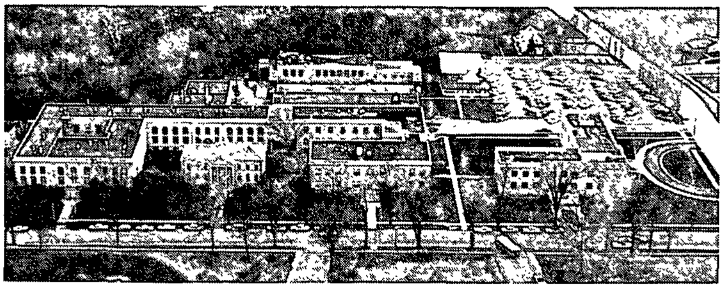

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 182

# SOLVENT PULPING — DISSOLUTION OR DISILLUSION?

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JUNE, 1986

**Solvent pulping - dissolution or disillusion?**

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Capital intensiveness, extensive pollution control requirements and a very large minimum economic mill size are well-known disadvantages of the otherwise desirable and well-established kraft process. Given the scarcity of alternatives, new processes invariably receive considerable attention and previously discarded ones are often reexamined in the light of new economic and environmental realities. Solvent pulping processes in both categories have recently begun to attract attention for these reasons.

The idea of physically dissolving the lignin in wood is not a new one. Kleinert proposed ethanol as a delignifying solvent more than fifty years ago (1). Since then numerous other solvents have been proposed, including butanol, glycerol, glycol, phenol, dioxane, dimethylsulfoxide, formic acid, and acetic acid. These have been variously proposed for use without any added catalyst, with acid catalysts, with added alkali or with added salts. A few examples of current interest are the APR process (2), in which wood chips are successively extracted with alcohol solutions of progressively lower lignin concentration; a process patented by Paszner and Chang (3), in which magnesium salts catalyze alcohol-water delignification; and the Battelle-Geneva process (4), which utilizes phenol as the solvent.

The most recent entry in the field is ester pulping, a process developed in the laboratory by R. A. Young of the University of Wisconsin and commercially by Biodyne Chemicals, Inc. of Neenah, Wisconsin (5). It has attracted vast media coverage, (e.g., 6-9) and has been promoted as a "revolutionary new pulping process." The pulping liquor is composed of water, acetic acid (to catalyze lignin hydrolysis), and ethyl acetate (to dissolve the resulting lignin fragments). The authors claim the process can delignify a variety of wood species to produce pulps with properties superior to those of the corresponding sulfite pulps.

In view of the significance of the benefits claimed and the wide publicity this process has received, we felt that it deserved a closer look. Consequently, we have carried out a limited number of experiments to gage its ability to pulp several softwood and hardwood species in addition to the two species, aspen and spruce, for which results have been reported (5). We report the results here.

**Results and discussion**

As shown by the data in Table I, aspen chips were easily pulped to a kappa number of 9.7 at 52.5% yield with good viscosity retention. Red oak, however, gave a pulp with a much higher kappa number, 71, when pulped under the same conditions. Eucalyptus was more readily pulped than oak, but the pulp had a much higher kappa number and a lower viscosity than the aspen pulp. Vacuum impregnation of the air-dried aspen chips had no effect on the results obtained with this species. These data support the previously reported effectiveness of this system for the pulping of aspen, a species that is also readily pulped by most conventional methods, but show that other hardwood species do not respond to ester pulping as well as aspen.

Attempts to pulp softwoods met with very limited success, as Table II shows. A liquor made up of equal volumes of the three components produced a coarse pulp of very high kappa number, 134, at a yield of 65% after 2 hours at 170°C. Changes in liquor composition, cooking time and liquor-to-wood ratio failed to reduce the kappa number to values below 100. Southern pine was even less responsive than white spruce.

Additional experiments, for which the results are not shown in Table II, were designed to exclude the possibility of lignin reprecipitation onto the pulp fibers during the fiberization or washing steps. After the cook, the digester charge was diluted with fresh liquor prior to fiberizing the cooked chips in a Waring Blendor, and the resulting pulp was washed either with further quantities of fresh pulping liquor or pure acetone. Pulping conditions were the same as those that produced the first pulp listed in Table II. The pulp fiberized and washed by dilution with fresh liquor had total yield 63.3%, screened yield 55.9%, and screened pulp kappa number 110; the corresponding figures for the acetone washed pulp were nearly identical.

On the basis of these results, it seems unlikely that this process is capable of converting softwoods to bleachable pulps. The manufacture of linerboard and similar grades would probably require longer cooking times than in the kraft process even if pulp properties were acceptable.

**Pulp properties**

The properties of triploid hybrid aspen ester pulp of 53% yield and kappa number 10 were determined after beating in a PFI mill to 420 mL Canadian Standard Freeness. They are compared to those of other aspen pulps in Table III. This pulp was superior to the sulfite pulp by all of the criteria listed; it was significantly stronger and had a much lower lignin content. In fact, this pulp was stronger and lower in lignin than the aspen pulp characterized by the inventors (5). Part of this difference may be attributable to the superior fiber properties of the triploid hybrid, relative to the more common varieties of aspen. The ester pulp was, however, significantly weaker than the corresponding kraft pulp, especially with regard to tear strength.

The literature data indicate that the ester pulps have properties that are similar to those of aspen pulps from the APR (ethanol-water) process. On the basis of very limited data, Paszner's modification of that process, using magnesium salts as catalysts, may produce a stronger pulp.

**Conclusions**

1. Ester pulping can be used to make aspen pulps of very low lignin content that have physical properties intermediate between those of kraft and sulfite pulps.

2. Other hardwoods are less readily pulped; conditions that resulted in an aspen pulp of kappa number 10 gave red oak and eucalyptus pulps of kappa number 71 and 30, respectively.

3. Softwoods are much less responsive. The process appears not to be capable of producing bleachable grades from either white spruce or southern pine.

**Experimental**

Air dried wood chips of triploid aspen, spruce, pine, red oak, and eucalyptus (Portuguese variety) were used for the purpose of this study. The pulping agent in all the experiments was a mixture of ethyl acetate, acetic acid, and water. Wood to liquor ratio was 1:6 and in some cases 1:8 and pulping temperature was 170°C. Pulping experiments were carried out in 500 mL batch type stainless steel autoclaves housed in an oil heated digester. The autoclaves rotate 360 degrees in the heated oil medium. The system is controlled by a Honeywell digital control programmer DCP-7700. Pulps were fiberized in a Waring Blendor after dilution with water (1:1 to simulate the effects of displacement of solvent with water in the pulp mill). An exception was the series of cooks in which fresh solvent was used for dilution prior to fiberization. The resulting pulps were washed with a 50:50 mixture of alcohol:water or acetone. Unscreened pulp yields were recorded and kappa number and handsheet properties were determined by TAPPI test methods.

**Acknowledgments**

The skilled experimental assistance of Mr. V. J. Van Drunen is gratefully acknowledged.

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I Ester pulping of hardwoods[a,b]

| Wood type | Kappa no. | Yield | Viscosity |
|---|---|---|---|
| Aspen | 9.7 | 52.5 | 31 |
| Aspen[c] | 9.5 | 52.8 | 33 |
| Red oak | 71.0 | 51.9 | -- |
| Eucalyptus | 30.0 | 51.5 | 19 |

[a]Liquor composition: 1:1:1 acetic acid-ethyl acetate-water by volume.
[b]Pulping conditions: 90 min to 120 min at 170°C, 6 mL liquor/g o.d. wood; air-dried chips; pulp washed with acetone.
[c]After vacuum impregnation of the chips.

II Ester pulping of softwoods[a,b]

| Species | White spruce | | | | | | | S. Pine | |
|---|---|---|---|---|---|---|---|---|---|
| % Acetic acid, vol. | 33 | 33 | 20 | 20 | 20 | 20 | 70 | 33 | 20 |
| % Ethyl acetate, vol. | 33 | 50 | 40 | 40 | 40 | 40 | 20 | 33 | 40 |
| Liquor-to-wood, mL/g | 6 | 6 | 6 | 6 | 6 | 8 | 8 | 6 | 6 |
| Time at 170°C, hr | 2 | 2 | 2 | 3 | 4 | 4 | 4 | 2 | 4 |
| Yield, % o.d. wood | 65.4 | 81.7 | 70.4 | 68.0 | 57.6 | 57.0 | 64.6 | 65.1 | 59.8 |
| Kappa no.[b] | 134 | -- | 164 | 178 | 118 | 108 | 101 | 141 | 141 |

[a]Pulping conditions: Air-dry chips impregnated with liquor in vacuum; 90 min to 170°C.
[b]Unscreened pulp.

III Comparison of aspen pulp properties of various solvent systems

| Property | Sulfite | Kraft | Ester | Biodyne | APR | Paszner |
|---|---|---|---|---|---|---|
| Yield | 44% | 54% | 52.6% | 64% | 53% | 60% |
| Kappa no. | 20 | 12.3 | 9.6 | 23 | 24 | 25 |
| Freeness (CSF) | 450 | 465 | 420 | 397 | -- | -- |
| Burst factor | 31 | 50.7 | 34.2 | 33 | 29.6 | 50 |
| Tear factor | 47 | 107 | 53 | 47 | 56 | 72 |
| Tensile, km | 5.9 | 8.7 | 7.1 | 7.1 | 5.6 | 9.0 |
| Bulk, cu cm/g | 1.36 | n.d.[a] | n.d.[a] | 1.34 | 1.5 | -- |
| Reference | (5) | --[b] | --[b] | (5) | (10) | (11) |

[a]n.d. = not determined.
[b]This work; triploid hybrid aspen.