

Tall oil recovery and the effects of solids content, β -sitosterol, acetic acid, and liquor source

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ABSTRACT *The minimum tall oil solubility (i.e., maximum tall oil recovery) occurs at a dissolved solids content of about 30% for pine liquor and at different solids contents for mixed pine and gum liquors. Temperature has a small effect, but settling time can have a substantial influence on the recovery of tall oil soap. Finally, the addition of β -sitosterol has no effect, while the addition of acetic acid in small amounts doubled tall oil solubility.*

KEYWORDS

Black liquor
Chemical analysis
Recovery
Solids content
Sterols
Tall oil

Approximately 80% of the available tall oil sent to the skim tank in a kraft mill is recovered, while the remainder is burned in the recovery furnace (1). Any increase in recovery efficiency in the skim tank translates directly into increased yield and profit. Moreover, the separation of tall oil soap from black liquors enhances the efficiency of subsequent chemical recovery from black liquors (2). The operational variables that dictate the extent of separation of soap from liquor are:

- Liquor source (softwood or hardwood)
- Temperature
- Settling time
- Liquor composition (dissolved salts, organic compounds, etc.).

The chemical variables that govern tall oil solubility are pH, salt concentration, and the proportions of fatty acids, resin acids, and unsaponifiables.

The source of the liquor determines the constitution of the tall oil and, to some extent, the resulting pH of the liquor. Tall oil from hardwoods, such as gum and oak, contain only trace amounts of resin acids and substantial

percentages (on a weight/weight basis) of unsaponifiables—typically 10–40%. Softwoods contain 30–50% resin acids and less than 10% unsaponifiables. The remainder of both hardwood and softwood tall oil is made up of fatty acids that are mostly unsaturated and that are well represented by oleic, linoleic, and linolenic acids. The unsaponifiables are largely long-chain alcohols, esters, and sterols, as well as some hydrocarbons (3). The most common sterol is β -sitosterol. One of the primary effects of adding hardwood liquor to softwood liquor is that it increases the percentage of unsaponifiables—i.e., it increases the mole ratio of neutral organics to soaps.

Despite the differences between softwood and hardwood liquors, there have been few studies dealing with the recovery of tall oil soap from liquor mixtures. Laboratory studies include the work by Lenz (4), who examined the effects of mixing fatty and resin acids with liquor mixtures, and Palonen *et al.* (5), who considered the behavior of model solutions composed of sodium abietate, sodium oleate, and sodium chloride. Attempts to quantify the effects of blending softwood and hardwood mixtures in mill operations are summarized by Drew and Propst (1). Rousseau *et al.* (6) discuss the difficulty in reconciling the differences between laboratory and plant data, and there remains considerable uncertainty in the quantitative influence

of the chemical variables that govern tall oil solubility.

In the study presented here, residual tall oil solubilities in pine and in mixtures of pine and gum liquors were determined as functions of solids content and pine-to-gum volume ratios. In associated experiments, small amounts of β -sitosterol, one of the main residual unsaponifiables in tall oil, and of glacial acetic acid were added to the liquors. Finally, although most of the results were derived at near equilibrium, there are implications from kinetic experiments about the approach to steady-state compositions.

Results and discussion

Settling time experiments

The first stage of the experimental program was to determine the time required for tall oil soap to form a cream from black liquor. There is evidence that tall oil soap separates as a colloidal dispersion. First, the settling times are long, implying that the soap particles are of colloidal dimensions. Second, by centrifuging, the sedimentation times can be decreased (7), and the total recovery can be enhanced.

The rates at which tall oil soaps separate at 60°C from black liquor samples that had been vigorously mixed and that contained 14.7% and 24.5% solids are shown by the data in Fig. 1. Even after 6 h of settling, the tall oil soap has not achieved equil-

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ilibrium between soap and residual aqueous phases. By contrast, Lenz (4) reports equilibration times of 10–20 min in pine and mixed pine and hardwood liquors. The differences in observations could be related to variations in mixing conditions or to an extreme sensitivity of soap particle density and size to changes in black liquor composition. Regardless of the reason, the data show the importance of designing for appropriate settling times in skimming tanks.

Solids content

The residual tall oil concentration in settled black liquor samples is a function of the total dissolved solids contents in the liquor (1). Based on the settling time experiments, residual tall oil concentrations were measured as functions of solids content for pure pine and pure gum liquors after 3 h of settling at 60°C to approximate steady-state conditions in the settled system. In Fig. 2, the results for pine liquor show a minimum residual tall oil concentration in settled black liquor at a solids content of about 28–30%. The tall oil content is expressed as mass units of tall oil per 1000 mass units of solids because the total amount of solids in the processing system is constant and the solids concentration is varied only by adding or removing water.

The decrease in residual tall oil with increasing solids content, below a solids content of about 30%, can be explained by simple salting out of the soap. Above 30% solids content, there is no obvious explanation for the increase in residual tall oil concentration with increasing solids content. Palonen *et al.* (5) have shown that the solubility of sodium oleate increases with increasing sodium chloride concentration when the separating soap-rich phase is a hexagonal liquid crystal. However, when the separating soap-rich phase is a lamellar liquid crystal, increasing the sodium chloride concentration results in a decrease in sodium oleate solubility. This conclusion holds true for one-to-one molar mixtures of sodium oleate and sodium abietate, the two main representatives of fatty and resin acids, respectively, in tall oil. In pure pine liquor, the separating soap-rich phase may switch in morphology from lamellar liquid crystalline to hexagonal liquid crystalline at a solids content of about 30%.

The residual tall oil in pure gum liquor is shown as a function of solids

content in Fig. 3. Within experimental uncertainty, the residual tall oil in settled gum liquor is constant at about 0.20 g of tall oil per 1000 g of solids. Therefore, there is not sufficient tall oil in gum to saturate the black liquor. The effect of evaporating water is to increase the tall oil concentration in proportion to the increase in solids concentration.

Mixed-liquor experiments

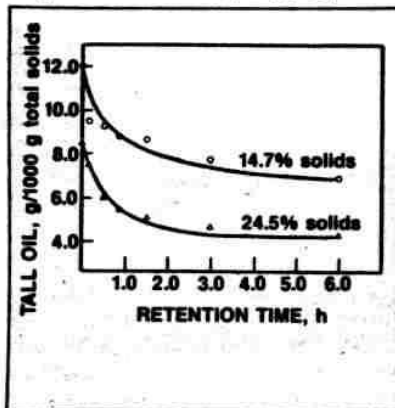
In addition to measuring residual tall oil concentrations in pure liquors, we also performed experiments with mixed pine and gum liquors. Three sets of stock black liquor mixtures were prepared to contain 12%, 25%, and 50% gum liquor by volume. Each stock solution initially had solids contents of about 14–15%. Portions of each

stock solution were concentrated by evaporation to contain solids contents of about 23–24% and of about 29–30%. Each of the samples was allowed to settle for 3 h at 60°C before analyses were performed to determine residual tall oil concentrations. The results are given both in Table I and in Fig. 3.

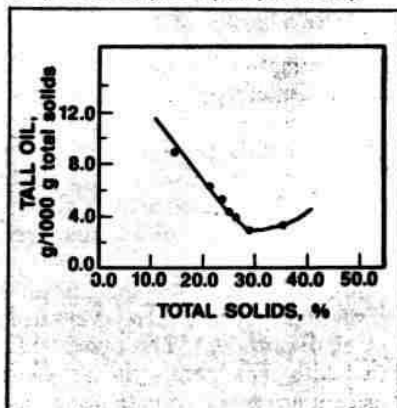
The general effect of adding gum to pine liquor was to decrease the residual tall oil concentration. However, this does not necessarily imply increased recovery of tall oil, because there may in fact be less total tall oil to recover upon dilution with gum liquor.

Second, the minimum tall oil concentration is at lower solids content (about 22% solids) for the 50% gum liquors than for pure pine liquor. As mentioned, this may be the result of a change in the morphology of the sep-

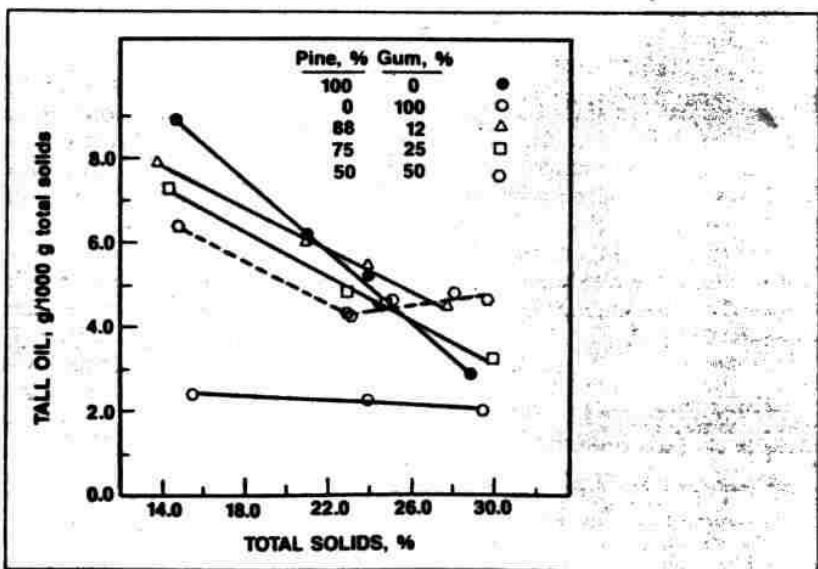
1. Dependence on settling time of residual soap content in black liquor (60°C).



2. The effect of solids content on residual soap in settled pine liquor (60°C, 3 h).



3. The effect of solids content on residual soap in settled mixtures of pine and gum liquors.



arating soap-rich phase from hexagonal to lamellar liquid crystalline. The physical explanation for the lowering in solids content of this phase transition from pure pine to a 50% pine and 50% gum liquor can be found in a change in the composition of the tall oil or in a change in the pH of the parent black liquor. According to Zinkel (8) and Rousseau *et al.* (6), the neutrals content and the strong acids content of the black liquor increases slightly in going from pure pine to a 50% pine and 50% gum liquor, while the weak acids content decreases slightly. This compositional change may also change the solids content at which a structural change in the soap-rich phase occurs. Table I shows that the pH of the parent black liquor is lower in liquors of higher gum content.

I. Solubility of tall oil soaps in mixtures of gum and pine black liquors

Specimen source	Initial solids content, %	Tall oil on solids, %	pH
Original pine	14.8	0.89	12.7
Original gum	15.5	0.24	9.3
12% gum	13.9	0.78	12.5
25% gum	14.4	0.73	12.3
50% gum	14.8	0.64	10.4
Original pine	21.2	0.62	12.8
Original pine	24.1	0.52	12.8
Original gum	24.0	0.22	9.4
12% gum	20.9	0.60	12.8
25% gum	23.0	0.49	12.7
50% gum	23.3	0.43	11.0
Original pine	29.1	0.28	12.9
Original gum	29.5	0.20	9.5
12% gum	27.8	0.44	12.8
25% gum	30.3	0.33	12.6
50% gum	29.8	0.46	11.0

60°C, 3 h

II. Solubility of tall oils as a function of pH

Sample	β -sitosterol on liq., wt. %	Total solids, %	Initial pH	adjusted pH	Tall oil on solids, %
1	...	25.7	12.9	...	0.43
2	...	27.9	12.9	11.0	0.79
3	0.1	26.1	12.8	...	0.42
4	0.1	30.7	12.8	11.0	0.77
5	0.4	26.2	12.8	...	0.41
6	0.4	30.3	12.8	11.0	0.72

The pH was adjusted by addition of an 8M solution of acetic acid.

Adding β -sitosterol and acetic acid

To explore the effects of neutrals content and pH on residual tall oil concentrations, experiments were performed in which β -sitosterol and acetic acid were added to black liquor solutions of varying solids content. Three samples of pure pine liquor of 26–30% solids content were intentionally doped with either β -sitosterol or acetic acid. The results of these experiments are presented in Table II.

The amount of added β -sitosterol is substantial at 0.4% by weight, based on total liquor mass, for Samples 5 and 6. (The total tall oil concentration in these two samples was only 0.1–0.2 wt. %, based on total liquor mass.) Nonetheless, the addition of β -sitosterol has a negligible effect on residual tall oil concentration.

III. Pulping conditions

Process variables	Sweetgum	Pine
Active alkali, %	18	20
Sulfidity, %	25	25
Liquor:wood	3.5:1.0	4.0:1.0
Max. temp., °C	170	170
Time to temp., min.	90	90
Time at temp., min.	60	105
Kappa no.	18	32

*As Na₂O, based on wood.

The addition of acetic acid, which results in a lowering of the black liquor pH from about 12.8 to 11, has a pronounced effect on tall oil concentration, with the residual tall oil concentration nearly doubled in all three cases. Whether this is caused by an increase in hydronium ion or acetate ion concentration is not known at this point. The acetate ion could function as a cosurfactant in stabilizing swollen micellar aggregates in solution, thereby increasing the residual tall oil concentration. Additional experimentation is necessary to determine the precise mechanism causing this behavior.

Experimental procedure

The wood, from local forests in North Carolina, was debarked, chipped, and stored prior to use in polyethylene bags in a cold room at 0°C. Stock solutions of black liquor were obtained by pulping pine and sweet gum chips according to the conditions shown in Table III. The washing procedure was designed to simulate pulp mill operation and to yield a stock black liquor solution of from 14% to 15% solids content. The details of the washing operation are given elsewhere (6).

Residual tall oil concentrations were measured by placing a well-mixed black liquor sample of known solids in a graduated cylinder and allowing gravity to separate the liquor and soap. An aliquot of separated liquor was carefully withdrawn, and tall oil soap and solids content were determined using the method in Ref. 9.

Literature cited

- Drew, J. and Propst, M., Tall Oil, Pulp Chemicals Association, New York, 1981.
- Drew, J., Pulp Chemicals Association Meeting, Point Clear, 1985.
- Conner, A.H. and Rowe, J.W., JAOCS 52: 334(1975).
- Lenz, B.L., Tappi 60(5): 121(1977).
- Palonen, H., Stenius, P., and Strom, G., Svensk Papperstid. 12:R93 (1982).
- Rousseau, R.W., Kassebi, A., and Zinkel, D.F., AIChE Symposium Series 239, 80: 1(1983).
- Drewsen, V., U.S. Pat. 1,778,523 (1930).
- Zinkel, D.F., Tappi 58: 109(1975).
- Saltzman, W. and Kuiken, K.A., Tappi 42: 873(1959).

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