wood parenchyma tissue. In pines and firs, these structures are organized as a network of interconnected radial and longitudinal ducts which store oleoresin at elevated pressure and transport it to injury sites. Oleoresin is especially abundant in certain pines, such as *Pinus elliotii*, *P. palustris*, *P. taeda*, and *P. ponderosa*.

Pine oleoresin is commercially produced from about 20 pine species in both natural and plantation forests in many developing countries. The crude oleoresin exudate is converted by steam distillation into its primary fractions of gum rosin (diterpenes) and gum turpentine (mono- and sesquiterpenes), which in turn are processed into chemical products such adhesives, coatings, printing inks, paper size, disinfectants, cleaners, food gums, pharmaceuticals, fragrances and flavorings [1]. Global production of gum rosin and turpentine is about 1 million Mg annually, with China accounting for about half of this amount. The United States was formerly a large producer of gum rosin and turpentine in the southeastern coastal plain region, but production has declined due to increased costs, foreign competition, and changes in management of the pine forest resource. Demand for gum rosin and turpentine has remained strong over the past two decades, in spite of competition from petroleum hydrocarbons, and tall oil rosin and crude sulfate turpentine recovered at softwood pulp mills.

The conventional method of oleoresin production, known as bark chipping, involves removing strips of bark up to 5 cm wide along one-third the tree's circumference. The exudate is collected in open cups affixed to the tree. Chemical preparations of sulfuric acid and the plant growth regulator *Ethephon* are applied to the freshly wounded cambium layer to enhance oleoresin yields and prolong the duration of flow. The treatment process is repeated at intervals of 3 to 4 weeks proceeding longitudinally along the stem to expose fresh resin ducts and remove resin-saturated tissue to renew the flow of oleoresin. Oleoresin yields with this method from *Pinus elliotii* averaged over 7 kg per tree annually from a series of 8 treatments [2]. Wood exposed by resin tapping is generally protected from decay by resinosis, however, the appearance of damage to the tree causes resistance to tapping by forest owners and managers. Resin tapping diverts materials from the tree's carbohydrate substrate pool to replace extracted oleoresins, and may decrease wood volume growth up to 22 percent during the tapping period.

The borehole method of oleoresin tapping was developed in attempt to overcome some of the limitations of bark chipping [3,4]. A key feature of the system is that a closed collection apparatus captures the volatile monoterpenes and prevents premature solidification of the resin acids, thereby maintaining oleoresin flow for an extended period of up to 6 months. Labor requirements and costs for borehole tapping are significantly lower than for conventional tapping. Product quality is higher due to reduced oxidation and gross contamination, and recovery of volatiles (turpentine) is about 50 percent greater. Tree mortality and wood volume growth loss are reduced as a result of lessened damage to the cambium and bark, and there is no damage to the merchantable portion of the tree stem.

The borehole method involves drilling holes into the sapwood xylem, application of stimulant chemical treatments (sulfuric acid, *Ethephon*), and installation of collection apparatus. Boreholes are made 2.5 to 3.8 cm diameter and 10 to 18 cm deep, at intervals of 10 to 30 cm around the tree's

circumference, at a height of 10 cm above ground. Trees must be at least 20 cm diameter at breast height for suitable application. Drilling boreholes may be accomplished with power or hand tools. Oleoresin collection is done with plastic bags or recycled plastic beverage bottles obtained from local sources. An automated system for borehole drilling and chemical treatment was developed and tested in 1999. Operating costs for this system, including machine capital, interest and repair, labor and supplies, were estimated at \$0.80 per tree or \$0.41 per kg of oleoresin produced [4]. Oleoresin yields from borehole tapping over 10 years of research trials with *Pinus elliottii* in Florida and Georgia, USA averaged 1.95 kg per tree. In commercial pilot operations, yields measured in sample plots averaged 769 kg per ha [4]. Yields vary dramatically due to genetic differences in anatomy and chemical composition of the oleoresin, and are sensitive to tree size and treatment variables of borehole size, orientation and chemical dosage. Large trees produce significantly greater yields due to both a greater volume of resinous tissue and higher concentration of oleoresins.

In addition to the traditional uses of gum turpentine and rosin for chemical products, there are potential new uses as biofuels. The volatile fraction can be used as a replacement for gasoline in conventional spark ignition, internal combustion engines. It has been demonstrated that a 50:50 blend of gum turpentine and gasoline can be used to fuel a small internal combustion engine without modification. The hindered nature of the structures of the major components of turpentine, α -pinene, β -pinene and 3-carene, suggest that they might impart octane-enhancing properties in more efficient and cleaner burning high compression engines. Rosin acids could be used in the same fashion as triacylglyceride derived fuels, with a fuel value comparable to that of fuel oil. Gum rosin might be superior to vegetable oil or animal fats as a source of biodiesel in that it is a mixture of free acids and saponification is not necessary for use as a blended fuel. Alternatively, industrial methylation and decarboxylation can convert it to a neat fuel. Pine oleoresin would be environmentally favorable as a fuel because of very low sulfur content.

References

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