

**MAXIMIZATION OF SOAP YIELD IN
ALKALINE PULPING**

Project 3267

**Report Two
A Final Report
to**

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 9, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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ABSTRACT

As reported previously, the crude, extractable tall oil (CTO) in commercial kraft black liquor was found to be stable over a period of at least 15 months when the liquor was stored in inert, sealed containers. Analysis of random samples from a series of such CTO by gas chromatography (GLC) showed the usual composition with respect to resin and fatty acids.

The solubility of synthetic mixtures of the soaps (sodium salts) of refined tall oil fatty and resin acids was determined in 1N sodium hydroxide, diluted skimmed kraft black liquor, and skimmed partially concentrated black liquor. The higher the relative content of resin acids and the stronger (higher concentration of solids) the liquor, the higher the solubility of tall oil soap. The lowest concentrations of soaps were present in the sodium hydroxide.

Crude tall oil was readily recovered from the laboratory kraft cooking of lightered wood (resin-soaked wood from a slash pine treated with Paraquat). When the lightered wood was pulped in the presence of additional tall oil fatty acids, the formation of skimmable soap was favored. Analysis by GLC of the CTO from lightered wood pulped in the laboratory under a variety of conditions gave results which were consistent with tall oils in general.

The fiberization of cooked chips with the concomitant exposure of the tall oil soaps to oxygen (air) was suspected as the cause of the increase of dehydroabietic acid at the expense of abietic acid. However, controlled experiments indicated that the resin and fatty acids are stable to mechanical fiberization of cooked chips even in the presence of pure oxygen.

Based on the results of the work on this project, the maximization of the yield of tall oil in the kraft process is dependent chiefly on the practice at each mill. The inherent nature of kraft black liquor may afford the recovery of 80-90% of the available CTO provided the equipment and engineering practice are designed and adjusted to take advantage of that potential.

STATEMENT OF THE PROBLEM

In the development of kraft recovery practices it was learned empirically that when fresh southern pinewood was pulped by the kraft (sulfate) process, maximum yields of soap skimmings are obtained if the black liquor is skimmed from a partially concentrated liquor of from 25-27% solids held in a tank at an elevated temperature for approximately one hour. The conditions necessary for maximized soap skimmings are operative when fresh southern pinewood is pulped by the kraft process, but such conditions no longer exist at a large number of kraft mills. For a variety of reasons many kraft mills have introduced parameters into their mill practice which cause the ideal conditions necessary for optimized soap skimmings to depart from the permitted range. Such parameters include use of hardwood in the kraft furnish (pulped together or separately with combined black liquors), outside chip storage, long-term roundwood storage, use of decayed and inferior wood, use of bark-containing and whole wood chips, use of resin-soaked chips, etc. As a result, most mills are experiencing much lower tall oil recoveries. A detailed account of the subject was reported by Bolger and Hopfenberg in 1965 (1).

OBJECTIVES

As set forth in our original proposal, the objectives of the experimental program of this Project are:

1. To determine the composition of kraft black liquors under conditions of low and high yields of soap skimmings.
2. To relate the yields of soap to mill operational parameters.
3. To establish empirically the effects of changes in operational parameters on maximization of the yield of soaps.
4. To make a theoretical analysis of the solubility behavior of low and high yield soap systems and establish how the implications of this analysis can be used to maximize the yield of tall oil in a given kraft mill system.

REVIEW OF OBJECTIVES AND PROGRESS TOWARD THEIR ATTAINMENT

- On Objective 1. The first objective proved to be unattainable due to the considerable day-to-day variation in the efficiency of recovery of tall oil soaps in a given mill. Cumulative data over a period of days (or weeks) would be required to sort out the efficient and inefficient mills. Such evaluations should be based on to-the-skimmer and from-the-skimmer soap contents of black liquor. Because the precipitation of soap undoubtedly begins before the stream of black liquor reaches the skimmer, representative samples of whole liquor are difficult to obtain and considerable scatter may be inherent in the analysis of such two-phased systems.
- On Objective 2. Without the evidence to classify a mill as "efficient" or "inefficient," no attempt could be made to relate "operational parameters" to yields of soap for a given mill. To attain this objective for a mill would require considerable study of a mill's equipment and processes. This would be mainly an engineering study.
- On Objective 3. In the absence of data for "operational parameters" (Objective 2), it was not possible to "establish empirically the effects of changes in operational parameters on maximization of the yield of soaps."
- On Objective 4. Wherever possible, basic and theoretical information was used in work on this project. The "solubility behavior" of the liquors proved to be quite uniform from mill to mill and is an unlikely factor in soap yields. The most important factor would appear to be the bulk density of the coagulated precipitate of the tall oil soap which would be critical in soap skimming. This, in turn, appeared to be partially dependent upon entrained air. Testing

of this hypothesis was beyond the scope of this project.

Some important theoretical factors in the recovery of tall oil were considered recently by Roberts, Österlund, and Axberg (2).

The presence of "liquid crystals in systems of rosin and fatty acids" may be evaluated eventually in schemes to increase the efficiency of tall oil recovery.

INTRODUCTION

The results of three sets of experiments were reported in Progress Report One (3): (a) crude tall oil contents (CTO) of commercial black liquors before and after skimming, (b) production of CTO in laboratory kraft cooks, and (c) preliminary work with high performance liquid chromatography in the analysis of CTO. Copies of the "Abstract" and "Summary and Conclusions" have been reproduced in Appendix I of this report.

Work covered in this report extended the study of tall oil present in commercial black liquors and that produced in laboratory kraft cooks which included lightered (resin-soaked) wood. Other experiments to complete the project included solubility measurements of CTO and of synthetic mixtures of fatty and resin acids in black liquors, and the possible effects of chip fiberization on compositional changes in the CTO. The results are summarized in the "Summary and Conclusions," which represent the findings of the entire project.

RESULTS AND DISCUSSION

RECOVERY OF TALL OIL FROM STORED COMMERCIAL BLACK LIQUORS

The possible loss of extractable, crude tall oil (CTO) upon prolonged storage of partially concentrated black liquor was investigated and, in part, the results were presented in Report One (3). Additional aliquots of these black liquors were analyzed in May, 1976, and the results are summarized in Tables I and II.

Some of the results summarized in Table I were reported previously (3), and errors in the first report were corrected.

The data in Columns 4 and 6, Table I, showed the general consistency of the results for the CTO contents of these black liquors with no apparent losses due to storage (see, also, Table II). In addition to total CTO contents, liquors were cleared of suspended solids by filtering through coarse cotton plugs and the filtrates were analyzed for dissolved CTO. The results are listed in Column 5 and show a marked uniformity. From these data and the data for total CTO in each sample (Column 6) the amount of skimmable soap (Column 7) present in both the unskimmed and the skimmed liquors was determined. Even though somewhat less soap may have remained in solution upon long standing in comparison with the liquors as received, these amounts of extractable CTO probably represent the limit upon which the efficiency of skimming may be based. Thus, the "skimmable soap" in the from-the-skimmer liquors (Column 7) represented 10-20% of the skimmable soap originally present and may be recoverable, in part, by additives and/or improved equipment and practice (1).

TABLE I
RECOVERY OF CRUDE TALL OIL (CTO) FROM COMMERCIAL BLACK LIQUORS
BEFORE AND AFTER ONE YEAR'S STORAGE

From Stored Black Liquors Analyzed 5-17-76											
Symbol	Company, location of mill	Solids Content % o.d. solids, weight basis of liquor ^a		CTO, % o.d. liquor solids ^{a,b}		CTO Dissolved in Black Liquor, % o.d. liquor solids (g/100 g)		CTO in Sample, (includes precipitated scaps), % o.d. solids		CTO as Skimmable Soap, % o.d. solids (by difference)	
		To Skimmer	From Skimmer	To Skimmer	From Skimmer	To Skimmer	From Skimmer	To Skimmer	From Skimmer	To Skimmer	From Skimmer
OI	Owens-Illinois, Inc. Valdosta, GA	28.7	31.7	1.24	0.39 (0.128)	0.34;0.31 (0.097;0.089)	0.33 (0.106)	1.88	0.64	1.57	0.31
TH	Thilmany Pulp and Paper Co. Kaukauna, WI	28.0	31.6	1.76	0.48 (0.138)	0.31 (0.088)	0.26 (0.081)	1.88	0.54	1.57	0.28
BR	Brunswick Pulp and Paper Co. Brunswick, GA	27.2	27.5	1.83	0.74 (0.204)	--	0.32 (0.089)	1.49	[3.91] ^c	--	[3.59] ^c
SC	Scott Paper Co. Mobile, AL	18.0	23.4	2.13	0.55 (0.129)	0.45 (0.081)	0.38;0.29 (0.073;0.067)	1.97	0.53 0.41	1.52	0.15 0.12
			19.3 22.5		-- 0.36		0.31 (0.069)		0.53		0.22
HM	Hammermill Paper Co. Selma, AL	21.3	20.9	1.99	0.78 (0.163)	0.30 (0.066)	0.34 (0.072)	2.87	0.84	2.57	0.50

^aInitial results, from Report One. Samples analyzed March-June, 1975.

^bNumbers in parentheses are CTO expressed as weight-percent of black liquor.

^cThis result appears to be in error due possibly to a sampling error.

TABLE II
EXTRACTABLE CTO FROM UNSKIMMED BLACK LIQUORS AFTER STORAGE^a

Experiment Company	1		2		3		4		5		6	
	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO, %	Date Analyzed	CTO % o.d. Solids
Thilmany	3-21-75	1.63	5-7-75	1.76	6-30-75	2.12	10-17-75	1.81	2-2-76	1.55	5-17-76	1.88
Owens-Illinois	3-26-75	1.26					10-17-75	1.90	1-30-76	1.51	5-17-76	1.88
Scott					6-9-75	2.12	10-21-75	1.54 1.97	2-4-76	2.30	5-17-76	1.97
Brunswick	3-25-75	1.83					10-20-75	2.03	2-2-76	1.15	5-17-76	1.49
Hammermill	4-15-75	1.98					10-20-75	2.45	2-3-76	1.68	5-17-76	2.87

^aMost of these data appeared in Report One, Table V, page 12.

In Table II data for the recovery of CTO from stored to-the-skimmer liquors were up-dated to include the final series of results obtained in May, 1976. The results support the previous conclusion (3) that tall oil components are stable indefinitely when black liquors are stored at room temperature in inert containers with the exclusion of air.

APPARENT SOLUBILITY OF REFINED TALL OIL ACIDS IN SODIUM HYDROXIDE
AND IN BLACK LIQUOR

One of the obvious parameters, which determine the amount of skimmable soaps on kraft black liquors, is the solubility of the soaps in the black liquor. Presumably the sodium salts (soaps) of fatty and resin acids, when present in excess of the saturation levels, barring cases of supersaturation, form precipitates which may be recoverable by skimming. Except for inefficient skimming and solid soap particles suspended in the body of the liquor beyond the reach of the skimmer, only dissolved, and, therefore, inaccessible, tall oil soaps would escape recovery.

In order to determine the possible role of solubility in soap formation and recovery, synthetic mixtures of refined tall oil fatty acids (FA) and resin acids (RA) were prepared in (a) sodium hydroxide, (b) dilute black liquor, and (c) partially concentrated black liquor. The results are summarized in Tables III-V and Fig. 1.

Solubility of Tall Oil Acids in Sodium Hydroxide

Stock solutions of the tall oil fatty and resin acids, as their sodium salts, were prepared in water. Synthetic mixtures of FA and RA were prepared from the stock solutions and were combined with sodium hydroxide at 90°C so that the final mixtures were 1N in sodium hydroxide. The results are shown in Table III and Fig. 1. The salts of the resin acids were somewhat more soluble than those of the

TABLE III
SOLUBILITY OF TALL OIL ACIDS IN SODIUM HYDROXIDE

Flask No.	Combined 1%, stock solutions, ml		Behavior Upon Mixing with Sodium Hydroxide Solution After 20 Hours Standing at Room Temperature	Solubility of FA and RA in Sodium Hydroxide, g/100 g soln.
	FA	RA		
1	0	100	Flocc. ppt. on bottom of flask	0.045
2	5	95	Ppt. of small flocs on bottom of flask	0.035
3	10	90	Ppt. of small flocs on bottom of flask	0.036
4	20	80	Finely divided ppt.; cloudy supernatant	0.032
5	40	60	Clear supernatant sticky (oily) ppt.	0.040
6	50	50	Flocculant ppt. from surface to bottom	0.026
7	60	40	Flocculant ppt. from surface to bottom	0.012
8	80	20	Fine ppt. with some foam on liquor surface	0.016
9	90	10	Flocculant ppt. in upper layer of liquor	0.012
10	95	5	Translucent, liquor; oily ppt. on sides of flask; foam and ppt. on liquor surfaces	--
11	100	0	Clear liquor; foamy ppt. on liquor surface	0.0092

TABLE IV

SOLUBILITY OF TALL OIL ACIDS IN DILUTE KRAFT BLACK LIQUOR

Flask No.	Combined 1% Stock Solutions, ml		Behavior Upon Mixing with Kraft Black Liquor and 20 Hours Standing at Room Temperature	Solubility of Combined FA and RA in Black Liquor, g/100 g
	FA	RA		
1	0	100	Finely divided brown ppt. (sludge) on bottom of flask	0.124
2	--	--		--
3	10	90		0.111
4	20	80		--
5	--	--		--
6	50	50	Finely divided brown ppt. in upper half of liquor; small amount of soap on the surface of the liquor	0.069
7	60	40		0.054
8	80	20		--
9	90	10		0.035
10	--	--	Definite soap layer; finely divided ppt. in the upper third of the liquor	--
11	100	0		0.029

TABLE V

SOLUBILITY OF TALL OIL ACIDS IN CONCENTRATED, SKIMMED KRAFT BLACK LIQUOR

Digester No.	Tall Oil Acids Added to 300 ml of Black Liquor		RA, g	Behavior After 20 Hours Standing at Room Temperature	Solubility of CTO Extracted, g/100 g
	FA g	Rel. Amount, %			
Control	0	0	0	Black liquor	0.115
1	0	0	2.0	Suspended soap >5 cm in upper part of liquor; no sludge	0.159
2	0.2	10	1.8	Approximately 4 cm finely divided soap in liquor; no sludge	0.157
3	0.5	25	1.5	Finely divided soap layer; no sludge	0.138
4	1.0	50	1.0	Foamy soap scum	0.124
5	1.5	75	0.5	Foamy soap scum	0.148
6	1.8	90	0.2	Foamy soap scum	0.138
7	2.0	100	0	Thin foamy soap scum	0.120

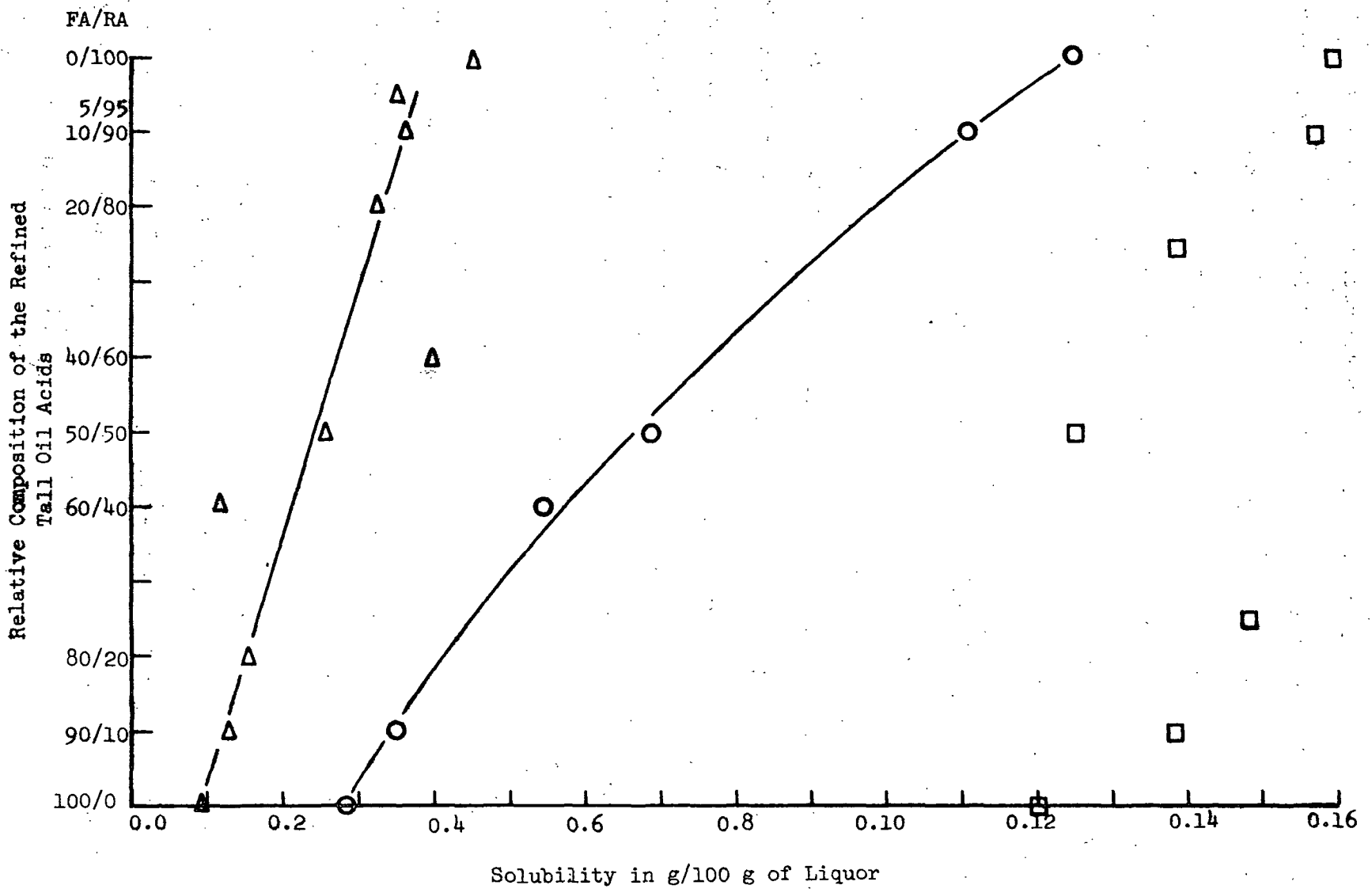


Figure 1. Solubility of Refined Tall Oil Acids in Sodium Hydroxide and in Kraft Black Liquor

fatty acids with the intermediate mixtures approximating arithmetical averages of the two types of acid. The appearance of the precipitated soaps was generally consistent with the previous observation (4) that resin acid soaps tend to form a sludge and that fatty acid soaps tend to entrain air to form a floating scum. The precipitates of mixtures tend to form floating soap layers when sufficient air (or other gases) becomes entrained in the precipitate. Otherwise the precipitates sink and form a sludge.

Solubility of Tall Oil Acids in Dilute Black Liquor

Synthetic mixtures of fatty and resin acids were prepared in a way similar to that described above with sodium hydroxide except that a skimmed commercial black liquor (21% solids) was used in place of the sodium hydroxide. The final solutions were approximately 11% o.d. solids. The results, shown in Table IV and Fig. 1, were similar to those obtained with sodium hydroxide except that the soaps were somewhat more soluble in the black liquor. This behavior may be due to a dispersant action of some of the organic substances derived from the wood, but this idea would require systematic testing to elucidate the point.

The appearance and behavior of the precipitates were consistent with the possible role of fatty acid salts in the formation of skimmable soaps. Thus, until the fatty acids in the mixture of FA and RA had increased to approximately 1:1 there was little tendency of the precipitate to float.

Solubility of Tall Oil Acids in Concentrated Kraft Black Liquor

In the third solubility experiment FA and RA mixtures were added directly to partially concentrated, skimmed black liquor (32% solids) according to the proportions listed in Table V. The mixtures in black liquor were sealed in seven digesters, raised to 170°C, held at 170° for ten minutes to attempt to dissolve the

acids, cooled to 90°, and the contents of each digester poured into a beaker. After standing at room temperature for twenty hours, the character of each precipitate was recorded and the dissolved CTO was determined. The results, Table V and Fig. 1, showed considerable scatter in the data, but the trends were similar to those observed for solutions of tall oil acids in sodium hydroxide and in dilute black liquor. Despite the high concentration of solids in the liquor, the tall oil soaps were more soluble per unit weight of solution than in the two previous experiments. Possible reasons for this behavior, such as the dispersant action of organic substances (1), were not tested. However, the solubility does not seem excessive with respect to the consequent losses of tall oil in practice.

Based on the measured solubilities and the observed nature of the precipitates, the presence of fatty acids in proportions of 50 to 100% of the mixtures appeared to favor the separation of skimmable soap layers.

In reviewing some of the implications of the solubility experiments, it seems likely that:

1. Optimum yields of tall oil soaps may depend more upon the mechanical efficiency of skimming than upon soap solubility.
2. Mixtures in which the ratios of fatty acids to resin acids are 1:1 or greater, may favor the formation of skimmable soap layers.
3. Based on tall oil soap solubility, the concentration of black liquor solids which is most efficacious for soap skimming may be of minor importance. Any salting-out of tall oil soaps appears to be more than balanced by some dispersant effect, possibly due to dissolved organics from the wood (1).

KRAFT PULPING OF LIGHTERED SLASH PINE WOOD AND EXTRACTIVE-
FREE LOBLOLLY PINE

A series of kraft cooks was run with lightered wood (LW), in this case, a resin-soaked wood approximately 30% extractives, from a slash pine which had been treated with "Paraquat" (5). The purposes were (a) to determine the suitability of such resin-soaked wood for the production of tall oil under the conditions of the experimental kraft process in hand, and (b) to test soap formation in systems low in fatty acids. The results are summarized in Table VI.

In digester A, Table VI, CTO was obtained for refined tall oil acids cooked as a control without wood. Approximately 75% of the original material survived the cook. In digester B, 5 g of LW chips produced a total CTO of 56% based on the extractives (1.5 g) present in the LW. In digesters C and D, LW chips were mixed with extractive-free loblolly pine chips (ELC), and the recovery of CTO, 46-52%, was consistent with that from LW chips alone. In digesters E and F, tall oil fatty acids (FA) were added. It may be noteworthy that the resins from lightered wood (digester D, especially) left much more CTO in and on the cooked chips than was found in the other cases. The addition of tall oil fatty acids, by contrast, in digesters E and F favored the recovery of CTO from the decanted liquors.

The aspen wood (digester G), naturally containing some fatty acids, was similar to the extractive-free loblolly pine (digester B) in the distribution of CTO between the decanted liquor and the fiberized chip washings. A relatively small proportion (<5%) of the CTO was retained by the washed pulp in all experiments. This appears to be consistent with practice.

TABLE VI

KRAFT COOKS OF LIGHTERED WOOD (SLASH PINE) IN THE PRESENCE
OF NORMAL SOFTWOOD AND HARDWOOD

Cooking Conditions: 22% active alkali; 30% sulfidity; 6:1 liquor/wood, 2 hours at 170°C

Digester Symbol	A	B	C	D	E	F	G
Description of Charge in Digester	0.5 g FA + 0.5 g RA (no wood) ^e	5 g Lightered wood (LW), ^c only ^e	5 g LW + 35 g extracted loblolly pine chips (ELC) ^d	10 g LW + 30 g ELC	5 g LW + 35 g ELC + 0.5 g tall oil fatty acids (FA)	5 g LW + 35 g ELC + 1.0 g FA	5 g LW + 35 g aspen chips
Pulp yield, ^a % a.d., extractive- free basis	--	33	46	46	47	43	45
o.d. Solids of decanted liquor, %	--	5.5	10.2	9.8	9.9	9.9	10.0
CTO dissolved in decanted liquor, g/100 g	0.040	0.024	0.090	0.082	0.086	0.103	0.021
CTO in decanted liquor, g	0.7849	0.7634	0.4505	0.4888	0.8845	1.2559	0.4739
CTO in fiberizing liquor, g	--	0.0699	0.3035	0.8866	0.2489	0.3921	0.4333
CTO in acetone extract of acidified pulp, g	--	0.0084	0.0247	0.0183	0.0328	0.0620	0.0530
Total CTO recovered, g/(%) ^b	0.78(78)	0.84(56)	0.78(52)	1.39(46)	1.17(59)	1.71(68)	0.96(48)

^aPulp yields were based on extractive-free wood; 5 g of lightered wood was equivalent to 3.5 g a.d. extractive-free.

^bSum of amounts in preceding three lines rounded to significant figures.

^cLW = Lightered wood chips from Paraquat-treated slash pine.

^dELC = Loblolly pine chips extracted with acetone.

^eThe amounts of cooking chemicals equal to those in digesters C-G.

By inspection of the line of data "CTO dissolved in decanted liquor," Table VI, the relatively small loss to the liquor is evident. Thus, the bulk of the tall oil in the decanted liquor would be expected to appear in a skimmable soap. These experiments, together with others dealing with the formation of floating soap scums (i.e., skimmable soaps) support the idea that the entrainment of air (or other gases) in the formation of the soap precipitate is essential for a practical skimming operation (1). Further, the presence of FA/RA in a ratio of 1:1 or higher may favor the entrainment process. Otherwise, precipitated soaps, rich in resin acids, tend to form sludges or slurries which cannot be skimmed. Thus, in the pulping of lightered wood, the formation of skimmable soap would be favored by the addition of fatty acids.

ANALYSIS BY GAS CHROMATOGRAPHY OF CTO FROM LIGHTERED
WOOD PULPED BY THE KRAFT PROCESS

All fractions of CTO obtained in the kraft cooking of lightered wood (see above section) were separated on DEAE-Sephadex (6) into neutrals (unsaponifiables) and acids. Unknown materials were lost in the DEAE-Sephadex treatment. Presumably these were not fatty or resin acids or the usual neutral substances (7). The acids were spiked with heptadecanoic acid ($C_{16}H_{33}CO_2H$) as an internal standard, and were converted to methyl esters with diazomethane. The esters were purified with aluminum oxide, and analyzed by gas chromatography. The neutrals were not investigated. The general procedures were described in Report One (8).

The fractions of CTO thus analyzed are listed in Table VII as "D" for decanted liquors, "F" for fiberized chip liquors, and "E" for the acetone extracts of the acidified pulps (fiberized chips). The separations of the CTO into acids and neutrals by DEAE-Sephadex were consistent with most tall oil analyses; the acids comprised 40-70% and the neutrals 10-20% of most CTO isolated from liquors.

TABLE VII

ANALYSIS BY GAS CHROMATOGRAPHY OF EXTRACTED CRUDE TALL OILS (CTO) FROM EXPERIMENTAL
KRAFT COOKING OF LIGHTERED WOOD (PARAQUAT-TREATED) OF SLASH PINE

Digester Symbol	A			B			C			D			E			F			G		
	0.5 g FA ^d + 0.5 g RA ^d (no wood)			5 g Lightered Wood (LW) ^e only			5 g LW + 35 g Extracted Loblolly Pine Chips (ELC) ^f			10 g LW + 30 g ELC			5 g LW + 35 g ELC Tall Oil Fatty Acids (FA)			5 g LW + 35 g ELC + 1.0 g FA			5 g LW + 35 g Aspen Chips		
Description of Charge in Digester	0.78(78)			0.84(56)			0.78(52)			1.39(46)			1.17(59)			1.71(68)			0.96(48)		
Total CTO recovered, g/(%) ^a	0.78(78)			0.84(56)			0.78(52)			1.39(46)			1.17(59)			1.71(68)			0.96(48)		
Liquor fraction analyzed ^{a,b}	D	D	F'	F''	E	D	F	E	D	F	E	D	F	E	D	F	E	D	F	E	
CTO recovered from fraction, g	0.785	0.763	0.0489	0.0210	0.0084	0.451	0.304	0.0247	0.489	0.887	0.0183	0.885	0.249	0.0328	1.256	0.392	0.0620	0.474	0.433	0.0530	
CTO fractionated on DEAE- Sephadex, acids, % CTO neutrals, % CTO	67.4 9.9	59.0 10.5	47.6 8.4	55.7 19.0	3.6 81.0	41.4 8.13	44.7 18.1	18.2 56.3	52.3 12.0	51.3 11.7	10.9 71.0	66.7 6.0	51.6 11.8	30.5 34.2	74.4 5.5	52.3 20.5	43.1 31.8	47.8 10.2	36.1 23.0	24.7 55.8	
Fatty and resin acid by GLC, relative basis, %, FA RA	73.1 24.5	1.6 98.4	4.7 95.0	6.0 93.8	86.9 13.1	3.9 95.8	5.1 94.5	30.6 68.4	3.1 96.7	4.7 95.4	43.7 57.0	52.4 47.7	46.5 53.4	62.6 37.4	66.6 32.4	66.0 33.8	68.2 31.7	10.9 89.1	29.8 69.3	53.5 45.0	
Fatty acids. Composition by GLC relative basis, %^c	Retention Time, min																				
<C ₁₆	1.5-1.8	t	0.1	t	t	11.5	0.65	t	2.27	0.45	t	3.51	0.45	t	t	t	t	t	0.34	t	t
Palmitic	2.3-2.4	t	0.32	1.53	0.72	24.8	0.79	0.97	7.30	0.38	0.69	10.6	0.45	0.58	2.34	0.36	0.70	1.14	2.30	2.90	6.2
Stearic	3.8	1.42	0.11	t	t	14.9	0.23	0.40	2.35	0.13	0	4.16	1.31	0.90	3.15	1.54	1.43	2.05	0.39	0.80	2.71
Oleic	4.5	40.0	1.06	2.38	2.84	33.0	1.57	2.55	16.2	1.51	2.88	22.6	27.6	23.6	44.9	35.1	34.0	41.1	2.86	12.53	25.4
Linoleic	5.5-5.6	9.9	t	0.41	1.49	2.65	0.30	0.37	0.25	0.63	0.87	1.27	12.9	12.6	7.21	19.6	20.3	16.4	2.27	7.8	9.2
Arachidic	6.2-6.3	0.28	t	0.35	0	t	0	t	t	0	0	0.30	0.50	0.76	t	0.83	0.79	0.35	t	0.38	0.85
Unknown	7.2-7.4	10.9	t	0	0.91	t	0.39	0.49	1.43	0	0.21	0.97	5.79	5.89	3.38	5.09	5.34	3.72	2.17	4.02	7.09
Unknown	8.3-8.5	10.6	t	t	t	t	0	0.32	0.82	0	0	0.30	3.36	2.16	1.66	4.12	3.41	3.47	0.61	1.43	2.09
Resin acids. Composition by GLC, relative basis, %	Retention Time, min																				
Unknown	12.0	0	1.15	0.67	0.58	0	0.18	t	t	t	t	t	t	t	0	t	0	0	t	t	t
Unknown	13.0-13.7	1.53	1.17	0.45	0.52	0	t	t	t	t	t	0	0	t	0	t	0	0	t	t	0.56
Pimaric	14.4-14.8	1.66	7.32	8.33	7.94	t	7.56	8.40	8.01	6.25	7.55	5.78	3.57	3.12	4.06	2.13	2.86	2.89	6.94	5.77	4.52
Sandaracopimaric	16.1-16.4	1.35	2.73	2.92	2.81	0	2.68	2.26	1.83	2.74	2.88	1.10	1.04	1.23	1.23	0.52	0.47	0.58	2.25	1.22	1.47
Unknown	17.7-18.5	0	0.72	1.62	1.21	0	1.69	1.00	t	1.11	1.65	t	0.52	0.88	t	0.62	t	0	1.34	0.80	1.55
Palustric + levopimaric	20.0	t	5.39	6.42	5.82	0	11.9	2.29	0	9.59	9.98	0	7.00	4.44	0	4.29	0.82	0	10.2	6.44	0
Isopimaric	20.7-21.8	2.12	26.5	30.4	27.2	4.80	27.4	33.2	28.8	25.0	29.1	20.1	14.1	16.8	12.76	9.03	11.1	13.3	26.0	25.2	18.3
Abietic	30.0-30.7	3.49	12.9	15.7	14.0	0	16.3	17.7	0	15.8	14.2	0	7.55	8.78	0	5.14	5.98	1.67	17.6	10.6	5.59
Dehydroabietic	32.5-33.7	13.4	35.0	24.6	30.4	8.34	20.8	28.8	29.8	28.9	25.5	29.0	9.02	14.7	19.3	6.35	10.7	13.3	17.1	16.4	13.5
Neobietic	35.4-36.0	0	5.49	3.91	3.23	0	7.28	0.83	0	7.40	4.47	0	4.83	3.36	0	4.34	1.92	0	7.70	2.55	0

^aThese data listed also in Table VI.
^bFraction designated as D = decanted digester liquor; F = fiberized chip washings; E = extracted (by acetone) from acidified pulp.
^ct = trace.
^dFA and RA = Refined tall oil fatty acids (FA) and resin acids (RA), respectively.
^eLW = lightered wood, a resin-soaked wood (approximately 30% extractives) from a slash pine treated with Paraquat (see p. 28).
^fELC = Extractive-free loblolly pine chips.

On the other hand, CTO isolated from acidified pulps contained mainly neutral materials with the acids as minor components. This behavior may reflect the inability of neutral materials, with limited solubility in the cooking liquor, to be washed from the pulp by hot water. Further, the small proportion of CTO present in these "F" fractions (<5% of the total CTO) would appear to be inconsequential in the recovery of tall oil.

The amounts of fatty and resin acids were determined by GLC rather than by the customary differential methylation. The results, Table VII, are expressed on a relative basis and show the marked range in composition from digester A, a control, throughout the several digesters containing lightered wood. Digesters B, C, and D show the very low proportion of fatty acids in the resins from lightered wood, and digester G showed the relatively small yield of fatty acids derived from the aspen.

The individual components of the fatty and resin acids are expressed in Table VII as the percentage of the total amount of acids measured by GLC. From these data comparisons may be made of the several experiments and their fractions of CTO. The relationships between individual components and the starting materials can be calculated from the data in Tables VI and VII, but were omitted in the interest of simplifying the interpretations.

With the exception of digester D, the decanted fractions ("D") produced the largest fraction of CTO. Therefore, the composition of CTO from decanted liquors with respect to individual acids may be assumed to be representative of the total CTO for the cook. However, by inspection of the composition with each digester B, C, D, G, the retention by the pulp (fraction "E") of fatty acids in preference to resin acids was not observed in digesters E and F in which fatty acids were added to the cooks. The neutrals, also, followed a similar trend with a pronounced

relative increase in the CTO from fractions "E," the acidified pulp extracts. The remainder of the fatty acid components were present in proportions usually expected in such materials.

The resin acids were present in approximately the expected proportions with the exception of those in the "E" fractions where palustric, levopimaric, and abietic were absent, or were present in small amounts. The reasons remain obscure.

Thus, the recovery of tall oil from the pulping of lightered wood appears to follow predictable patterns.

FIBERIZATION OF COOKED CHIPS AND ITS POSSIBLE EFFECT ON THE ABIETIC ACID/DEHYDROABIETIC ACID RATIO

It was observed in previous work that the fiberizing of pine chips cooked by the kraft process produced resin acid fractions in which dehydroabietic acid appeared to have been formed from abietic acid (9). This behavior had not been observed previously in our work. An experiment was then performed in which alkaline solutions of tall oil fatty and resin acids were agitated violently in a Waring Blendor in the absence of wood, to simulate the action during fiberizing. Blending actions in the presence of air, nitrogen, and oxygen were used to attempt to highlight any effect, particularly that of oxidation. The results are shown in Table VIII.

By inspection (fourth column) the fatty acids were recovered quantitatively and the resin acids in a yield of approximately 80% based on the original resin acid mixture (tall oil resin). The blending step was without effect on either the oleic/linoleic acid or abietic/dehydroabietic acid ratios. Therefore, the original observation that the possible effect of fiberizing on these ratios might have been produced by the vigorous mechanical agitation was not supported. Presumably, some

TABLE VIII

FATE OF TALL OIL FATTY AND RESIN ACIDS IN SIMULATED FIBERIZING MIXTURES

Aqueous solutions contained 1.0 g fatty acid (FA) or resin acid (RA), in 1.0 liter of 0.1N sodium hydroxide. Blending was at "low" speed for 2 minutes, either at room temperature or "hot" (65-80°C).

Experiment No.	FA or RA	Experimental Conditions	Recovered by Extraction as CTO, %	Oleic Acid, % of FA	Linoleic Acid, % of FA	Oleic/Linoleic Ratio	Abietic Acid, % of RA	Dehydroabietic Acid, % of RA	Abietic/Dehydroabietic Ratio
1	RA	Control ^a	80.5	--	--	--	32.8	31.4	1.04
		Blended in air; hot	79.1	--	--	--	36.2	32.6	1.11
2	FA	Control	101.3	52.1	39.8	1.31			
		Blended in air; hot	100.6	53.0	39.8	1.33			
3	RA	Control	77.0	--	--	--	35.5	31.0	1.14
		Blended in air; cold	78.8 ^b	--	--	--			
4	RA	Blended in oxygen; hot	80.5	--	--	--	29.2	27.6	1.06
5	FA	Blended in oxygen; hot	99.5	57.3	42.7	1.34	--	--	--
6	RA	Blended in nitrogen; hot	81.7	--	--	--	37.4	35.3	1.06
7	FA	Blended in nitrogen; hot	104.7	57.1	42.9	1.33	--	--	--

^aFA and RA reagents analyzed without heating or blending.

^bNot chromatographed.

factor, at present unknown, may have promoted the oxidations, especially of abietic to dehydroabietic acid.

On the other hand, the CTO recovered from pulps by extraction with acetone after acidification, as shown in Table VII, contained little or no abietic acid. This result was reminiscent of the previous observation for fiberized chip washings (9), but the corresponding liquors in the latter case, Table VIII, showed no such drop in the amount of abietic acid.

In an effort to pin-point the cause of such losses, the effect of exposure of CTO to air during the analytical process was examined. This appeared logical in view of the consistent increases in dehydroabietic acid at the expense of abietic acid during oxygen/alkali pulping (10). Samples of "old" and "new" CTO isolated from commercial black liquors were analyzed by GLC. The results, shown in Table IX, indicated no marked influence of the action of air on neat CTO during analysis. To date the most consistent conversion of abietic to dehydroabietic acid was found in oxygen/alkali pulping. Otherwise, the disappearance of abietic acid in favor of dehydroabietic acid remains sporadic and unaccounted for.

TABLE IX

ANALYSIS BY GLC OF CTO FROM TWO COMMERCIAL BLACK LIQUORS.
POSSIBLE DETERIORATION OF ISOLATED CTO ON STANDING

	$\frac{10C^a}{\text{"Old"}}$	$\frac{10D^b}{\text{"New"}}$	$\frac{11D}{\text{"Old" "New"}}$	
	Fatty acid, methyl esters, %, relative basis			
Palmitic	2.3	3.5	3.6	3.4
Oleic	8.7	21.0	24.5	22.5
Linoleic	8.7	17.9	17.9	17.7
Linolenic	1.1	3.5	1.7	2.9
Resin acids, methyl esters, %, relative basis				
Levopimaric and palustric	none	10	2.6	10.6
Isopimaric	8.2	3.4	10.3	10.9
Abietic	23.6	13.0	13.7	11.0
Dehydroabietic	36.6	7.7	9.9	4.8
Neoabietic	none	5.6	4.7	5.3

^aRepresents only the CTO in the supernatant black liquor (excludes the precipitate). The CTO was purified with 95% ethanol to remove sulfur; 10D was not so treated.

^bRepresents the entire aliquot of black liquor.

EXPERIMENTAL

RECOVERY OF CTO FROM STORED COMMERCIAL BLACK LIQUORS

Analytical procedures were described in Progress Report One. The results of the analysis of black liquors which had been stored for approximately 15 months are summarized in Tables I and II.

STOCK SOLUTIONS OF TALL OIL ACIDS

Stock solutions of tall oil fatty acids and resin acids, respectively, were prepared from 10.0 g of the acids dissolved in 35 ml of 2N sodium hydroxide diluted with 300-400 ml of water and the mixture heated to 80-90°C. When solution was complete, the mixtures were cooled and diluted to 1 liter.

SOLUBILITY OF TALL OIL SOAPS IN SODIUM HYDROXIDE

Sodium hydroxide, 100 ml of 2N NaOH, was placed in each of eleven 250-ml Erlenmeyer flasks and the flasks were heated to approximately 90°. The acid mixtures 100 ml, were then poured into the alkaline solutions, mixed thoroughly by hand, and the flasks set aside to cool. After standing overnight at room temperature, a portion of each mixture was filtered through a loose plug of cotton and the clear filtrate was analyzed for dissolved tall oil acids. The results are shown in Table III and Fig. 1.

APPARENT SOLUBILITY OF TALL OIL SOAPS IN DILUTE KRAFT BLACK LIQUOR

Solutions of the sodium salts of tall oil acids, total of 100 ml, were mixed with 100 ml of black liquor by the general procedure described above. The black liquor was "from-the-skimmer" (21% solids) furnished by Hammermill. The results are listed in Table IV and Fig. 1.

APPARENT SOLUBILITY OF TALL OIL SOAPS IN PARTIALLY CONCENTRATED BLACK LIQUOR

Fatty acids and resin acids, refined from tall oil, were weighed directly as received into each of seven experimental digesters. Black liquor, partially concentrated (32% solids) "from-the-skimmer," furnished by Owens-Illinois, was fortified with sufficient sodium hydroxide to compensate for the tall oil acids to be added (50 ml of 2N sodium hydroxide in 2500 ml of the black liquor). An amount of 300 ml (350 g) of the black liquor was added to each digester with the tall oil acids, the digesters were sealed, heated to 170°, held at that temperature for 10 min, cooled to 90°, and the contents of each was poured into a tared 400 ml beaker. After standing overnight, a portion of each liquor was filtered through a cotton plug and analyzed for dissolved CTO. The results are summarized in Table V and Fig. 1.

KRAFT PULPING OF LIGHTERED SLASH PINE WOOD AND EXTRACTIVE-FREE LOBLOLLY PINE

A series of kraft cooks was run with lightered wood (LW), a resin-soaked wood (approximately 30% extractives) from a slash pine which had been treated with Paraquat (5). In some experiments the lightered wood was mixed with extractive-free loblolly pine chips, and, in one cook, with aspen chips. A control cook consisted of refined tall oil fatty (FA) and resin (RA) acids cooked in the absence of wood. The conditions for the kraft cooks and the extractable tall oils (CTO) recovered are listed in Table VI.

ANALYSIS OF CTO BY GAS CHROMATOGRAPHY

The main details of the experimental procedures were reported previously (3). The results of the analysis of the CTO from the current kraft series are tabulated in Table VII.

SUMMARY AND CONCLUSIONS

1. Whole black liquor was stored in sealed inert containers for 15 months without measurable loss of crude tall oil (CTO). This leads to the assertion that such materials may be stored indefinitely without loss of CTO or deterioration of the quality of refined products.
2. The analysis of black liquor may not be reliable unless representative samples are analyzed. Considerable care must be observed because tall oil soaps precipitate readily from the black liquor and true reconstitution (redissolving of the soaps) is practically impossible.
3. Although tall oil soaps were slightly more soluble in partially concentrated black liquor than in dilute black liquor, the difference was small and not a significant factor in the maximization of CTO yields. Tall oil soaps were least soluble in sodium hydroxide in comparison with black liquors. The common ion influence on solubility appeared to be more than balanced by the dispersant components of the black liquor.
4. The formation of skimmable soaps was favored when the ratios of fatty acids (FA)/resin acids (RA) were greater than 1:1. This fact supported the possibility that CTO from lightered wood (resin-soaked wood) may be recovered readily by raising the fatty acid content of the system to the 1:1, FA/RA ratio.
5. Laboratory-scale pulping of lightered wood with added fatty acids produced crude tall oils which were normal in composition when analyzed by gas chromatography.
6. The mechanical fiberization of cooked chips was not responsible for chemical changes in the tall oil acids.
7. Maximization of tall oil yields at a given mill appeared to be dependent upon the process equipment and engineering practice.

SUGGESTIONS FOR FUTURE WORK

Based on the results of the work on this project and on other recent studies (1,2), the most important factor in tall oil soap skimmings appears to be the bulk density of the coagulated soaps. In turn the optimum density appears to depend upon (a) the composition and concentration of electrolytes, (b) the nature and concentration of organic substances, (c) the temperature and duration of the skimming step, and (d) the composition of the soaps, themselves. Through physico-chemical studies of the composition and structure of tall oil soap precipitates at the molecular level, critical variables relevant to tall oil soap skimmability may be identified.

ACKNOWLEDGMENTS

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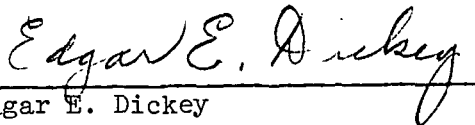
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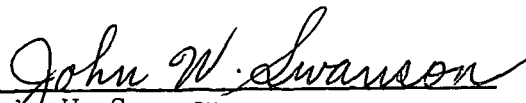
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APPENDIX I

from Project 3267, Report One

ABSTRACT

Partially concentrated black liquors were procured from five kraft mills and were analyzed for extractable, crude tall oil (CTO). Due to the small number of samples the results were statistically insensitive to the relative efficiencies from mill-to-mill. Aliquots of the liquors which had been stored for as long as a year were unchanged in the amount and composition of CTO. An isolated sample of black liquor was exposed repeatedly to air at room temperature, but no change was observed in the CTO or its composition.

Liquors were analyzed by conventional chemical methods and by a combination of chemical and ion-exchange material, DEAE-Sephadex (a diethylaminoethyl ether of a cross-linked dextran). The DEAE-Sephadex was preferred for most analyses of CTO.

Laboratory kraft cooks of loblolly pine chips (and aspen as a resin-free control) were used to evaluate the production of skimmable soap under controlled conditions. Although precipitated soap formed skimmable scums in all cooks except the aspen and extractive-free pine chips, cooks with resin acid:fatty acid ratios of >3:1 retained somewhat higher levels of CTO in solutions than normal cooks. The CTO from fiberized chip washings was similar to other fractions of CTO except that the abietic acid:dehydroabietic acid ratio was very much smaller and resembled that from CTO obtained in oxygen-alkali pulping of pine. These observations are consistent with the known sensitivity of abietic acid to oxidation.

Preliminary experiments with high performance liquid chromatography were conducted with tall oil components, chiefly fatty and resin acids. A Varian model 8500 liquid chromatograph with a Perkin-Elmer Model LC-55 variable wavelength spectrophotometric detector were used with assorted columns. The results indicated that the separation of tall oil components may be efficient and reasonably rapid, but the spectrophotometric detector limits the sensitivity and versatility of the method. For the evaluation of tall oil mixtures it is obvious that a universal type of detector (such as a moving wire type) is required.

SUMMARY AND CONCLUSIONS

Five kraft mills furnished both to-the-skimmer liquors and from-the-skimmer liquors which were analyzed for extractable crude tall oil (CTO) and ranged from 1.24 to 2.13% to-the-skimmer and 0.39 to 0.78% from-the-skimmer, based on o.d. liquor solids. Fractionation of the CTO and analysis of the acids by gas chromatography were within the normal ranges for commercial tall oils.

The analysis of aliquots of black liquors stored at room temperature in air-tight, polyethylene bottles showed no significant loss of CTO upon storage for approximately one year.

In one experiment, air was bubbled through the black liquor but no loss of CTO due to air-oxidation was observed.

Two series of laboratory-scale kraft cooks were performed with loblolly pine chips; one cook with aspen chips was included in the series. The black liquors were drained from the cooked chips and, after standing overnight, were analyzed for CTO in an upper fraction which included the soap scum, and a lower fraction. The

results from the first series produced approximately half the CTO known to be present in the cooks. In the second series, the washings from the mechanical fiberizing of the chips were included in the analyses and resulted in nearly quantitative recovery of CTO. The distribution of CTO between the decanted black liquor and the fiberized chip washings indicated that CTO salts are held preferentially by the cooked chips over the cooking liquor. Analyses by gas chromatography of the CTO indicated that manipulations which expose the resin acid salts to high concentrations of air (oxygen) may be responsible for the marked conversion of abietic to dehydroabietic acid in such cases.

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