

**EFFECT OF OXIDATIVE PULPING CONDITIONS
ON THE TALL OIL AND TURPENTINE COMPONENTS
OF SOUTHERN PINEWOOD**

Project 3266

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

December 31, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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AND TURPENTINE COMPONENTS OF SOUTHERN PINEWOOD

ABSTRACT

In laboratory scale equipment, loblolly pinewood chips were pretreated with soda (sodium hydroxide) which involved impregnation under pressure followed by steaming. In other experiments chips were pulped by the kraft, soda, and alkali-oxygen (soda-oxygen) processes. More skimmable tall oil soap was obtained from a kraft cook than from soda or alkali-oxygen cooks. However, due to the solubility of the tall oil components in the kraft black liquor, approximately one-third of the tall oil could not be recovered as skimmable soap.

The extractable crude tall oil obtained from the pretreatment liquors was 55-65% of that obtainable from the kraft cooks with a higher yield recovered when a higher concentration of sodium hydroxide was used in the impregnation liquor. Presumably, the balance of tall oil remained in the pretreated fiberized chips. When alkali-pretreated chips were pulped by the kraft process, tall oil was recovered in an amount which, together with that from the pretreatment step, accounted for most of the tall oil potentially available.

The addition of oxygen to a soda cook caused relatively little more loss in tall oil components over that of the soda cook alone. The main change in tall oil components was the marked increase in dehydroabietic acid at the expense of abietic acid. Although the unsaturated fatty acids, oleic, linoleic, and palmitoleic, might be expected to oxidize to other compounds under soda-oxygen conditions, this did not occur, suggesting that these compounds may be as stable in oxygen-alkali pulping as are other tall oil components.

Slash pinewood chips from a normal tree and lightwood (resin-soaked) chips from a Paraquat-treated tree, were pulped by the alkali-oxygen process to exaggerate possible changes in the tall oil components. The analytical procedures were designed to recover all extractable tall oil as well as to measure skimmable soaps. Aspen was included to afford a comparison with a hardwood in which resin acids were absent. Aspen and the lightwood produced no skimmable tall oil soap. In all cases except the lightwood, the largest fraction of extractable tall oil was recovered from relatively dilute liquors which were obtained in fiberizing the chips in a Waring Blendor. Also, substantial amounts of extractable tall oil were recovered from the pulps upon acidification with dilute sulfuric acid and extraction with acetone. The total extractable tall oil in soda-oxygen pulping suggested that no significant losses of tall oil components occurred as a result of the pulping process.

OBJECTIVES

The objectives are: To determine the effect of oxygen-alkali pulping conditions on the tall oil and turpentine precursors (extractives) of southern pinewood, to characterize the products of reaction of these extractives under a variety of such pulping conditions, and to determine if possible, the conditions under which tall oil and turpentine components can be salvaged. Possible recovery of tall oil and turpentine components from preoxygen stages of multistage oxygen-alkali pulping processes will also be considered.

CURRENT STATUS OF PROJECT 3266

To date the first phase of the experimental program included (a) comparison of effects of kraft, soda, and alkali-oxygen pulping processes on tall oil yields, (b) overall inspection (by gas chromatography) of possible changes in composition of recoverable tall oil, and (c) study of suitability of lightwood (resin-soaked wood) as a raw material for pulp and tall oil production. No attempts have been made to study the fate of turpentine components. Such studies will require the modification of available apparatus and/or the addition of new equipment and procedures. Introductory experiments were performed to test the feasibility of alkaline pretreatment steps for the recovery of tall oil prior to alkali-oxygen pulping.

Throughout the work reported herein, the term "tall oil" refers to a mixture of organic acids and unsaponifiable substances which is obtained by a controlled extraction procedure (1). These methods of analysis are described by Saltsman and Kuiken (2) and by Zinkel (3).

RESULTS AND DISCUSSION

GENERAL COMMENTS

Three series of alkali-oxygen pulping experiments were performed in half-liter stainless steel reactors using 45 g of oven-dry (o.d.) wood. In an additional experiment, loblolly pinewood chips were pretreated with sodium hydroxide in an effort to recover tall oil more readily than may be possible with alkali-oxygen pulping liquors. In some of the experiments skimmable soap was determined in digester-strength liquor as the difference between the dissolved soap and the total of such components in the sample. [In some cases soaps precipitated and floated at the surface but no effort was made to skim the precipitate for a quantitative estimation of "skimmable soap."]

According to Bolger and Hopfenberg (1) the solubility of tall oil soaps in kraft skim tank feed appears to be about 0.29% based on total solids. The solubility of tall oil soaps in alkali-oxygen black liquors has not been reported, but appears to be in the range of 0.4-0.8% based on the oven-dry (o.d.) solids content of the digester-strength liquor. In our work no equipment or techniques were available for concentrating liquors to 28-30% solids prior to skimming as is done in commercial practice. Hence, we obtained no data in regard to the solubility of tall oil soaps in simulated skim tank feed liquors.

COMPARISON OF KRAFT, SODA, AND ALKALI-OXYGEN PROCESSES

One series consisted of one each of a "short" kraft, a "long" kraft, a soda, and an alkali-oxygen cook. As shown in Table I the black liquors were analyzed for extractable tall oil. In these experiments the contents of each digester was transferred to a Waring Blendor, the chips were fiberized, and the resulting pulp was filtered and washed with a minimum of water. The combined

TABLE I
ALKALINE PULPING OF LOBLOLLY PINE CHIPS
AND ANALYSIS OF TALL OILS

	"Short" Kraft	"Long" Kraft	Soda	Alkali- Oxygen
Digester charge, g o.d. wood	90	90	90	45
Active alkali, Na ₂ O, % o.d. wood	18	18		
Active alkali, NaOH, % o.d. wood			22	22
Sulfidity, %	28	28		
Liquor-to-wood, ml/g			3.75	3.75
Oxygen pressure, psig				140
Time to temp., min/deg.	90 to 174	90 to 174	30 to 160	30 to 160
Time at temp., min	41	83	120	120
Heat factor	1000	2000		
Yield of pulp, % o.d. wood	52.4	46.6	78.7	53.9
Tall oil, % black liquor solids	2.40	2.83	1.90	1.07
Tall oil, % o.d. wood	1.70	2.16	0.82	0.74
Unsaponifiabiles (neutrals), % tall oil	23.3	23.9	11.6	35.2
Fatty acids, % tall oil	44.0	43.8	45.8	45.6
Palmitic ^{a,c}	9.8	11.2	9.3	11.8
Palmitoleic	2.8	3.1	2.7	4.8
Stearic	4.0	6.6	3.5	6.3
Oleic	43.2	42.8	42.9	42.5
Linoleic	24.0	21.5	20.6	22.9
C ₂₀	2.4	1.6	2.0	3.1
C ₂₀ unknowns, combined	11.4	11.2	17.6	9.0
Resin acids, % tall oil	29.4	34.2	34.1	27.3
Pimaric ^{b,c}	12.1	9.1	9.4	8.9
Dihydroabietic	1.5	2.1	3.0	1.7
Palustric	4.1	4.1	3.0	2.2
Abietic	23.8	43.9	32.7	6.8
Dehydroabietic	54.1	35.8	47.6	77.8

^a Individual acid yields based on total fatty acid fraction.

^b Individual acid yields based on total resin acid fraction.

^c The quantitative data were calculated on the basis of presumptive identification of components by gas chromatographic retention time and authentic compounds chromatographed under the same conditions. Data for major components (anything over 1%) are given in Table I.

filtrate (black liquor) was then analyzed for solids and tall oil. An estimate of the total solids present in the black liquor was made from the known amount of solids added and from the amount of wood dissolved. From these data the yields of tall oil on the basis of the o.d. wood were estimated (Table I). The procedure afforded no basis for observing or estimating skimmable soap.

Based on tall oil yields, the alkali-oxygen process appeared to have destroyed nearly two-thirds of the tall oil which was available in the "long" kraft process.

By inspection of the composition of the tall oil acids isolated from these cooks (Table I) the relative amounts of the main components were not changed significantly with the exception of abietic and dehydroabietic acids. In this case, the alkali-oxygen process produced relatively large amounts of dehydroabietic acid at the expense of abietic acid. To account for the lower yields of tall oil in soda and alkali-oxygen processes, in comparison with the kraft process, two possible factors may be considered: (1) general oxidation may have occurred and/or (2) the recovery of tall oil was more efficient in the kraft cooks compared with the soda and alkali-oxygen cooks. Future experiments will be designed to furnish more information about such possibilities.

ALKALI-OXYGEN PULPING OF LOBLOLLY PINWOOD CHIPS

To examine further some of the factors which may affect the recovery of tall oil, four lots of loblolly pinewood chips were cooked by the same procedure used previously (Table I, last column). As shown in Table II, in addition to unextracted and acetone-extracted chips two additional lots of extracted chips impregnated with tall oil fatty acids and tall oil rosin, respectively, were pulped. The yields of pulp were similar to those obtained previously (Table II, second column).

TABLE II

LOBLOLLY PINEWOOD CHIPS PULPED BY KRAFT AND BY ALKALI-OXYGEN PROCESSES

	Kraft Process		Alkali-Oxygen Process					
	Unextd. Chips ^a	Pretreated Chips ^b	Unextd. Chips ^a 1	Unextd. Chips 2	Extd. ^c Chips	Extd. Chips + Rosin	Extd. Chips + FA	
Pulp yield, % o.d. wood	47	38	54	58	60	62	62	
Kappa number	36	35		97	98	97	97	
Tall oil (TO), % o.d. wood	2.16	0.86-1.05 ^d	0.74	0.99	0.34	0.82	1.53	
Tall oil in skimmable soap, % of TO in decanted black liquor	--	--	--	44	--	14	35	
Tall oil in the fiberized chip washings, % of total tall oil available	--	--	--	71	--	80	84	
Tall oil fractions, % total TO								
Neutrals	24	Not Analyzed	35	41	Not Analyzed	37	19	
Fatty acids (FA)	44		46	42		30	77	
Resin acids (RA)	34		27	16		30	3	
Fatty acids, % total FA								
Palmitic acid	11		12	12		3	20	
Stearic acid	7		6	5		<3	10	
Oleic acid	43		43	42		55	15	
Linoleic acid	22		23	21		30	5	
Resin acids, % total RA								
Pimaric acid	9		9	11		30	7	
Palustric acid	4	2	3	2	17			
Abietic acid	44	7	4	3	10			
Dehydroabietic acid	36	78	74	16	55			

^aThese data are from Table I for comparison.

^bPretreated chips from column 3 of Table V.

^cThe chips were extracted by leaching with acetone at room temperature.

^dBased on original wood.

The extractable tall oil followed a pattern consistent with the amounts and character of extractives known to be present. The unusually large yield (1.53%) of tall oil obtained when the chips were impregnated with tall oil fatty acids may reflect the fact that the impregnation of the chips was possibly non-uniform with comparatively high levels of fatty acids near the surface of the chips.

ATTEMPTED MEASUREMENT OF SKIMMABLE SOAPS

In order to test the skimmable soap potential of alkali-oxygen pulping, the digesters were cooled to 80-90°C, opened, and the black liquor was decanted from the cooked chips. Upon standing overnight at room temperature skimmable soap collected on the surface of all liquors except that of the extracted chips (Table II). In this case the absence of skimmable soap was consistent with the probable solubility of such soaps in the black liquor precluding the possibility of soap separation (Table II). The skimmable soap represented a minor amount of the total tall oil recovered, and ranged from 14-44% of the total available in the decanted black liquor. However, the proportion of skimmable soap based on the total contained in the liquor from which it precipitated may be regarded as a realistic measure of the skimmable soap potential. Also, proportionately less soap (14%) was precipitated in liquor from chips impregnated with rosin than in the liquors from unextracted chips (44%), or those impregnated with fatty acids (35%).

The amount of tall oil removed in fiberizing the chips represented the major portion (71-84%) of the available tall oil. This result was unexpected. Apparently the liquor outside the chips received less tall oil soaps by diffusion than was assumed previously. Thus, fiberizing the chips in a Waring Blender at a consistency of approximately 2% resulted in a comparatively efficient (71-84%)

removal of the remaining tall oil from the pulp. These considerations would be obviated under conditions of commercial operation comprising digester blowing and brown stock washing.

As observed previously and shown in Table III, the main effect on individual components was the apparent increase in dehydroabiatic acid at the expense of abiatic acid. Differences in composition between the tall oil isolated from black liquors as compared with that from the fiberized chip washings were minor.

ASPEN AND PARAQUAT*-TREATED SLASH PINE PULPED BY THE ALKALI-OXYGEN PROCESS

During the evaluation of the experiments noted in Table II on spiked samples of loblolly pinewood it became evident that the aged samples of tall oil rosin and tall oil fatty acids used for spiking no longer represented the resin acids and fatty acids of fresh pinewood. Before fresh samples of authentic tall oil resin acids and fatty acids could be obtained, and in order to obviate problems of adequate distribution of spiked components, a series of four cooks was made employing naturally occurring "spiked" samples. This series included aspenwood (containing only fatty acids and no resin acids), normal slash pinewood (control), and the resin-soaked (lightwood) and nonresin-soaked portions of Paraquat-treated slash pinewood. In order to compensate for the abnormally high extractives content of the Paraquat-treated samples, the digesters were charged with 45 g of chips on the basis of o.d. unextracted wood, but the pulp yields were estimated on the o.d. extractive-free basis. As shown in Table IV the yields of pulp may reflect the possibility that when proportionately large amounts of the chip charge are dissolved in the cooking liquor, the attack on the lignin may be diminished somewhat. In

*"Paraquat" is a trade name (Chevron Chemical Co.) for 1,1'-dimethyl-4,4'-bipyridinium dichloride.

TABLE III

ANALYSIS BY GLC OF LOBLOLLY PINEWOOD TALL OIL ACIDS
(AS METHYL ESTERS) FROM ALKALI-OXYGEN COOKS

Fatty Acids	Retention Time, min	Composition, % of the Fatty Acid Fraction ^a					
		Unextracted Chips		Extracted Chips + 2% Rosin		Extracted Chips + 2% Fatty Acids	
		Up	W	Up	W	Up	W
<C ₁₆	--	6.6	4.3	27.3	24.6	<1	<1
Palmitic	4.6-4.7	12.0	12.0	20.5	19.0	3.1	3.0
Palmitoleic	5.4-5.6	4.1	3.5	11.4	7.7	1.2	1.2
Unknown	6.2	<1	<1	2.2	2.6	<1	<1
Unknown	7.3-7.4	<1	<1	3.1	1.6	<1	<1
Stearic	8.2-8.3	4.8	5.2	9.7	10.2	2.6	2.3
Oleic	9.8-10.0	41.9	39.2	13.9	17.1	57.2	50.0
Unknown	11.1-11.2	1.0	1.3	1.7	<1	<1	1.5
Linoleic	12.5-12.6	20.8	21.4	4.6	9.0	29.2	32.6
C ₂₀ (?)	14.2-14.8	2.8	4.0	2.4	3.6	1.3	3.3
Unknown	17.2-17.5	0.9	1.5	1.2	4.0	1.8	2.5
Unknown	25.0-25.1	2.5	2.4	--	--	1.2	<1
<u>Resin Acids</u>							
Fatty acids ^b	--	11.3	3.5	12.8	9.9	Mainly Fatty Acids	43.5
Unknown	13.0-13.2	--	<1	--	--	6.0	12.5
Unknown	14.0-14.2	1.3	1.7	<1	3.3	4.7	10.7
Pimaric	15.8-16.5	10.8	11.1	8.3	6.7	47.6	22.7
Sandaraco-pimaric	17.7-18.1	2.2	2.4	2.0	2.5	<1	3.6
Unknown	20.0-20.4	1.7	1.3	1.2	1.6	12.4	10.2
Palustric	23.3-23.6	2.8	2.8	12.9	20.1	<1	4.0
Unknown	25.2	--	--	--	--	3.1	3.5
Isopimaric	27.2-27.5	--	<1	<1	<1	--	--
Abietic	33.9-34.5	1.7	4.8	<1	15.8	<1	4.2
Dehydroabietic	37.5-38.4	76.0	72.8	65.2	44.4	14.0	20.5
Neobietic	44.0-44.6	3.1	2.7	8.6	3.4	1.3	2.0
Unknown	46.6-47.0	<1	<1	--	--	9.6	6.0

^aUp = From upper fraction of decanted black liquor and

W = From fiberized chip washings.

^bFatty acids remaining with the resin acid fraction due to incomplete fractionation.

the case of aspen, the hemicelluloses are readily dissolved by the aqueous alkali and in the case of the slash pine, especially the Paraquat-treated samples, the extractives supply much organic material.

TABLE IV

ASPEN AND PARAQUAT-TREATED SLASH PINEWOOD CHIPS (45 g o.d.) PULPED
BY THE ALKALI-OXYGEN PROCESS

	Aspen	Slash Pine, control	Paraquat-Treated Tree	
			Nonresin-Soaked Wood	Resin-Soaked Wood
Extractives (acetone), % o.d. wood	3.3	3.9	8.2	34.1
Chips pulped, o.d., extractive-free basis, g	43.5	43.2	41.3	29.7
Yields of pulp, % o.d., extractive-free wood	73	59	71	69
Tall oil in decanted black liquor, % o.d. wood	0.11	0.31	0.70	14.2
Tall oil in fiberized pulp washings, % o.d. wood	0.92	1.20	1.34	4.76
Tall oil extracted from acidified pulp with acetone, % o.d. wood	0.27	0.42	0.54	0.80
Total tall oil (sum), % o.d. wood	1.30	1.93	2.58	19.8
Tall oil in fiberized chip washings, % total tall oil	71	62	52	24
Total tall oil, % of extractives in wood	39	48	31	58
Apparent tall oil from saponification of extractives, % of extractives	31	43	82	99
Tall oil in pulp, % of total tall oil	21	22	21	4.0
Soap separation observed	no	yes	yes	no

As observed in the series with loblolly pine (Table II), the largest proportion of tall oil was recovered from the fiberized chip washings except for the lightwood sample (Table IV). Apparently a minor amount of the available tall oil was diffused from the chips into the cooking liquor, but the accessibility was greatly increased by fiberizing the chips. Also, the tall oil soap remaining with the pulp was greater than that obtained in the decanted black liquor for normal wood. Only pulps from the samples abnormally high in extractives retained proportionately less tall oil in the pulp than was recovered from the black liquor or the fiberized pulp washings.

The failure of the Paraquat-treated sample to precipitate tall oil soap from the digester-strength liquor (Table IV) was consistent with the general behavior of lightwood in kraft pulping. This is usually attributed to the low level of fatty acids in comparison with resin acids. In contrast, normal wood contains fatty and resin acids in approximately equal amounts which favors the precipitations of skimmable soaps. Consistent with these facts, the digester liquor decanted from the lightwood sample contained a copious, heavy precipitate which formed a sludge on the bottom of the vessel. In working up the sample in the tall oil analysis the precipitate appeared to be rich in the salts of resin acids. Further experiments will be designed to test such precipitates as sources of resin acids. If the sodium resins can be combined with the sodium salts of fatty acids, skimmable soap mixtures may be formed.

The total tall oil recovered from the alkali-oxygen pulping of aspen and normal slash pinewood (Table IV) was approximately equal to the simulated tall oil formed from the saponification of isolated extractives. The recovery from Paraquat-treated wood was less efficient. However, the results indicated that in the case of normal wood, alkali-oxygen pulping resulted in no significant

loss of potential tall oil. This finding must be checked by further experimental study, but is in contradiction to the results published by Erickson and Dence (4). These workers found that a 60% reduction of tall oil occurred in alkali-oxygen pulping of Scotch pine in comparison with the kraft pulping of southern pine, a comparison of questionable validity. Furthermore, the results reported herewith were obtained with a liquor-to-wood ratio of 3.8:1 with chips whereas Erickson and Dence (4) used a 30:1 ratio with thermomechanical pulp.

ALKALI PRETREATMENT OF LOBLOLLY PINEWOOD CHIPS

As an alternative approach to the salvaging of tall oil and turpentine components in an oxygen-alkali pulping scheme, we are concerned with the possible recovery of these components from pretreatment liquors such as those from alkali impregnation processes as employed in the concurrent Institute Funded Formal Project 3264 on the oxygen-alkali pulping of loblolly pinewood defiberized in an alkali impregnation and steaming operation. Accordingly, three lots of loblolly pinewood chips were treated with sodium hydroxide and steam in an effort to recover tall oil prior to alkali-oxygen pulping. As shown in Table V, the impregnation liquor, the liquor from subsequent steaming of the chip charge, and the fiberized chip washings were analyzed. The tall oil recovered from the impregnation and steaming liquors appeared to be less than 30% of that expected, based on the saponified extractives of the wood. The main fraction of the tall oil was retained by the pretreated chips and was recovered, in part, in the subsequent long kraft cook (see Table II, column 2 for the data for experiment 3). Thus, the combined recovery of tall oil from the pretreatment and the kraft cook accounted for 1.6% tall oil in experiment 3 and 1.5% tall oil in experiment 2, based on the original o.d. wood chips. In comparison, 2.2% tall oil was recovered when loblolly pinewood chips were pulped directly by the long kraft cook (Table II,

TABLE V
ALKALI PRETREATMENT OF LOBLOLLY PINEWOOD CHIPS^a

	Pretreatment Experiment		
	1	2	3
Digester charge, o.d. wood, kg	5.51	2.75	2.75
Yield of pulp, % o.d. wood	--	84	82
Impregnation liquor, g NaOH/liter	22	22	39
Impregnation liquor added, kg	28.8	18	18
Impregnation liquor recovered, kg	22.2	15.7	16.3
Liquor from steaming, kg ^b	18.2	7.6	9.1
Tall oil from impregnation liquor, % o.d. wood	0.47	0.51	0.38
Tall oil from steaming liquor, % o.d. wood	0.21	0.17	0.39
Total tall oil recovered from pretreatment, % o.d. wood	0.68	0.68	0.77
Tall oil from fiberizing liquor, % o.d. wood	0.54	0.50	0.65
Total tall oil available, including fiberizing liquor, % o.d. wood	1.22	1.18	1.42
Tall oil recovered from long kraft cook of pretreated chips, % o.d. wood		0.85-1.01	0.86-1.05
Total available tall oil from pre- treatment and kraft cooking, % o.d. wood		1.53-1.69	1.63-1.82

^aThe chips were steamed at 15 psi for two minutes, the condensate was replaced with the sodium hydroxide impregnation liquor under 100 psi of nitrogen for 30 minutes, the liquor was drained from the chips, and the charge was steamed for 5 minutes at 75 psi.

^bCondensate from the steam line accumulated in this liquor.

column 1). Furthermore, it seems noteworthy that the recovery of tall oil from such dilute pretreatment liquors would be impractical in commercial practice. On the other hand, countercurrent principles, as in continuous digesters, may improve the efficiency of the recovery of tall oil from alkaline pretreatment liquors.

A comparison of the results of experiments 2 and 3 suggest that more concentrated impregnation liquors might increase tall oil component recovery from pretreatment liquors.

SUMMARY

1. Even under the optimum conditions of the long cook kraft, approximately one-third of the tall oil components cannot be recovered.

2. Using the long cook kraft yield as the maximum possible commercial tall oil yield, less than 40% of this amount of crude tall oil could be recovered from the soda cook, suggesting that a first-stage soda cook would be unsatisfactory for the commercial production of tall oil.

3. The addition of oxygen to the soda cook caused relatively little more loss in the amount of crude tall oil recovered over that of the soda cook alone. This conclusion must be qualified by the fact that the pulp yield in the soda cook was 79%, while in the soda-oxygen cook, it was 54%.

4. The oxidation by oxygen-alkali of the extractives of loblolly pine-wood appears to be a minor factor in the available tall oil.

5. Although the unsaturated fatty acids, oleic acid, linoleic acid, and palmitoleic acid might be expected to oxidize to other compounds under alkali-oxygen conditions, this did not occur, suggesting that these unsaturated acids are stable under conditions of oxygen-alkali pulping to the same extent that other tall oil components are.

6. All of the resin acids were relatively stable to oxygen-alkali pulping conditions except abietic acid which was converted almost entirely into dehydroabietic acid, a major component of tall oil under all conditions.

7. The total crude tall oil yields obtained from the pretreatment (alkaline) liquors amounted to 55-65% of that obtained from the long cook kraft

pulping experiment with the higher yield coming from the experiment with a higher concentration of sodium hydroxide in the impregnation liquor. Presumably, the balance of the tall oil remained in the pretreated fiberized chips.

8. When alkali-pretreated chips were pulped by the kraft process, tall oil was recovered in an amount which, together with that from the pretreatment step, accounted for most of the tall oil potentially available.

9. In an attempt to exaggerate the possible effects of the alkali-oxygen process on tall oil components, slash pine lightwood (34% extractives in the resin-soaked wood from a Paraquat-treated tree) was cooked. No skimmable soap was produced. This may be due to the very small proportion of fatty acids relative to resin acids in the extractives.

10. Aspen chips were included in the series to test the survival of hardwood fatty acids (no resin acids were present) in the alkali-oxygen process. No precipitate of soap was formed.

11. In an effort to account for all the extractable tall oil, the analytical procedure was revised to include tall oil present in cooking and washing liquors and adsorbed or occluded on the final pulp. When the procedure was applied to normal aspen and slash pine, the total extractable tall oil indicated that only minor losses of potential tall oil (based on saponified extractives) had occurred. Thus, losses through the action of alkali-oxygen may be less than were indicated originally. The recovery of tall oil from the Paraquat-treated samples was less efficient than from normal wood. With the exception of the lightwood sample, the largest fraction of the extractable tall oil was recovered from the fiberized chip washings. This may be due, in part,

to a slow or repressed diffusion of the tall oil soap from the chips into the cooking liquor. In the kraft process diffusion may be more efficient than in the alkali-oxygen system.

EXPERIMENTAL

PULPWOOD SAMPLES

Loblolly Pine - Loblolly pinewood bolts were supplied by Champion International in Canton, North Carolina. This is the same wood that is being used in the concurrent Funded Formal Projects 3264 and 3267 on oxidative pulping and maximization of tall oil soaps, respectively.

Trembling Aspen - Trembling aspen logs were supplied by Wausau Paper Mills Company from their forest in the vicinity of Rhinelander, Wisconsin.

Slash Pine - Bolts of normal and Paraquat-treated slash pine were supplied by Mr. William Peters of the U.S. Forest Service from trees cut in the Owens-Illinois, Inc. forest near Olustee, Florida.

Production of Chips for Pulping - The loblolly pinewood and the aspen-wood were chipped in a mechanical chipper to produce commercial type chips. The slash pinewood was cut into discs which were chipped by hand with a hinged knife. In the case of the Paraquat-treated slash pinewood, the resin-soaked portions were separated from the discs before chipping.

PULPING EQUIPMENT AND CONDITIONS

All pulping was done in stainless steel cylindrical digesters 53 mm in inside diameter by 240 mm in height and 3.5 mm wall thickness, and 530 ml volume. Each digester is closed by a two-piece threaded cap sealed with a teflon ring gasket. As many as seven such units can be mounted in a rotating rack and immersed in an electrically heated oil bath. Four of the units are equipped with valves for degassing and for pressurizing with gases. The cooking conditions for the kraft and the alkali-oxygen experiments are listed in Table I.

The pretreatment of chips noted in Table V was done in stationary stainless steel digesters with the liquor pumped through the chip charge. The fittings enabled the digester to be degassed, pressurized with steam, or depressurized as needed.

DETERMINATION OF TALL OIL

The procedure described by Saltsman and Kuiken (2) was used to isolate the crude tall oil from pulping and washing liquors. The crude tall oil was separated into unsaponifiables, fatty acids, and resin acids by the procedure of Zinkel (3).

ANALYSIS OF TALL OIL FRACTIONS BY GAS CHROMATOGRAPHY

Benzene solutions (1%) of the methyl esters of fatty and resin acids were injected onto a column (6 ft x 1/8 inch, stainless steel) packed with 10% EGSS-X, at a temperature of 180°C for fatty acid esters and 200°C for resin acid esters. A hydrogen flame ionization detector was used with helium carrier gas in the column at 25 ml per minute.

Individual components were identified presumptively by relative retention times and by comparative behavior with authentic references.

SIMULATED SKIMMING OF TALL OIL SOAPS

At the end of each cook, the reactor was cooled to 80-90° and opened, and the hot liquor was decanted from the chips through a 150 mesh, stainless steel screen into a beaker. After standing undisturbed overnight at room temperature, the lower 40-60% of the liquor was removed by a siphon to another vessel and both portions were analyzed for extractable tall oil. The amount of tall oil

in the upper portion, corrected for dissolved tall oil, was defined as skimmable tall oil soap. The method is similar to that reported by Bolger and Hopfenberg (1).

RECOVERY OF TALL OIL FROM PULPS

The recovery of tall oil from pulps was based on a general method outlined by Laundrie and Zinkel (4). After the fiberizing liquor was filtered from the pulp, the pad, without further washing, was pressed as free of liquor as possible under a rubber sheet. The wet pad was broken by hand and was leached overnight with 100 ml of sulfuric acid in acetone (10 ml of 5N aqueous sulfuric acid and 50 ml of water diluted to 500 ml with acetone). The mixture was filtered on a sintered glass funnel and washed with 200 ml of fresh acetone applied in 50 ml portions. The pulp mat was pressed with a rubber sheet and oven-dried for the determination of pulp yield. The acetone extract was analyzed in the usual manner for tall oil content.

PLANNED FUTURE EXPERIMENTS

Since one of our most important and unexpected findings was the fact that under the conditions of experiment employed in our last alkali-oxygen cooks of aspenwood and slash pinewood chips only minor losses of potential tall oil (based on saponified extractives) occurred when tall oil was recovered from the black liquor, the fiberized chip washings, and the pulp, we will attempt to confirm these findings under a variety of conditions and with loblolly pinewood.

The experiments will be performed in sets of four because four digesters are available with valves for degassing and admitting oxygen. Most experiments will be based on loblolly pine, but aspen and slash pine will be used to augment the tests required. All cooks with alkali-oxygen will be conducted at 160°C and with 140 psi oxygen pressure.

The last set of experiments may be repeated to test the validity of the results of the first series and to extend our knowledge concerning the possible fate of extractives in alkali-oxygen pulping. In addition, the following sets of experiments are planned, subject to change as new data may indicate the need for changes.

Set I

1. Two parts unextracted normal slash pinewood + one part resin-soaked slash pinewood.
2. Two parts extracted loblolly pinewood + one part resin-soaked slash pinewood.
3. Three parts extracted loblolly pinewood spiked with 3% tall oil fatty acids + one part resin-soaked slash pinewood.
4. Unextracted loblolly pinewood, control.

Set II

1. Extracted loblolly pinewood spiked with 3% tall oil rosin.
2. Extracted loblolly pinewood spiked with 3% resin-soaked slash pinewood extractives.
3. Extracted loblolly pinewood spiked with 3% tall oil fatty acids.
4. Unextracted loblolly pinewood, control.

Set III

1. Unextracted normal slash pinewood, control.
2. Unextracted loblolly pinewood, control.
3. Extracted loblolly pinewood spiked with 1% tall oil fatty acids and 2% resin-soaked slash pinewood extractives.
4. Extracted loblolly pinewood spiked with 2% tall oil fatty acids and 2% resin-soaked slash pinewood extractives.

Each cook will be separated into (1) decanted black liquor, (2) fiberized chip washings, and (3) undried pulp as in the last set of experiments described in this report. By determining the extractable tall oil in each portion as outlined, the over-all attack on the tall oil components can be assessed. Analysis of the acid fractions by gas chromatography will provide information about the attack of the alkali-oxygen system on individual components.

The experimental results from the three above sets of cooks should (1) indicate the degree to which alkali-oxygen pulping reduces the potential tall oil, and (2) refine our knowledge concerning the attack on specific tall oil components. In addition, we hope to learn something about the influence of tall oil component content of the chips on the results obtained.

The recovery of tall oil from the pretreatment of chips with sodium hydroxide and from the alkali-oxygen black liquors was lower than might be expected from the known extractive content of the pinewood chips. Furthermore, the major portion of tall oil was found in the fiberized chip washings. These data indicated that a disproportionate fraction of the tall oil soaps remained within the chips through the pretreatment or alkali-oxygen cooking cycles. In order to test this hypothesis, experiments are planned to recover tall oil as completely as possible, as noted earlier, from the decanted black liquor, from the fiberized chip washings, and from the pulp. A comparison of the alkali-oxygen process with the kraft process may reveal any differences in diffusion between the two processes. Additional experiments are planned to test the effect of dispersants (such as Busperse 47) on the production of tall oil in alkali-oxygen pulping.

Other experiments are planned to determine whether tall oil yields can be improved in an alkali pretreatment stage.

Although the aspenwood and resin-soaked slash pinewood cooks gave no skimmable soaps (Table IV), a combination of the two black liquors may do so. Such an experiment is planned.

Due to the considerable retention of tall oil soaps found on the pulps from our fiberizing process performed at a consistency of 2-3% in water, experiments on fiberizing in dilute sodium hydroxide are indicated.

In the course of collecting the aqueous acetone extract from the resin-soaked slash pinewood pulp, crystals of a substance believed to be vanillin were observed. However, in the processing for recovery of tall oil, any vanillin

would have been discarded. Experiments designed to measure the total vanillin formed in alkali-oxygen pulping of such wood are included in our plans.

Development studies on the use of high performance liquid chromatography for the evaluation of alkali-oxygen reaction mixtures are underway. These are being continued.

ACKNOWLEDGMENTS

We gratefully acknowledge the work of staff members Mrs. Bruce Alward and Mr. John Peckham without whose assistance this work could not have been done.

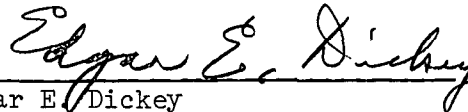
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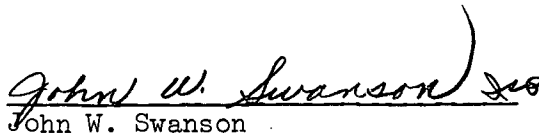
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