Extraction of wood with solvents

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ABSTRACT *We have assessed the commercial usefulness of extract products from* Pinus pinaster *following extraction with propanone, ethanol, trichloromethane, or diethylether as solvents on the pilot plant scale. Extraction products were similar between solvents and were ready for commercial use. The extracted wood can be used for papermaking, with a reduction in the digestion reactants consumed in comparison to conventional pulping. The rate of rosin extraction and pulp yield were greater when diethylether and trichloromethane were used as solvents. However, propanone and ethanol consumed less digester reactant and produced pulp with greater whiteness and lower kappa number.*

KEYWORDS
Ethanol
Extraction
Fatty acids
Pulping
Rosin
Solvents

Wood extraction from dead trees for the production of chemicals is carried out using stump wood. For commercial exploitation, the extract content must be over 15%, which is only possible with century-old tree wood (*1*). Today, it is difficult to find this raw material, because shorter shifts are used in forestry. Nevertheless, some treatments with phytocides used today can increase considerably the quantity of extracted products (*2*).

Extraction of *Pinus pinaster* prior to pulping can yield chemicals such as rosin, fatty acids, and turpentine (*3*). The commercial viability of this process depends on the quantity and quality of the extraction products (*4–6*), on the capacity of extracted chip wood towards paper production (*2, 7–9*), and on the effectiveness of solvent recovery.

Our purpose was to study the extraction products and the capacity of the treated wood towards paper production after extraction using different solvents.

Experimental procedures

Materials

The wood chips were from *Pinus pinaster*, 45 years old, and were conditioned at 20°C and 60% RH. The chip size distribution was: 33% under 18 mm, 23% in the range of 18–20 mm, and 44% in the range of 20–26 mm.

The different solvents are listed in **Table I**, together with the extractables obtained according to TAPPI T 204.

Wood extraction

We employed a 20-L stainless steel extractor. Inside the extractor, wood chips were contained in an 11-L basket able to hold up to 3 kg of chips immersed in the solvent (**Fig. 1**). The extractions were carried out in batches. The extractor was heated by a closed circuit jacket to the boiling temperature of the solvent, and the flux of the solvent was steady. The total time was 2 h, with 60 min in heating and 60 min in boiling.

The extract solution was continuously collected in a 50-L evaporator and was partially recirculated to the extractor. Flow rate, pressure, and temperature were measured and regulated at the levels required to maintain boiling. After 0.5, 1.0, 2.0, and 3.0 h of extraction, samples of the extract solution were collected from the evaporator through a valve (extraction was made during 9 h, and samples were collected every 30 min, although here only the results of 3 h are given). These samples were dried and weighted.

The results indicated the concentration of solid extract and were expressed in units of grams of extract per liter of extract solution (g/L). From the concentration of extract and the volume of extract solution, the total amount of extracted product was calculated and expressed as a fraction of the initial rosin in wood. This amount was estimated from the values listed in Table I.

At the end of each 9-h extraction, a sample of the extract solution was distilled by steam and separated into two phases. The organic phase of the distillate was analyzed by gas chromatography, using an UCOM-LB-550X column 2 m long and 1/8 in. in diameter, employing a thermal conductivity detector, at an oven temper-

ature between 100°C and 170°C, and heating at 2.5°C/min. The results of the analysis were compared to those of natural turpentine. The waste of the steam distillation was analyzed according to the list in **Table II.**

Paper production

The wood chips were washed with water and were broken up in a disc mill, a Sprout Waldron Model 105. A 25-L pilot plant digester with a stainless steel inner lining from ABC J. Wennbergs of Karlstad, Sweden, was used for cooking.

The digestion took place in neutral or alkaline medium without the addition of a buffer solution. The cooking liquors were heated by direct steam or by indirect heating, in a tubular exchanger. Vapor was generated in a Wabcock-Vaporax-300 S-15, which could work at a pressure of 14 kg/cm² and produce 300 kg/h of steam. Flow rate, pressure, and temperature were controlled and measured. Samples were collected by coil under 80°C, to avoid loss by evaporation.

Pulp properties were analyzed according to TAPPI methods. Kappa number was analyzed by T 236, extractables were determined by T 204, and whiteness was analyzed by T 217. The reactant sulfite consumed and the initial and final pH were also measured.

Experimental results

Wood extraction

Results of the analysis of samples collected from the evaporator at different time intervals are shown in **Table III** for the different solvents employed. Ethanol extracted the least amount of total rosin at every time interval. Among the remaining three solvents, trichloromethane demonstrated the greatest extraction rate after 2 h of extraction. This early high extraction rate could be due to the greater ability of trichloromethane to penetrate the wood.

After 9 h of extraction, the amounts of rosin extracted by diethylether and trichloromethane were approximately equal, and these amounts were greater than that extracted by propanone.

For all solvents, the concentration of extract in the extract solution increased in the first hour of the extraction and later progressively

I. Extractives content using different solvents

Solvent	Extractables, % on o.d. wood
Diethylether	2.73
Ethanol	2.60
Propanone	2.61
Tricholoromethane	2.57

TAPPI T 204.

Initial amount of wood = 2.0 kg.

II. Waste analysis of steam distillation from the liquid evaporator

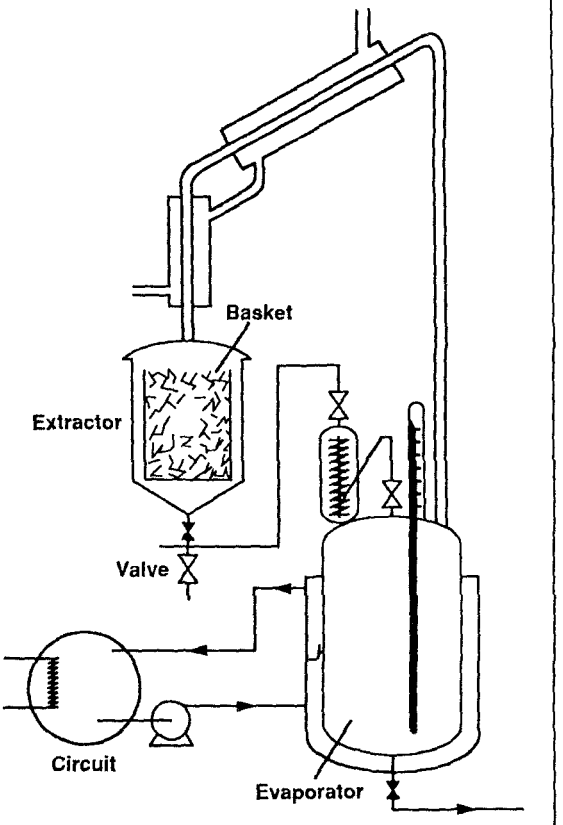
	ASTM*
Solids, %	D 269-52
Acidity	D 465-59
Saponification	D 464-59
Nonsaponification products, %	D 1065-56
Rosinic acid, %	D 1585-63
Fatty acids, %	D 1585-63
Abietic and neoabietic acids, %	D 3008-72
Ashes, %	D 1063-51

*American Society for Testing and Materials.

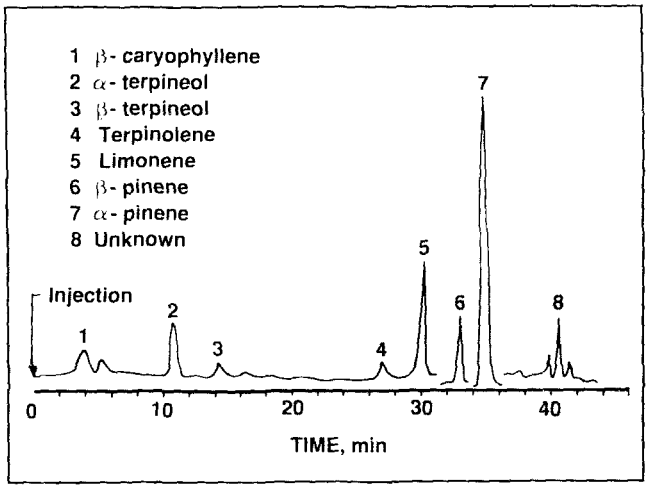
III. Experimental results in wood extracted with different solvents

Time, h	Extracted conc., g/L	Rosin extracted, g	Rosin in wood, g	Rosin fraction extracted
		Diethylether		
0.0	...	...	54.57	0.00
0.5	1.22	3.36	51.21	0.06
1.0	1.60	10.70	43.87	0.20
2.0	1.23	25.45	29.12	0.47
3.0	0.68	34.89	19.68	0.64
		Ethanol		
0.0	...	....	53.00	0.00
0.5	0.97	1.52	51.48	0.03
1.0	1.13	4.24	48.76	0.08
2.0	0.82	9.25	43.75	0.17
3.0	0.69	12.96	40.04	0.24
		Propanone		
0.0	...	...	52.20	0.00
0.5	1.50	3.49	48.71	0.07
1.0	1.76	12.85	39.35	0.25
2.0	0.35	24.46	27.74	0.47
3.0	0.33	28.71	23.49	0.55
		Trichloromethane		
0.0	...	...	51.40	0.00
0.5	1.46	3.37	48.03	0.07
1.0	1.89	13.33	38.07	0.26
2.0	0.61	26.95	24.45	0.52
3.0	0.40	32.17	19.23	0.63

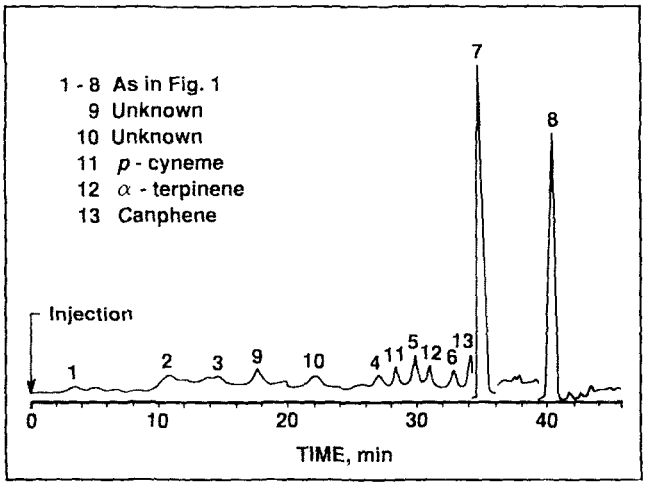
1. Diagram of the apparatus.



2. Analysis of a natural turpentine



3. Analysis of volatile products of wood extraction with trichloromethane



IV. Characteristics of solid products of extraction for different solvents and comparison with natural products

	Colophony	*Tall oil*	*Propanone*	*Ethanol*	*Trichloromethane*	*Diethylether*
Solids, %	0.05	4.0	6.43	3.16	7.36	3.04
Acidity index	170	162	151	157	150	147
Saponification index	175	168	189	186	181	180
Nonsaponification products, %	5.50	7.00	7.55	10.04	8.76	5.81
Oxidation products, %	0.50	3.0	17.00	18.02	16.20	15.40
Rosinic acids, %	93.00	33.0	48.71	57.93	61.26	61.13
Fatty acids, %	...	60.0	43.74	32.03	29.98	26.09
Abietic acid, %	26.00	33.0	7.15	5.23	...	6.80
Neo-abietic acid, %	24.00	...	8.79	9.77	...	6.32
Ashes, %	0.02	0.10	0.12	0.51	...	0.01

decreased. Thus, the rate of extraction increased up to 1 h but decreased thereafter. This finding is in agreement with the results of other researchers (*10–12*).

Extraction products

The chromatographic analyses of the volatile extract products were similar between the different solvents. This finding is in agreement with the results of others (*5, 6, 13–15*). **Figure 2** presents the analysis of natural turpentine; **Fig. 3** presents the analysis of product extracted by trichloromethane, as representative of all the solvents. The chromatograph of extracted product reveals more peaks,

and thus more impurities, than the natural turpentine.

The characteristics of the solid products are shown in **Table IV**, where they can be compared with those corresponding to a natural colophony (rosin) and a commercial tall oil. The characteristics of the extraction products are similar to those of a commercial tall oil. The acidity and saponification indices are lower for the extracted products than for those obtained from the live tree. Solid extraction products present a light amber color, and these products would be suitable for commercialization, even though it would be necessary to remove the fatty and rosinic acids.

V. Paper production with wood chips extracted with different solvents and nonextracted chips

	Blank	*Propanone*	*Ethanol*	*Trichloromethane*	*Diethylether*
Sodium sulfite consumed,[a] %	10.58	8.57	8.25	10.10	9.90
pH					
Initial	9.5	9.5	9.6	9.8	9.6
Final	6.7	7.2	7.7	7.0	7.0
Kappa no.	150.3	127.6	76.2	...	138.2
Yield,[a] %	83.2	82.5	82.5	91.2	88.5
Extractables,[b] %	2.91	0.44	0.54	0.48	0.31
Whiteness, %	41.15	44.55	43.36	42.12	42.4

[a]Percentage on unextracted dry wood.
[b]Percentage on dry pulp.

Paper production

After NSSC pulping ("neutral sulfite semichemical"), we obtained the results shown in **Table V**. The results with nonextracted chips have been included for comparison.

The extraction procedure with any of the solvents reduced the consumption of digestion reactants and decreased the drop from initial to final pH of the black dyes. Kappa number was reduced with all the solvents, decreasing as the polarity of the solvents increased.

Pulp yield was somewhat less with the use of hydrophilic solvents (ethanol and propanone) than the yield of nonextracted wood. Yield was much higher with the use of hydrophobic solvents (trichloromethane and diethylether).

The extracted contents of the pulp was decreased by 80–90%, and the whiteness of the pulp was greater with extracted wood. (Editor's note: The maximum amount of rosin extracted was 6%, and these percentages of 80–90% are not supported by data presented here. However, the authors maintain that these percentages are correct because 63% was obtained at 3 h and the work was continued until 9 h.) Other researchers (*16, 17*) have found similar results.

Conclusions

Wood extraction with solvents makes possible the recovery of some minor wood compounds that are ready for commercial use. Products produced with hydrophobic solvents have a higher content of rosinic acids.

The extracted wood chips can be used for paper production. The pulp obtained by NSSC process, from *Pinus pinaster* wood previously extracted is of a good quality and can substitute for unbleached bisulfite pulp in the production of newsprint grades. If hydrophilic solvents are employed, less consumption of reactant occurs, and the pulp presents a greater whiteness and a lower kappa number. On the other hand, hydrophobic solvents produce a greater pulp yield.□

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