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A Study of Tall Oil from Green and Seasoned Slash Pine Wood

by Keith W. Max

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A STUDY OF TALL OIL FROM GREEN AND SEASONED SLASH PINE WOOD

A thesis submitted by

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INTRODUCTION

To anyone in the field of sulfate pulping the term tall oil is undoubtedly very familiar, for this by-product is evident whether or not it is recovered. In fact, sulfate soap (the sodium salts of tall oil components) is an important constituent of black liquor, adding to the fuel value in the recovery system as well as to the problems arising during the concentration stage. In explanation of this statement, it should be pointed out that sulfate soap has been found to be responsible for a large amount of fouling and plugging of pipes, tubes, and valves. Furthermore, this substance is suspected of being one of the chief factors causing foam difficulties during the handling of black liquor.

Because tall oil has commercial possibilities and, indeed, has been produced in Europe for several decades, the chemical composition and properties of both crude and refined oils have been studied. For a review of the information relating to tall oil, reference may be made to a recent paper by Wise (1). Some of this information is given in the historical section of this report, but only the data pertinent to the immediate problem are included.

Because the information reported in the tall oil literature by nearly all investigators is derived from studies of commercial products, little or nothing is known about the history of the material used for analysis. It appears logical, therefore, to study tall oil produced under accurately controlled conditions from wood, the history of which is also known.

A further object of the proposed study has been the determination of the effect of wood seasoning on the characteristics and properties of the tall oil therefrom. Practical observers have noted that the difficulties arising from black liquor foam are considerably more pronounced when green wood is used for pulping. Because the sulfate soap in black liquor probably contributes to this foaming, the question arises as to whether a wood-seasoning period produces any change in the tall oil which would reduce the foam trouble. Special emphasis has been placed on the fatty acid fraction during the study of the wood-seasoning effect.

Since the nature of tall oil is dependent upon the characteristics of its precursors in the wood, another aim of this investigation has been the comparison of the composition of the ether-extractive material from wood with that of the tall oil produced by pulping another portion of the same wood.

An integration of the individual objectives produced sufficient data to draw some conclusions as to the effect of pulping conditions on the extractives, the effect of seasoning on the extractives and the resulting tall oil, and the reason for decreased foaming in the black liquors from the pulping of seasoned wood. At the same time, the attack used to fulfill the aims stated above also yielded information about tall oil produced under controlled conditions from a known wood.

HISTORICAL REVIEW

When a resinous wood is pulped by an alkaline process, the organic acids and esters present as extraneous components are converted to sodium salts. The extent of this conversion is not known, but it is probable that even most of the esters are saponified. These sodium salts, which are actually soaps, are soluble in water, but the electrolytes in the black liquors exert a salting-out action on the organic salts which is sufficient to render them much less soluble. Indeed, as the black liquors are concentrated, this effect becomes marked and there is a gradual separation of a floating soap.

The presence of these floating soaps was noted as early as 1890, and in 1893 Klason (1a) pointed out that these soaps contained rosin. This material is now commonly called sulfate soap, as the sulfate pulping process is generally used with resinous wood. The Swedish call it *sulfattval* or *sulfat sopa*, and the Germans term it *Sulfat Seife*. This foreign nomenclature persists in the literature because most of the interest in tall oil has been centered in Europe.

At the beginning of the twentieth century, the oil produced by acidification of sulfate soap aroused commercial interest in Sweden. Larsson (2), working at Skutskär, Sweden, in 1902 began the pioneer work on the commercial production of tall oil (*Tallöl* or *tallolja* in German and Swedish, respectively). It is of interest to note at this point that he employed a vacuum distillation method for purification, a process in use today.

Fahrion (3), prominent German rosin chemist, was requested by Larsson to analyze samples of tall oil; however, he failed to recognize the presence of acids other than several rosin acids. It is probable that the term liquid rosin (flüssiges Harz, flystande harts), another common name for tall oil, dates from this time. Because Bergström and his coworkers (4, 4a) subsequently reported the presence of fatty acids, it is unfortunate that the term liquid rosin is applied to tall oil, for the name is misleading.

Tallolja is the Swedish designation for oil of pine which, indeed, is the source of tall oil; however, it is not to be confused with the pine oil of this country, which is a distillation product of the wood turpentine industry.

Since the early beginning of the work on tall oil, many investigators, prompted by both scientific and commercial interests, have studied this by-product of the sulfate pulping process. In addition to the many academic studies, there are over 200 patents relating to the production, purification, and applications of tall oil. West (5) has prepared an extensive annotated bibliography on the subject.

The sulfate soap which separates from black liquor is a dark brown sticky material containing considerable water and having the characteristic odor of the sulfate process. Drying of this soap is difficult because of the formation of a tough film of rosin acids on its outer surface. This acid film is produced by the action of carbon dioxide from the air on the rosin salts.

Although floating soaps separate from the strong black liquor taken immediately from the digester, the amount is greatly increased upon concentration of the black liquor: according to Drewsen (6), the specific gravity of the soaps is approximately 1.05, a value close to that of the original black liquor. As the specific gravity of the liquor is increased by concentration, the separation becomes more complete for two reasons: the difference in density between the soaps and the liquor is greater and, secondly, the salting-out effect, mentioned above, is more evident. It is a common commercial practice to separate sulfate soap at an intermediate point in the evaporator system by gravity skimming or by centrifugal processing. Drewsen stated that a typical sample of soap contained 36 per cent rosin acid salts, 23 per cent fatty acid salts, and 34 per cent moisture. The remainder was probably unsaponifiable matter.

The presence of unsaponifiables in sulfate soap may seem surprising; however, the components of the unsaponifiable portion separate with the soaps in an emulsified form. This non-soap portion may be removed by solvent extraction (7) of the dried sulfate soap.

Tall oil may be produced from sulfate soap by acidification. Various procedures have been proposed for carrying out this operation, and many chemicals have been suggested as acidifying agents--sulfuric acid, sulfur dioxide gas, sodium bisulfate, sodium bisulfite, waste sulfite liquor, etc. However, commercial practice generally accepts only those chemicals which will be useful in the recovery system.

It is a well-known fact that crude sulfate soap contains occluded ligneous materials which are precipitated upon acidification: therefore, it is desirable to remove as much of these impurities as possible prior to acidification, to obviate the formation of very stable emulsions of finely divided foreign matter. In order to purify sulfate soap before acidification, sodium sulfate solution is used as a wash or the soap is salted out from a fresh water solution with sodium sulfate. Although sodium chloride is more effective for this purpose, its presence is undesirable in the recovery system.

The acidification is generally carried out on a hot solution of sulfate soap to a pH of about 5 (8). Agitation is important to insure proper mixing without danger of emulsion formation; however, proper purification of the soap eases the latter difficulty. The liberated crude tall oil may be separated directly or extracted with an immiscible solvent and then separated and concentrated.

The product isolated in this manner is a crude oil--that is, it contains some objectionable, foreign components; however, this material is the by-product of the sulfate industry known as tall oil. The composition of this odoriferous, viscous, yellow to brown oil is far from constant. For many years chemists have known that tall oil contains many compounds which may be classified in groups as unsaponifiables, rosin acids, and fatty acids. The first class (unsaponifiable matter) includes phytosterols, complex alicyclic alcohols, and resenes. Little is known about the individual components of the resene material, but it is probable that it consists principally of hydrocarbons related to those found in petroleum and others similar to terpenes or their derivatives. The phytosterols have been studied in greater detail, and some information on their nature is available in the literature. Sandquist and coworkers (9 - 11) found a mixture of phytosterols which melts at 137 - 139° C. (acetyl derivative, melting at 122 - 123° C.); from this two crystalline compounds, dihydrositosterol (melting at 139° C., $[\alpha]_D$ +25.6°) and a sitosterol (melting at 138.5° C., $[\alpha]_D$ -32.2°), were isolated and assigned the formulas $C_{29}H_{52}O$ and $C_{29}H_{50}O$, respectively. Bergström (12, 13) also found a phytosterol with a melting point of 134° C., and Dittmer (14) reported a melting point of 136° C. for the phytosterol from tall oil. It is probable that long chain alcohols, resulting from the saponification of waxes, are present in tall oil, and Sandquist and colleagues (15) have isolated such a compound which they believed to be lignoceryl alcohol.

The unsaponifiable matter in tall oil adds very little to the value of the product. For most industrial purposes, however, its presence is not greatly objectionable. The mechanism by which a nonsaponifiable material is included in the sulfate soap, as stated above, seems to be one of emulsion; thus, after acidification of the soap, these noncarboxylic substances become an integral part of the tall oil.

Little is known regarding the identity of the compounds composing the rosin acid group. The difficulties involved in the study of these rosin acids have prevented intensive investigation of their isolation and identification. In spite of this lack of information, these acids are undoubtedly related to those found in pine rosin (colophony). Aschan and associates (16, 17) have reported pinabietic acid, $C_{20}H_{30}O_2$ (melting at 176- 178° C.), as being present in black liquor and a series of acids (termed colophenic acids) which differ from ordinary rosin acids by the ready solubility of their sodium salts in cold water and the stability of the solution toward carbon dioxide. Hasselström, McPherson, and Hopkins (18) also found a pinabietic acid which they considered to be a mixture of Steele's abietic acid, dehydroabietic acid, and dihydroabietic acid. Dittmer (14) found abietic acid only, and Frankel (8) stated that the rosin acid fraction contained about 90 per cent abietic acid. Other rosin acids reported by Becher (24) are oxyresinic and aboetinic acids. On the other hand, some investigators have proposed the term tallic acid for the rosin acids in tall oil, feeling that there is some difference between them and the ordinary rosin acids.

It is sufficient to say that the individual compounds comprising the rosin acids are probably closely related and are undoubtedly conversion products or derivatives of any one of the family of rosin acids originally present in the wood.

By far the most important class of compounds found in tall oil are the fatty acids. Of this class, the unsaturated acids of eighteen carbons (the oleic acid series) predominate. At least three compounds--oleic acid ($C_{17}H_{33}COOH$), linoleic acid ($C_{17}H_{31}COOH$), and linolenic acid ($C_{17}H_{29}COOH$)--have been identified. It is significant that these acids have the same chain length, differing only in the degree of unsaturation. Most investigators have found that linoleic acid is usually present in the largest quantity (14, 19-21). However, this is not necessarily true, because many factors may influence the proportion of these acids in tall oil. As an example, Hasselström (22) found only a small quantity of linoleic acid in refined tall oil. Other unsaturated fatty acids (ricinoleic acid, a hydroxy acid with one double bond, and erucic acid ($C_{21}H_{41}COOH$), a singly unsaturated acid) have been reported by Pyhälä (23), and Becher (24) found brassic acid (an isomer of erucic acid).

The presence of saturated fatty acids is a controversial question, with some investigators reporting solid acids and others not. Sandquist and colleagues (15) have reported lignoceric acid ($C_{23}H_{47}COOH$), and Keghel (25) identified myristic acid ($C_{13}H_{27}COOH$). Many workers (13, 19, 22, 23, 25) have found palmitic acid ($C_{15}H_{31}COOH$), whereas others have denied its presence. Hasselström (26) concluded that the palmitic acid, which he had previously reported (22), was formed from oleic acid during the cooking process. However, it is difficult to understand how the chain length could be reduced by two carbon atoms, rather than be split at the double bond.

Hodges (27) lists a large number of compounds which have been reported by various authors as present in tall oil. The presence of some of these is problematical, but the list is of interest in that it indicates the variety involved.

It is not difficult to understand that different compounds and analyses have been reported by different investigators, because the number of variables influencing the composition of tall oil is large. It is obvious that, with the exception of compounds possibly formed during the pulping operation, the composition of tall oil is dependent largely upon the composition of the ether-extractive material in the wood, which may be considered its precursor. It is also evident that the extractives in wood will vary from one species to another; however, the extraneous material is likely to vary to a considerable extent in the same species. According to Kurth (28), the composition of the extractives of pine sapwood differs greatly from those in the heartwood. Moreover, the age, season of cut, climatic conditions, position in the tree, etc. are factors influencing the composition and amount of extractives in any one species of wood.

It should be noted at this point that a considerable amount of the extractive material in the wood is not recovered as tall oil after cooking. The losses appear to occur during wood storage, during pulping, and as a result of the partial solubility of the sulfate soap in black liquor. Bergström and Cederquist (29) found that the yield of tall oil amounted to about 41.6 per cent of the material extracted with benzene from the same amount of wood.

Table I contains several typical tall oil analyses taken from West's bibliography (5):

TABLE I

TALL OIL ANALYSES

Sample	Acid No.	Saponification No.	Unsaponifiable %	Rosin Acids %	Fatty Acids %
A	145.0	165.0	10.0	57.0	33.0
B	157.3	167.9	8.2	43.4	48.5
C	164.4	174.9	6.0	32.0	58.0
D	163.0	173.0	8.2	38.4	52.0
E	151.0	174.0	10.5	48.0	40.8
F	160.0	169.0	9.5	41.4	48.3
G	156.0	172.0	8.5	38.7	51.2
H	161.0	168.0	6.8	32.2	59.0

Although the history of the materials used as a source for the data presented in Table I is not available, one is struck immediately with the wide variations in the analyses. The data serve to emphasize the dependency of the composition and properties of tall oil upon its precursors and preparation.

It is interesting to observe the general difference commonly found between acid and saponification values. This difference, which might be termed an ester number, indicates the presence of esters in tall oil. At first glance, it appears odd that any esters should be present in a material which has been subjected to such strong saponifying action as that of an alkaline pulping process. On the other hand, the possibility of re-esterification after the isolation of tall oil from sulfate soap gives some reason to expect an ester number for tall oil.

Analyses for rosin acids and fatty acids show that the latter are generally present in greater proportion. There are exceptions, of course, as in the cases of A and E (Table I). These data give further evidence that the composition of tall oil is not constant.

From the amount of study on tall oil, one would consider the substance a useful and vital commercial product. For that matter, considerable amounts have found a market in Europe, but in this country relatively little tall oil is used. The greatest incentive to spur research is the vast amount of tall oil available as a by-product, which, at the moment, is generally burned in the recovery system. Estimates of the yield of tall oil range from 50 to 100 pounds per ton of pulp produced. A rough estimate indicates that 125,000 to 250,000 tons of tall oil could be produced each year in the United States alone.

The brief description of the isolation of tall oil from black liquor previously given is but a general scheme, and many variations are in practice; however, regardless of the method by which the crude product is obtained, the objectionable odor and color characteristics of the sulfate process are inherently present. These drawbacks have retarded the use of tall oil in this country and, in consequence, many investigators have labored to devise methods to produce a marketable oil which could compete with natural fats and oils. Many types of purification schemes have been suggested to alleviate the difficulties mentioned above, and other methods have been proposed to obtain an oil which has special properties, such as a high concentration of fatty acids. To enumerate and describe the individual methods for purification would lead to a voluminous description and extensive bibliography; therefore, only the principles involved, including several typical references for each case, will be classified. A list of methods of improving the quality of crude tall oil follows:

1. Distillation with superheated steam (30, 31).
2. Vacuum distillation (30, 32).
3. Heat treatment to 250 - 350° C. to effect a pyrolysis of oxidized rosin acids, the principal color bodies, and to expel odor and water (33, 34).
4. Heat treatment above the melting point of tall oil salts in the absence of air and water, accompanied by a flushing stream of hot inert gas to carry away volatile materials (35, 36).
5. Treatment with oxidizing or bleaching agents (hydrogen peroxide, chlorine, hypochlorous acid, bleaching powder, hydrosulfites, nitric acid, oxygen gas, etc.) (37 - 40).
6. Precipitation of color bodies from hydrocarbon solvents (benzine or naphtha), with further utilization of decolorizing agents (charcoal, fuller's earth), furfural or its derivatives, ethylene glycol, etc., to remove impurities (41 - 45).

7. Treatment of tall oil salts with strong alkali or of the oil itself with strong mineral acids (45 - 47).

Such purifications have as their purpose the removal of the objectionable characteristics of odor, color, moisture, etc., but the resulting product has a composition only slightly modified. In order to obtain a product with a high percentage of fatty acids with little rosin or vice versa, further treatment is necessary. Frequently the use requirements prohibit mixtures such as normally occur in tall oil; consequently methods for separating fatty acids from rosin acids have been devised. After a separation of unsaponifiable matter, a further separation of the acids may be carried out by the following briefly outlined principles:

1. Selective glycerol or alcohol esterification of fatty acids; separation by distillation (48 - 50).
2. Complete glycerol esterification with tin catalysts, followed by a zinc-catalyzed hydrolysis of the fatty esters; separation by distillation (51).
3. Selective esterification of fatty acids with an aliphatic monohydric alcohol of less than 6 carbon atoms and a subsequent esterification of rosin acids with glycerol; separation by distillation (52).
4. Complete esterification of both acid fractions with glycerol, followed by a transesterification of the fatty esters with a low boiling monohydric alcohol; separation by distillation (53)
5. Selective esterification of the fatty acids with methyl or ethyl alcohol, followed by a neutralization of the rosin acids with aqueous alkali and an extraction of the fatty esters with an immiscible solvent. This method may be combined with the furfural purification method previously outlined to accomplish both a purification and a separation in one step (42, 54, 55).
6. Separation by forming water-soluble sulfuric acid esters at the unsaturations of the fatty acids (45).

7. Separation by the selective liberation of the rosin acids from sulfate soap by carbon dioxide gas or by a calculated amount of acid. Separation is accomplished by extraction. Hot secondary amyl alcohol dissolves both fatty acid soaps and rosin acids; on cooling, relatively pure crystals of fatty acid soaps separate (56).

8. Solution in liquefied propane and heating under pressure causes the crystallization of rosin acids, which may be separated (56a).

9. Fractional distillation of the acids (50, 57).

The above methods are not the only ones available, but they comprise the more important proposals for the commercial separation and purification of tall oil.

The fact that tall oil has not been commercially marketed in this country is largely the result of the inability of the chemical industry, at the present time, to produce purified oils at a cost substantially lower than the commercial prices of natural oils. Methods are available for the manufacture of such products, and it is possible that, because of the demand for and the lack of supply of natural products, tall oil may find application in certain fields now utilizing common fats and oils.

APPROACH TO THE PROBLEM

Approximately 1000 pounds of green slash pine wood were obtained directly from the stump to insure its freshness and divided into two equal portions. Half of each bolt was placed in each portion, one of which was used as received and the other was seasoned.

By ether extraction of the green wood meal, the precursors of the tall oil produced by pulping the green wood were isolated for examination. A sulfate cook on another portion of this green pine wood under well-defined conditions produced a black liquor from which sulfate soap and ultimately tall oil were likewise isolated.

After a prescribed seasoning period, the remaining half of the pine wood was treated in the same manner as the green wood. Extraction gave a product containing the precursors to the tall oil produced by cooking the seasoned wood.

As a result of such wood treatments, four products were obtained--ether extractives and tall oil from green wood, and ether extractives and tall oil from seasoned wood. The attack on the problem involved the examination of these four materials.

Because primary emphasis was to be placed on the fatty acid fraction of both extractives and tall oil, this fraction was isolated from the other classes of materials present. After such a separation, those tests which give information as to the composition and the effects of treatment were run on the fatty acid fraction.

EXPERIMENTAL PROCEDURES

TREATMENT OF THE WOOD

The wood used in the study of extractives and tall oil was slash pine (Pinus caribaea Morelet), one of the common yellow pines which ranges throughout the southern seaboard and gulf states. Approximately 1000 pounds (twelve 5-foot bolts) of this species were sent by express in a green condition directly from Brunswick, Georgia, to Appleton, Wisconsin. To protect the wood from drying out during the brief period of shipment, it was wrapped in asphalt laminated paper.

Each bolt was cut in half, one end of which was used for green wood studies and the other was stored for seasoning. This seasoning period was of four months' duration, but the conditions of storage only approximated those of actual practice. Because the winter months in Wisconsin are not conducive to outdoor seasoning, it was necessary to store the peeled wood indoors where the temperature averaged about 70° F. Every week during the 4-month storage time, the wood was periodically showered with water. This wetting was necessary to prevent too rapid drying of the wood; furthermore, it probably gave a closer approximation to actual southern seasoning conditions.

The green half of the wood was used immediately for pulping, extraction, analysis, etc. The data pertinent to the wood, as determined on the green wood only, are given in Table II.

TABLE II

DATA ON SLASH PINE

*Average specific gravity	0.569
Average growth rate, rings per inch	5.17
Average age, years	15.0
Wood analysis (oven-dry unextracted wood basis)	
Cross and Bevan cellulose, %	54.50
Lignin, %	28.20
Pentosans, %	12.60
Uronic acids, %	0.55

* Based on oven-dry volume.

The procedures for the determinations given in Table II were taken from Institute Group Procedures 31 and 30 and Institute Methods 14a, 13, 23a, and 25, respectively. From these data, the wood appears to be a normal sample of a typical sulfate pulpwood.

GENERAL METHOD OF PREPARING EXTRACTIVES

From sections of each bolt of wood so chosen as to obtain a representative sample, sawdust was prepared on a rotary saw fitted with a box for collecting the product. This sawdust was further disintegrated in a Mikro-Pulverizer and then fractionated. A small amount of 40 to 60-mesh material was separated for analysis, and a considerable quantity of 20 to 100-mesh wood meal was prepared for large-scale ether extraction.

Using a large Soxhlet apparatus, 8- 10-hour ether extractions were made until about 10 pounds of 20 to 100-mesh wood meal had been extracted. Water was removed from the combined extracts by means of a separatory funnel, and the ether solution was dried with anhydrous sodium sulfate. The dry ether solution was concentrated to a small volume on a steam bath and transferred to a suitable round-bottom flask with a standard ground-glass mouth. A fitting of this flask with a Claisen distilling head and proper condensing and receiving flask permitted the removal of most of the remaining ether *in vacuo*. During the distillation, carbon dioxide, dried by bubbling through concentrated sulfuric acid, was passed through a capillary into the solution to prevent oxidation. A final drying period of 3 hours in an oven at 105° C. in a stream of dry carbon dioxide gave the dry extractives which were used for analysis.

PRODUCTION AND ISOLATION OF TALL OIL

The conversion of the extractives in wood to sulfate soap by the sulfate pulping process has been reviewed in the historical section of this paper. The same process was carried through in this investigation.

The peeled slash pine wood was chipped in a small commercial chipper with the knives set to produce a 3/4-inch chip. The moisture content of the chips was determined (49.6% for green wood and 11.7% for seasoned wood), and a sufficient quantity of chips was placed in the digester to fill it to about three fourths of its capacity. Generally, this required about 100 to 110 pounds of wood (oven-dry basis).

In order to produce sufficient tall oil for the projected study and still work on a laboratory scale, a 13-cubic foot tumbling digester manufactured by the A. O. Smith Corporation was employed. It is equipped for use with ~~direct or~~ indirect steam; indirect heating is accomplished by means of a jacket.

The sulfate cooking liquor was made up in a small steel tank which was fitted in such a manner that the liquor was transferred to the digester from a side outlet about 6 inches from the bottom. By this means, the impurities settling from the strong liquor (260 grams per liter as sodium hydroxide) were not introduced into the digester.

All cooks were made under practically the following conditions:

Active alkali (as NaOH), %	25.0
Sulfidity, %	31.2
Water ratio, ml./g.	5.0
Average maximum temperature, ° C.	175
Time up to maximum temperature, hr.	1.5
Time at maximum temperature, hr.	3.5
Relief: at 100° C. and to 60 lb./sq. in. before blowing	
Heating: indirect	

At the end of the cook the pressure was relieved to 60 lb./sq. in., and the pulp and liquor were ~~then~~ blown into a pit with a false bottom separated by a perforated steel plate. The hot black liquor was withdrawn from this false bottom and stored in clean 50-gallon drums. Two such cooks were made ~~on~~ using both green and seasoned wood, and in each case the second cook was blown on top of the first. As much of the hot liquor as possible was drained from the pit. An overnight drainage period, followed by some pressing, removed more liquor from the pulp. After pressing, the pulp was approximately 15 per cent dry. No washing was done.

The pulp from the green wood had a permanganate number of 15.5, whereas that from the seasoned wood showed a permanganate number of 16.9.

The raw black liquor ~~obtained in such a manner~~ had a specific gravity of 1.05- 1.06, which is approximately the same as that of sulfate soap reported by Drewsen (6). In order to build up the specific gravity to approximately 1.10, which ~~point~~ Drewsen claims to be optimum for the separation of sulfate soap, the liquor was concentrated to about one half of its volume.

The concentration on a laboratory scale of about 70 gallons of black liquor (~~the~~ approximate volume recovered from two cooks) is a long and arduous process. Therefore~~,~~ a special distilling head, employing a change of direction trap principle, was designed and constructed on a larger scale. It was necessary to incorporate a foam trap in the distilling head to remove water under reduced pressure without loss of soap in the distillate.

The design of this apparatus ~~can~~ be seen from the photograph (Figure 1) and from the cross-sectional diagram (Figure 2).

When this distilling head was attached to a stainless-steel resin kettle and connected through a multitube condenser to two aspirator-type vacuum pumps in parallel, the assembly for concentrating black liquor was complete. The kettle was equipped with a steam jacket for indirect heating and a motor-driven stirrer to insure more uniform heating of the liquor. The distillate was collected in two 9-liter bottles inserted in parallel between the condenser and the vacuum pumps (Figure 1).

Operation of this apparatus was relatively smooth between 125 and 145° F. at pressures of 35 to 90 mm. of mercury. Foam from the kettle passed through the expansion chamber a (Figure 2) into trap b where it dropped to the bottom, vapors passing on through f into trap c. If any foam entered f, then trap c provided a further barrier to its entry into condenser h. The foam in traps b and c eventually broke and returned to the kettle through legs d and e.

It should be pointed out that certain features of the distilling head are essential to efficient trapping of the foam. The expansion chamber a is necessary to prevent foam from passing into the trap system in the form of slugs. In other words, it gives the foam an opportunity to break before entering the traps. The legs d

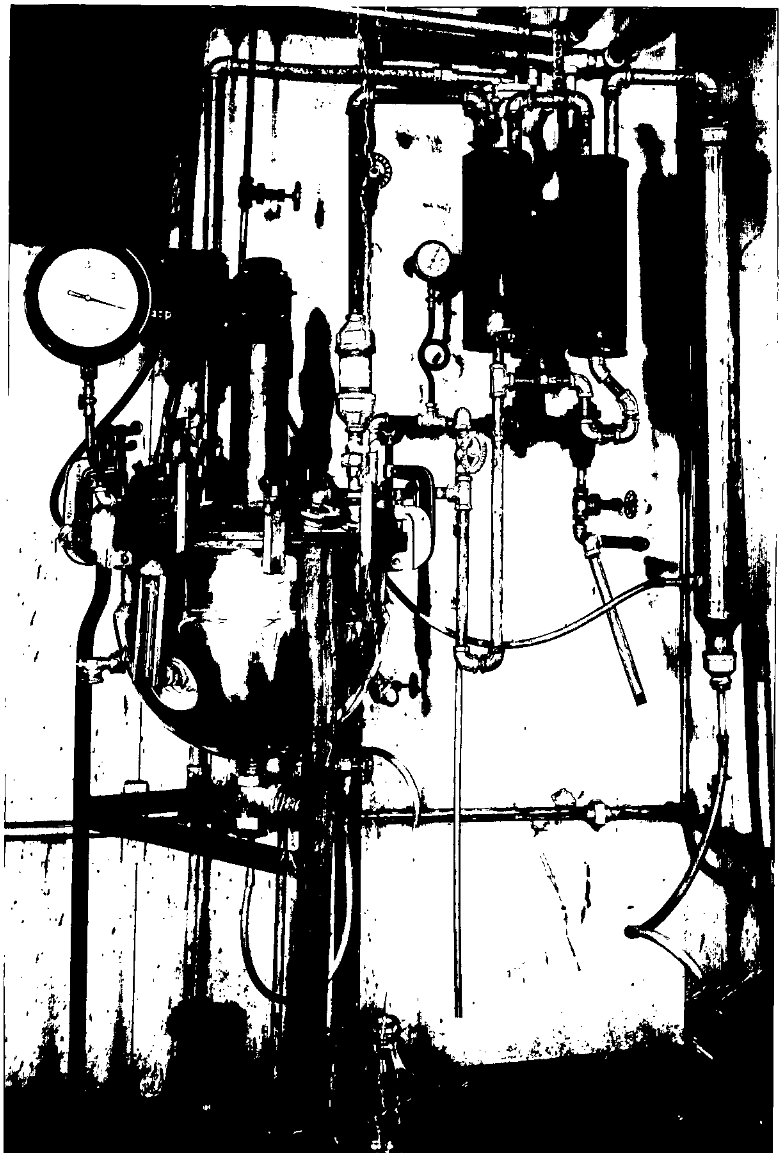

Figure 1

BLACK LIQUOR CONCENTRATION ASSEMBLY

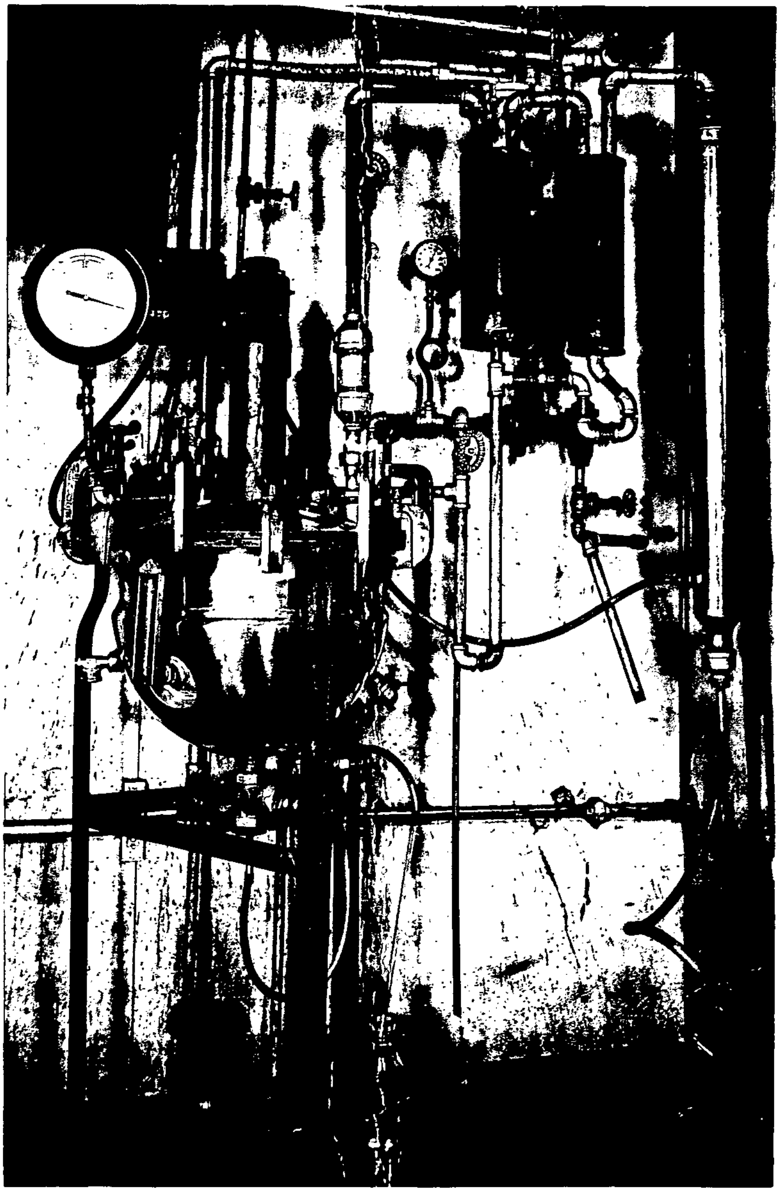

Figure 1

BLACK LIQUOR CONCENTRATION ASSEMBLY

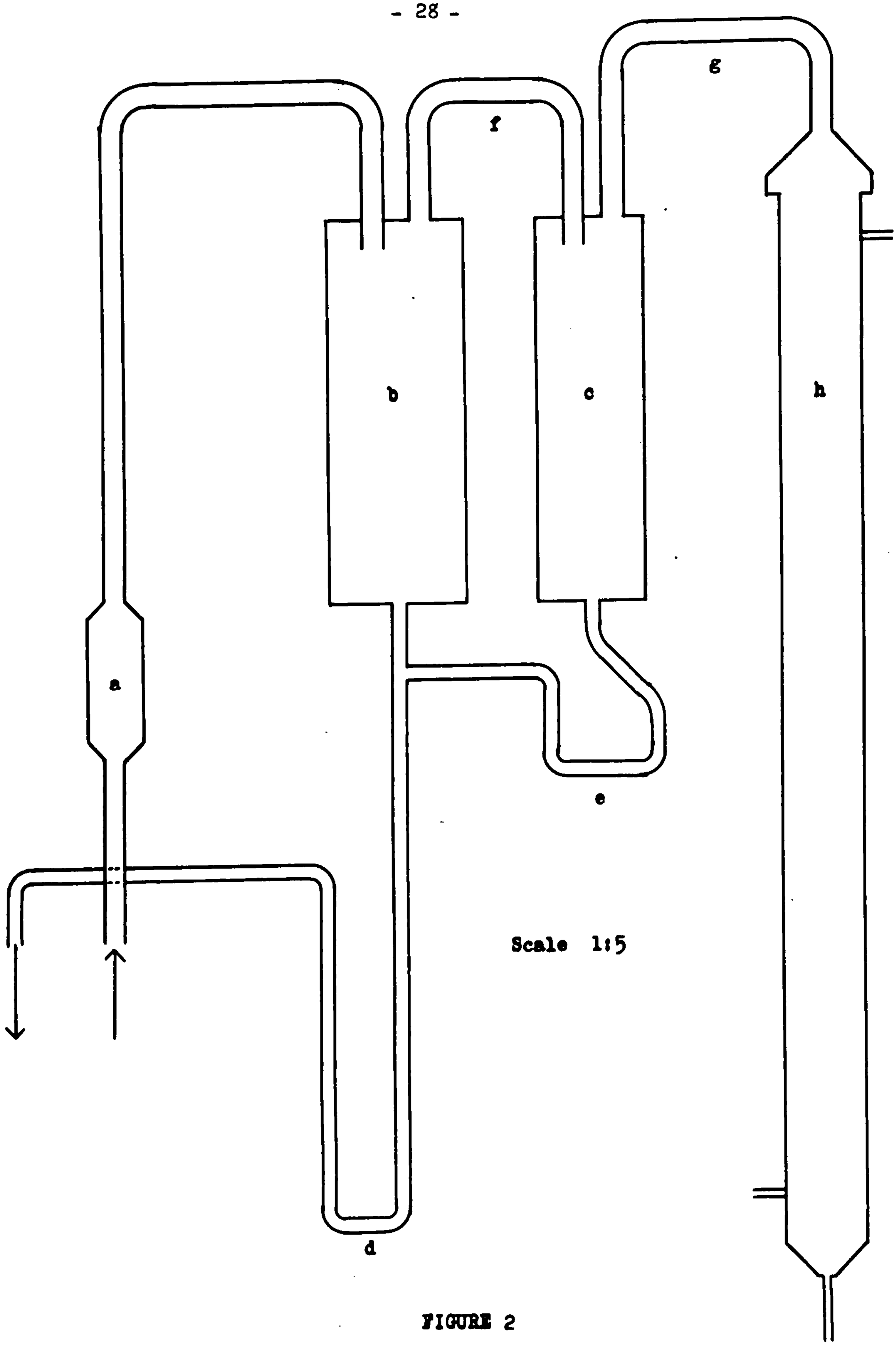

FIGURE 2

and e in the return system, which retain liquor, prevent vapor from entering the traps from the bottom. This is very important. Vapors entering from the bottom of ~~the~~ traps ~~would~~ cause further expansion of the foam in the traps until it passed over through g into condenser h.

At first glance, leg d appears to be exceedingly long; however, it was found that the foam in expansion chamber a increased the friction to vapor passage to such an extent that a back pressure was exerted through leg d. Thus, it is necessary to have a hydrostatic head in leg d greater than this back pressure.

The construction of a complex trap system in the distilling head was necessary, because it was undesirable to incorporate antifoaming agents in the liquor.

Although the kettle used had a capacity of about 5 gallons, only about half this volume was maintained. As the distillation proceeded, additions were made through the valve in the bottom of the kettle (Figure 1). When the liquor became too thick for efficient operation, it was returned to ~~the~~ storage drum and another portion added. In such a manner, the concentration of the liquor in the drum was built up to the desired point. It was observed that the degree of foaming decreased as the liquor became more concentrated. An average rate of distillation was about 1 gallon of distillate per hour. Roughly, a concentration to approximately half volume gave a specific gravity of 1.12.

The drum containing the concentrated black liquor was placed on a suitable rack, so that the temperature of the liquor could be raised to 42° C. (<u>6</u>) by heating with a small burner. When this temperature was reached and maintained, the liquor was drawn off from the bottom and run through the separator bowl of a Sharples supercentrifuge from a head of 5 feet. The use of a No. 7-1/2 ring and a medium injection nozzle gave a volume separation of about 5:1 with respect to the heavy and light fractions, the soaps being contained in the light fraction.

After 24 hours, the soaps floating on the smaller fraction were skimmed off and combined with the major portion of the soaps which remained in the drum as the liquor was withdrawn.

The crude sulfate soaps were purified to a considerable extent by a ~~triple~~ salting-out process. A ~~water~~ solution of the soaps, prepared by using the minimum amount of hot water, ~~was~~ filtered through a finely woven cloth and then treated with solid sodium chloride in sufficient amount to give a salt concentration of 200 grams per liter. With that concentration of salt, the soaps are salted out and float on the surface. The liquor was withdrawn from the bottom of the separatory funnel. This salting-out process was repeated twice, the maximum amount of liquor being withdrawn during the last treatment.

Such treatment effects a considerable purification of the soaps, which are now suitable for the liberation of the tall oil, ~~The~~ acidification was accomplish~~ed~~ by the addition of sulfuric acid to a hot water solution (70° C.) until a pH of approximately 5 was reached (8). Unfortunately, the liberation of tall oil was accompanied by a flocculation of alkali-soluble impurities. ~~This is~~ an indication of incomplete purification of the soaps, ~~but~~ further salting out of the soaps was ~~not~~ practical, as will be explained. Ether extraction of the acidified solution gave a solution of tall oil contaminated with ~~flocculated~~ ligneous material; however, these impurities were effectively removed by filtration. ~~In~~ explanation, it should be pointed out that, on a small scale, it is more effective and simpler to filter off small amounts of these impurities from the ether solution of tall oil than to attempt a complete purification of sulfate soaps.

Any undissolved water was removed from the ether solution of tall oil in a separatory funnel, followed by drying the ether solution with anhydrous sodium sulfate. The dried solution was concentrated on a steam bath to a small volume and transferred to a tared 1-liter round-bottom flask with a standard ground-glass mouth. The remainder of the solvent was removed by vacuum concentration with dry carbon dioxide passing through the capillary. After a 3-hour drying period in an oven at 105° C. in a stream of dry carbon dioxide, the flask and tall oil were weighed.

SEPARATION OF COMPONENT CLASSES

In order to separate either tall oil or the extractives of wood into component classes, such as unsaponifiables, rosin acids, and fatty acids, well-known methods of analysis were used. Kurth (58) has reported a general scheme for the separation and analysis of the extraneous components in wood. His outline for the analysis of the ether extractives is generally applicable to the products encountered in this investigation. Some modifications were made, but the principles involved are the same.

The dry sample of extractives or tall oil was saponified by refluxing with alcoholic potassium hydroxide solution, prepared according to Jamieson (59), using 10 ml. of the alcoholic alkali per gram of substance. After the addition of a suitable amount of water, the unsaponifiable matter was extracted with ether from the potassium salts of the saponifiable material. This ether solution was washed with water, dried over anhydrous sodium sulfate, filtered, and concentrated. The concentrated unsaponifiable solution was transferred to a tared Erlenmeyer flask, further concentrated, and then dried in an oven in a stream of dry carbon dioxide. After cooling and weighing, the percentage was calculated.

The salts of the acids ~~were~~ transferred to a large separatory funnel and acidified with sulfuric acid. An ether extraction removed the acids from glycerol and water. After washing the ether solution with water to remove excess mineral acid, it was dried with anhydrous sodium sulfate, filtered, and concentrated.

For the separation of rosin and fatty acids, the preferential esterification method ~~has~~ been recommended. Considerable controversy has been raised over the choice of a catalyst. Twitchell (60), Fahrion (61), Wolff and Scholze (62), and Schulz (63) advocated either hydrochloric or sulfuric acid as a catalyst, but considerable disagreement is found among these authors. ~~However~~, the fact remains that the sulfuric acid method of Wolff and Scholze gives a better degree of separation than the hydrochloric acid method. Kurth (58) recommended the Wolff and Scholze method. Blengsli (64) studied the degree of sulfuric acid ester formation (the controversial drawback against the use of sulfuric acid as a catalyst) by following the amount of free sulfuric acid in the esterification mixture. He concluded that, below 35° C., substantially no sulfuric acid esters ~~was~~ formed. Because the same degree of esterification of the fatty acids can be obtained with a sulfuric acid catalyst at room temperature in 2 to 18 hours as by refluxing (62), the Wolff and Scholze method appears satisfactory.

For the purpose of this study, however, it was essential that no sulfuric acid esters result during the esterification, because such a reaction would reduce the degree of unsaturation according to the following mechanism:

$$-CH=CH- \; + \; H_2SO_4 \longrightarrow -CH_2-\underset{\displaystyle OSO_2OH}{\underset{|}{CH}}-$$

$$-CH_2-\underset{\displaystyle OSO_2OH}{\underset{|}{CH}}- \; + \; H_2O \xrightarrow{\text{hydrolysis}} -CH_2-CHOH- \; + \; H_2SO_4$$

Further, because the degree of unsaturation and the amount of oxidation (as hydroxy or keto acids) are fundamental ~~measures~~ measure of the effect of wood seasoning, no products should be formed during the analyses which would cause a misinterpretation of the results. It was decided, therefore, to determine whether sulfuric acid esters are formed during esterification.

Relatively pure oleic acid (Hanus iodine number 91.2) and a c.p. abietic acid (Eastman Kodak product) were mixed in known amounts. Wolff and Scholze's method produced a 98.37 per cent separation, which is entirely satisfactory for this type of analysis. The iodine number of the separated oleic acid was 93.8 after an approximate correction for the rosin acids in the fatty acid fraction. This is a ~~good~~ substantiation of Blengsli's ~~titration~~ ~~evidence~~ that no sulfuric acid ester is formed below 35° C. It was decided, therefore, to use Wolff and Scholze's method at room temperature for the separation of rosin and fatty acids. The method employed ~~is as~~ follows:

The amount of dry acids was estimated from the original sample weight and the percentage of unsaponifiables, allowing for glycerol loss in the case of extractives. Absolute ethyl alcohol (7 ml. per gram of acids) was added to the acids and solution accomplished by agitation. Then a 5:1 volume mixture of absolute alcohol and concentrated sulfuric acid (3.5 ml. per gram) was carefully added, the mixture stirred, and allowed to stand for 20 to 24 hours.

At the end of this period, the mixture was carefully neutralized to phenolphthalein with dilute (approximately normal) aqueous sodium hydroxide solution. After transferring to a separatory funnel, the fatty esters were extracted with ether, adding more water, if necessary, to obtain a sharp interface.

The water solution containing rosin salts was acidified with sulfuric acid and extracted with ether. This ether solution was washed, dried, filtered, concentrated, and transferred to a tared flask. After removal of the ether in vacuo and drying in a carbon dioxide atmosphere, the rosin acids were weighed and the percentage calculated.

The ether was evaporated from the fatty ester solution and alcoholic potassium hydroxide solution (10 ml. per gram) was added. After refluxing for 30 minutes, a large volume of water was added and the solution acidified with sulfuric acid. An ether extraction removed the fatty acids, which were isolated and weighed in the same manner as rosin acids.

The oxidized fatty acids, which may be removed as a result of their insolubility in petroleum ether, were not isolated at this point, as Kurth advocated. Rather, these oxidized acids were determined in the saturated and unsaturated acid fractions after separation.

Because of the difference in solubility of the lead salts of saturated and unsaturated fatty acids in ether or alcohol, more or less standard methods for their separation have been devised. The lead salt-ether method, as described in detail by Jamieson (59), was used in these analyses.

The general scheme of analysis, as described above, is diagramed in Figure 3.

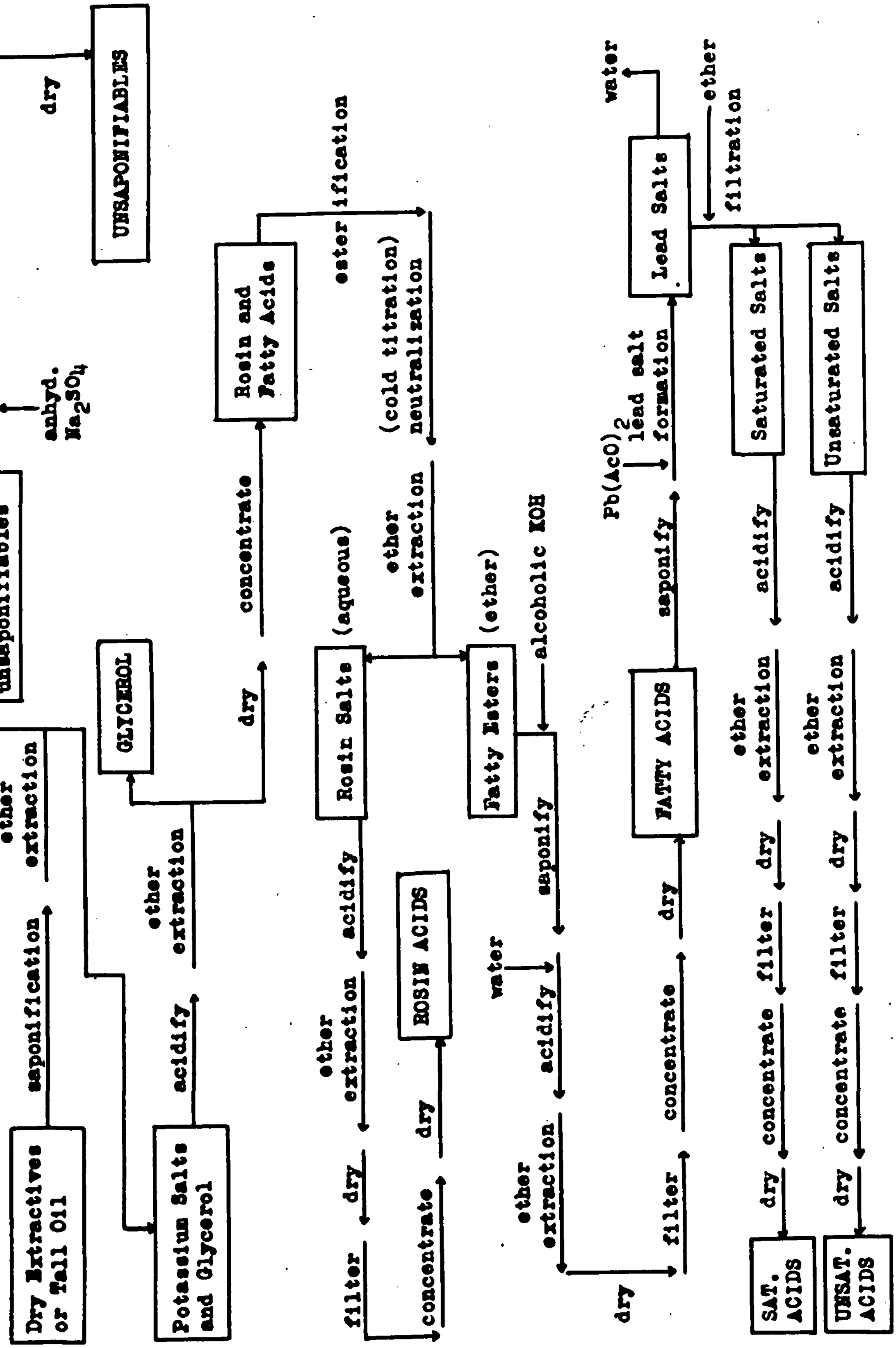
Dry Extractives or Tall Oil
saponification
ether extraction
ether solution of unsaponifiables
dry
anhyd. Na_2SO_4
filter
concentrate
dry
UNSAPONIFIABLES
Potassium Salts and Glycerol
acidify
ether extraction
GLYCEROL
dry
concentrate
Rosin and Fatty Acids
esterification
(cold titration) neutralization
ether extraction
Rosin Salts
(aqueous)
Fatty Esters
(ether)
alcoholic KOH
acidify
ether extraction
dry
filter
concentrate
dry
ROSIN ACIDS
saponify
water
acidify
ether extraction
filter
concentrate
dry
FATTY ACIDS
saponify
$Pb(AcO)_2$
lead salt formation
Lead Salts
water
ether filtration
Saturated Salts
Unsaturated Salts
acidify
ether extraction
dry
filter
concentrate
dry
SAT. ACIDS
acidify
ether extraction
dry
filter
concentrate
dry
UNSAT. ACIDS

FIGURE 3

METHOD FOR ISOLATING PHYTOSTEROLS

Although a quantitative determination of the phytosterols was not carried out, a small amount was isolated for the purpose of confirming the presence of such material in pine extractives and tall oil.

A sample of the unsaponifiable matter was dissolved in a small amount of hot alcohol and several ml. of a 1 per cent alcoholic solution of digitonin added (65). After cooling in a refrigerator, the crystals of phytosterol digitonide were filtered off and air dried. To obtain the acetate from the digitonide, the air-dry crystals were heated in about 5 ml. of acetic anhydride until solution was complete. When cold, 30 ml. of 60 per cent alcohol were added, the precipitated crystals filtered, and washed with 60 per cent alcohol. Hot 80 per cent alcohol was used to dissolve the crystals and wash the filter. After allowing the phytosteryl acetate to crystallize in a refrigerator, the product was further purified by recrystallization from small volumes of hot absolute alcohol until a constant melting point was obtained.

METHOD FOR DETERMINING PETROLEUM ETHER-INSOLUBLE MATERIAL

As mentioned in the procedure for the separation of components, the oxidized fatty acids are difficultly soluble in petroleum ether. Instead of separating these insoluble materials from the whole fatty acid fraction, they were separated from both the saturated and the unsaturated acids. By this modification, the degree of unsaturation remaining in the oxidized acids could be determined separately.

An arbitrary method for a quantitative estimation of petroleum ether insolubility was devised. The method, which gives comparative but not absolute values, is as follows:

One-gram samples of unsaturated acids and 0.5-gram samples of saturated acids were weighed into small Erlenmeyer flasks. Petroleum ether of a boiling range of 30-60° C. (50 ml. per gram) was added, the flasks stoppered, swirled to dissolve or disintegrate the sample, and the whole allowed to stand at room temperature for 24 hours. At the end of this time, the precipitate was filtered through a tared porous porcelain crucible, using suction. The flask was washed out with five small portions of petroleum ether, which were run through the filter. When the nature of the insoluble material was such that it remained, for the most part, in the flask, no attempt was made to transfer it to the filter; in that case, the residual petroleum ether was evaporated off and the residue weighed. After drying the crucible and contents in a vacuum desiccator, this residue was also determined. From the combined weights of crucible and flask residues, the percentage of petroleum ether-insoluble material (the oxidized fatty acids) was calculated.

DETERMINATION OF FOAM STABILITY

The foam stability of soap solutions was measured by the rate of foam volume decrease. It was desired to determine the foam stability of soap solutions of tall oil and unsaturated fatty acids from both green and seasoned wood. To saponify the acidic components, 50 ml. of 0.5 N aqueous sodium hydroxide were added to 2.5-gram samples of the oils; after heating on a steam bath until solution was complete, the soap solution was transferred to a 250-ml. volumetric flask and diluted to the marked graduation. One hundred ml. of the resulting (approximately 1 per cent) solution were added to a 1-liter graduated cylinder fitted with a ground-in glass stopper. After shaking the cylinder 20 times in an up-and-down-lengthwise fashion at the rate of one complete shake per second, a stop watch was started and readings of the foam and solution levels were made at intervals throughout a 10-minute period. When the liquor level reading was subtracted from the foam level reading, the foam volume at any particular time was obtained. A curve of foam volume plotted against time gave comparative data on foam stability.

EXPERIMENTAL DATA AND DISCUSSION

The first step in the investigation involved an examination of the wood. It is obvious that there is some relation between the nature of the tall oil and that of the wood from which it is obtained. Because the precursors of tall oil are found in the extraneous part of the wood, it seemed logical to accumulate some information about the nature and amount of these materials in the wood.

Dominant proportions of the extraneous matter in wood may be classed as extractives, removable with various organic solvents. From previous studies, it is known that the ether extractives are composed of the same type of compounds which are found in tall oil. On the other hand, alcohol and benzene remove these same materials, as well as others not extracted by ether. That some of these extracted substances are volatile is to be expected, and the degree to which such volatile compounds are found in tall oil depends to a considerable extent on the conditions of pulping. It was not intended to investigate the pulping variables, but preliminary studies were made to determine the volatile material in the wood. This value was taken as the difference between the yields of ether extractives from the original wood and the steam-distilled wood.

Various extractions were carried out on the green 40 to 60-mesh wood meal and also on the seasoned wood meal. The results of these analyses are shown in Table ~~III~~.

TABLE III

EXTRACTION DATA*

	Green Wood	Seasoned Wood
Alcohol-benzene, %	3.0	2.1
Ether, %	2.3	1.4
Hot water (on alcohol-benzene extracted wood), %	0.6	1.0
Ether (on steam-distilled wood), %	1.1	0.8
Alcohol (on steam distilled-ether extracted wood), %	0.2	0.3
Volatile (calculated), %	1.2	0.6

* Percentage based on the oven-dry unextracted wood.

The alcohol-benzene and hot water extractions were made according to Institute Methods 11 and 10a; the ether extractions were carried out for 8 hours, following the general procedure of Institute Method 11. The scheme reported by Kurth (58) for separating volatile matter, ether extractives, and alcohol-soluble material was followed in obtaining the last two sets of data. After steam distilling 40 to 60-mesh wood meal for 1 to 1.5 hours, the residual meal was filtered through an extraction thimble, air dried, and extracted with ether and then with alcohol. The difference between the ether extractives from the original wood and those from steam-distilled wood represents a calculated percentage of volatile matter.

The data in Table III show that the seasoning of wood reduces the total extractives. An interesting increase in hot water solubility was found, but whether this increase is a result of changes in the extractives or in the wood substance is uncertain. The most important result is the decrease in the percentage of nonvolatile ether extractives from 1.2 to 0.8. This is a certain indication that seasoning has altered the fatty and rosin acids in such a manner as to decrease their solubility in ether. Although the percentage of volatiles is decreased, the total loss of extractives cannot be attributed to this class of compounds.

Kurth (58a) found little difference in the percentage of ether extractives between green and air-dried slash wood meal. He used the term green wood to describe wood which had been received in the fall and stored outside through a Wisconsin winter. His air-dried wood was this particular wood after conversion into wood meal and air drying for 20- 30 days. It is difficult to compare these samples with those reported in the present study.

The attack on the problem involved the investigation of four materials--ether extractives and tall oil from green wood and the same products from seasoned wood. These products were isolated from the wood and separated into component groups in the manner described above. The data are given in Table IV.

The first section of Table IV shows the percentages of the various groups as they were determined on the oil. The second section

TABLE IV

COMPARISON OF EXTRACTIVES AND TALL OIL FROM GREEN AND SEASONED WOOD

	From Green Wood		From Seasoned Wood	
	Extractives	Tall Oil	Extractives	Tall Oil
On Basis of the Oil				
Unsaponifiable, %	11.3	7.2	13.9	11.0
Rosin acids, %	42.8	36.9	47.3	34.4
Fatty acids, %	38.4	55.4	34.3	53.7
Total, %	92.5	99.5	95.5	99.1
*Saturated fatty acids, %	2.3	4.7	2.1	2.7
*Unsaturated fatty acids, %	36.1	50.7	32.2	51.0
On Basis of the Oven-Dry Unextracted Wood				
Unsaponifiable, % x 10^2	25.7	7.8	18.9	2.9
Rosin acids, % x 10^2	97.2	40.1	64.3	9.0
Fatty acids, % x 10^2	87.2	60.2	46.7	14.0
*Saturated fatty acids, % x 10^2	5.1	5.1	2.8	0.7
*Unsaturated fatty acids, % x 10^2	82.0	55.1	43.8	13.2

* Values corrected approximately by the iodine number method outlined by Jamieson (59).

shows the percentage, multiplied by 100, as calculated to the oven-dry unextracted wood basis. To illustrate the changes which occur on cooking and seasoning, both sets of data are necessary to avoid confusion. The first section shows the proportions of the components in the oil, whereas the other section indicates the proportions in the wood.

An important consideration in a comparison of the tall oils from green and from seasoned wood is the yield. The method of isolation used necessarily yielded only a fraction of the tall oil available, for only part of the liquor was recovered. The percentage of the liquor employed for tall oil recovery was determined by analyzing the black liquor for total sodium (Institute Method 104). From the volume of liquor and its soda analysis, the total sodium (as sodium hydroxide) in the liquor recovered was calculated. The ratio of this figure to the total alkali (as sodium hydroxide) introduced into the cook gives the percentage of the black liquor actually used. It is true that such a calculation is based on the assumption that the sodium and sulfate soap were not preferentially absorbed in the pulp, but this assumption is reasonable. In Table V, the yield data (both actual and calculated) are reported for the tall oils from both green and seasoned wood.

As can be seen from Table V, a very marked reduction in the yield of tall oil resulted from the seasoning of the wood. The calculated percentage of tall oil yield on the basis of the oven-dry unextracted green wood corresponds closely to the percentage of

TABLE V

TALL OIL YIELD DATA

	Green	Seasoned
Actual yield (on oven-dry unextracted wood basis), %	0.50	0.12
Actual yield (on basis of ether extractives), %	22.10	8.74
Calculated total yield (on oven-dry unextracted wood basis), %	1.087	0.26
Calculated total yield (on basis of ether extractives), %	48.00	19.10
Calculated total yield, lb. per ton of air-dry pulp	43.25	10.40

nonvolatile ether extractives from green wood (Table III). This may be coincidental but, on the other hand, the nonvolatile ether extractives may represent the maximum possible yield of tall oil. A comparison of the characteristics and properties of the tall oils is given in Table VI.

TABLE VI

TALL OIL CHARACTERISTICS

	Green	Seasoned
Saponification No.	180.5	173.3
Acid No.	171.3	154.9
Ester No.	9.2	18.4
Iodine No. (Hanus)	118.1	90.0
Index of refraction ($\underline{n}_D^{20}$)	1.5001	1.5200
Specific gravity, 20° C.	0.9687	0.9856
Optical rotation $[\alpha]_D^{20}$	10.87	13.34

The procedures for the determination of these data were taken from Jamieson (59).

The fatty acid fractions of both the ether extractives and the tall oils were subjected to further study. The effect of wood seasoning on the unsaturated fatty acids is illustrated by the data in Table VII.

V

TABLE ~~VII~~

CHARACTERISTICS OF UNSATURATED FATTY ACIDS

	From Green Wood		From Seasoned Wood	
	Extractives	Tall Oil	Extractives	Tall Oil
Saponification No.	195.8	197.6	178.4	183.7
Acid No.	190.9	189.2	165.5	176.6
Ester No.	4.9	8.4	12.9	7.1
Iodine No. (Hanus)	132.8	116.4	95.5	98.6
Thiocyanogen No.	89.9	89.9	63.5	70.4
Petroleum ether-insoluble, %	1.31	0.57	10.68	3.02

The data in Tables III, IV, V, VI, and VII give a good over-all picture of the relationship of the extractives to tall oil, the effect of cooking, and the effect of wood seasoning.

Several important conclusions can be drawn from Table IV. The decrease in ether extractives after seasoning, as was previously pointed out, is marked in all three fractions: unsaponifiables, rosin acids, and fatty acids. Although some groups decrease to a greater degree than others, no one class of compounds can be said to be the sole source for the decreased yield of extractives in seasoned wood. The loss in fatty acids is most outstanding. It should also be noted that the percentage of glycerol (as esters), determined by subtracting the total extractives in Table IV from 100, decreases on seasoning the wood.

A comparison of the data for the unsaturated fatty acids from green and seasoned wood (Table VII) shows the large decrease in saponification number, acid number, iodine number, and thiocyanogen number; on the other hand, the ester number and petroleum ether insolubility increase. Thus, during the seasoning period the unsaturated acids undergo an increase in average molecular weight, a decrease in unsaturation, and an increase in petroleum ether insolubility and ester formation. All of these changes would be accounted for by the formation ~~of~~ hydroxy acids through reaction of the double bonds.

The difference between saponification number and acid number (termed ester number) is ~~good~~ evidence for the presence of esters. However, the method followed in the isolation of the unsaturated fatty acids (i.e., precipitation from an alkaline aqueous solution as lead salts) gave little opportunity for ester formation because alcohols were not present. Therefore, it seems logical to assume that the esters present are inner esters of the hydroxy acids or represent a condensation of two molecules of hydroxy acids. If this is the case, an increase in ester number indicates the formation of hydroxy acids as a result of the oxidation of double bonds. This would be proved by an increase in acetyl number.

In discussing the comparison between extractives and tall oil, it is necessary to treat separately the products from green and seasoned wood, because it was observed that quite different relationships were found for the two woods. This is especially true for the characteristics of the fatty acids.

The data of Table IV show that all component groups decrease in the amount recovered as tall oil from green wood, and that the unsaponifiable matter and rosin acids decrease to a greater degree than do the fatty acids. The result of this difference is indicated in the relative proportions of the components on the basis of the oil, where the percentage of fatty acids increase in tall oil. The change in the fatty acids during pulping is best shown in Table VII. Saponification and acid numbers are changed but slightly, with the former rising and the latter decreasing. However, the ester number shows a significant increase, whereas the amount of petroleum ether-insoluble material decreases. It is difficult to explain the conflicting indications of these data. However, there is some reason to believe that the unsaturated acids have, to a considerable extent, lost their unsaturated nature (through oxidation of the double bonds) and are isolated in the saturated fatty acid fraction. The iodine number and the percentage of petroleum ether-insoluble materials for the saturated fatty acids isolated from green and seasoned extractives and tall oil are given in Table ~~VIII~~.

TABLE VIII

DATA ON SATURATED FATTY ACIDS

	Petroleum Ether-Insoluble, %	Iodine No. (Hanus)
Green wood extractives	1.56	13.68
Green wood tall oil	37.60	53.70
Seasoned wood extractives	39.42	44.90
Seasoned wood tall oil	9.64	71.60

The amount of oxidized fatty acids, as shown by the quantity of the petroleum ether-insoluble material in the saturated fatty acids fraction, is seen to increase to a very substantial proportion after pulping the green wood. Keeping in mind that the same treatment increases the ester number of the unsaturated acids and lowers the percentage of oxidized acids, it appears that the cooking conditions change the nature of the oxidized acids so that either they are destroyed or their lead salts become insoluble in ether.

Thiocyanogen theoretically adds at the one double bond in oleic acid, at one of the two double bonds in linoleic acid, and at two of the three double bonds in linolenic acid. On the other hand, iodine adds at all the double bonds. Because the thiocyanogen value is represented in terms of the iodine equivalent, the thiocyanogen and iodine values for oleic acid are the same, 89.9. The theoretical thiocyanogen value of linoleic acid is 90.5--a value close to that for oleic acid, and that for linolenic acid is 182.5. Therefore, the values from thiocyanogen and iodine determinations give some indications as to the individual acids present in an oil.

The data in Table ~~VII~~ V indicate that the iodine number decreases, whereas the thiocyanogen number is unchanged. This is an indication that decreased unsaturation results from a destruction of one of the two double bonds in a portion of the linoleic acid. Furthermore, it appears that no linolenic acid is present in the original wood extractives.

Another point of interest is the increase of the iodine number of the saturated acid fraction. Theoretically, a saturated acid should have no iodine number; in this case, however, where oxidized acids are involved, some degree of unsaturation is found in the ether-insoluble lead salts. There are some unsaturated acids whose lead salts are difficultly soluble in ether; therefore, the saturated acid separation is not always absolute. The cause for part of the iodine number in the saturated acid fractions may be found in incomplete separation, but a large proportion of the iodine absorption probably results from the presence of slightly unsaturated oxidized acids.

The total result of the alkaline pulping conditions on the fatty acids from green wood appears to be a decrease in the degree of unsaturation of the more unsaturated acids (i.e., linoleic acid), wherein oxidized products are formed which are isolated with the saturated acid fraction. Although the petroleum ether insolubility of the unsaturated fraction decreases, greater esterification is possible as a result of a greater proportion of hydroxyl groups in the oxidized acids present.

A loss of unsaponifiables is to be expected. Part of this loss ~~is likely~~ due to volatility. Furthermore, the unsaponifiables are retained in sulfate soap through an emulsification mechanism, and it is not probable that such an occlusion would give a quantitative recovery.

No efforts were made to study the changes occurring in the rosin acids during the pulping operations, but the decrease in these substances is more evident than that of the fatty acids. Here, again, the pulping conditions probably change the nature of the rosin acids so that they are not effectively recovered as soaps from the black liquor.

Turning now to a comparison of the extractives and tall oil from seasoned wood, an entirely different result is found in the characteristics of the fatty acid fractions. First of all, the yield of tall oil on the basis of the extractives present is less than half that from green wood (Table V). Although the proportions of the component groups in the tall oil from seasoned wood are roughly the same as those in green wood tall oil, the relationship of these components to their precursors in the seasoned extractives is considerably different from that observed in the case of green wood (Table IV).

The fatty acids isolated from both extractives and tall oil from seasoned wood were studied in greater detail than the other components (Table VII). Saponification and acid numbers increase, ester number decreases, iodine and thiocyanogen numbers increase slightly, and the petroleum ether-insoluble matter decreases. These trends indicate an increase in unsaturation and a decrease in average molecular weight. Furthermore, the degree of ester formation was decidedly less, as was the amount of petroleum ether-insoluble material, which points to a loss of oxidized fatty acids during pulping. This effect is in contrast to the results noted for green wood, but the nature of the extractives before subjection to drastic alkaline conditions was also considerably different. In seasoned extractives, the unsaturated fatty acids have undergone an oxidation at the double bonds. It is possible that these oxidized acids are unstable and under cooking conditions are split at the point of oxidation into fragmentary compounds. Such a decomposition would result in the loss of petroleum ether-insoluble material, a decreased ester value, and increased acid, saponification, iodine, and thiocyanogen numbers. These results are shown in Table VII.

A further evidence that the high state of oxidation of the seasoned extractives is reduced, probably by destruction of oxidized acids, is shown by the decrease in petroleum ether-insoluble material of the saturated fatty acids (Table VIII).

The thiocyanogen numbers on the unsaturated fatty acids from extractives and tall oil from seasoned wood are exceedingly low

(Table VII). Indeed, these figures are lower than theoretical for oleic acid, the least unsaturated of the acids which normally are present in this fraction. This is a very interesting result and raises the question as to the reason for such low values. Although no experimental data can be given to illustrate the following hypothesis, there is reason to suggest that the oxidized acids present may be the cause. Thiocyanogen is known to add at one of the two double bonds in linoleic acid and at two of the three double bonds in linolenic acid. This is an indication that some of the unsaturated linkages are more reactive than others. The point of oxidation of the unsaturated acids may be these more sensitive double bonds. If so, then the reactivity with thiocyanogen would be reduced. Whether or not the remaining double bonds would absorb thiocyanogen is, of course, uncertain; however, it is possible that the oxidized acids present, which are somewhat unsaturated, do not add thiocyanogen. ~~In this~~ theory the answer to the low thiocyanogen values may ~~be found.~~

The effects of the cooking conditions on the seasoned extractives are in contrast to those noted for green extractives. The chief effect seems to be a destruction of oxidized acids.

One of the principal objectives of the investigation was to determine the difference between tall oil from green wood and that from seasoned wood. The characteristics of the whole tall oil crudes are given in Table VI. It should be pointed out that seasoned wood tall oil shows very marked differences from green wood tall oil. Since the cooking conditions were almost identical, these differences must be the result of the seasoning of the wood. It appears, therefore, that oxidation during the seasoning period alters the nature of these acids before pulping; consequent cooking introduces further changes and, as a final result, the tall oil from seasoned wood is decidedly different from the green wood product.

In addition to substantial decreases in acid, saponification, and iodine numbers, the ester value is doubled and ~~the physical-chemical constants~~--refractive index, specific gravity, and optical rotation--are likewise increased. Visual differences were also observed; the seasoned wood product had a darker color and a greatly increased viscosity. All of these differences point to decreased unsaturation, increased average molecular weight, and increased influence of functional groups. It ~~appears likely~~, then, that oxidation and perhaps some kind of polymerization are the chief reactions which have taken place. The fact that the entire nature of tall oil is dependent on the degree of wood seasoning is very definitely shown by these data.

The fatty acid fractions from green and seasoned wood tall oils (the characteristics of which are presented in Table VII) show the same indications of oxidation at the double bonds. This is supported by the percentage of petroleum ether-insoluble material.

After both green and seasoned wood tall oils were isolated, tests on the foam stability of their sodium soaps were made according to the procedures outlined ~~earlier~~. Curves indicating the rate of foam volume decrease for 1 per cent soap solutions of both tall oils are shown graphically in Figure 4.

The obvious conclusion from these curves is that green wood tall oil soaps form a much more stable foam.

The same stability tests were then applied to 1 per cent soap solutions of the unsaturated fatty acids isolated from the two tall oils. The curves representing their foam stability are shown in Figure 5.

It is very interesting to note that the foam volume of 1 per cent sodium soaps of unsaturated fatty acids from the two tall oils decreases in a manner similar to that of the tall oil soaps. The difference between the green and seasoned wood fatty acid soaps is somewhat more pronounced, but the general result is the same.

The nature of these foams was also quite different, the more stable being compact, whereas the weaker foams were loose and friable.

From these curves it appears that the decreased foaming of the black liquor from seasoned wood is, at least in part, a result of changes in the nature of the tall oil soaps therein. Furthermore, the fatty acid fraction of these tall oils is a principal factor influencing this effect.

Further evidence for this conclusion is found in the surface tension of 1 per cent soap solutions of these oils. The data as determined on the du Noüy precision tensiometer are shown in Table ~~IX~~ V.

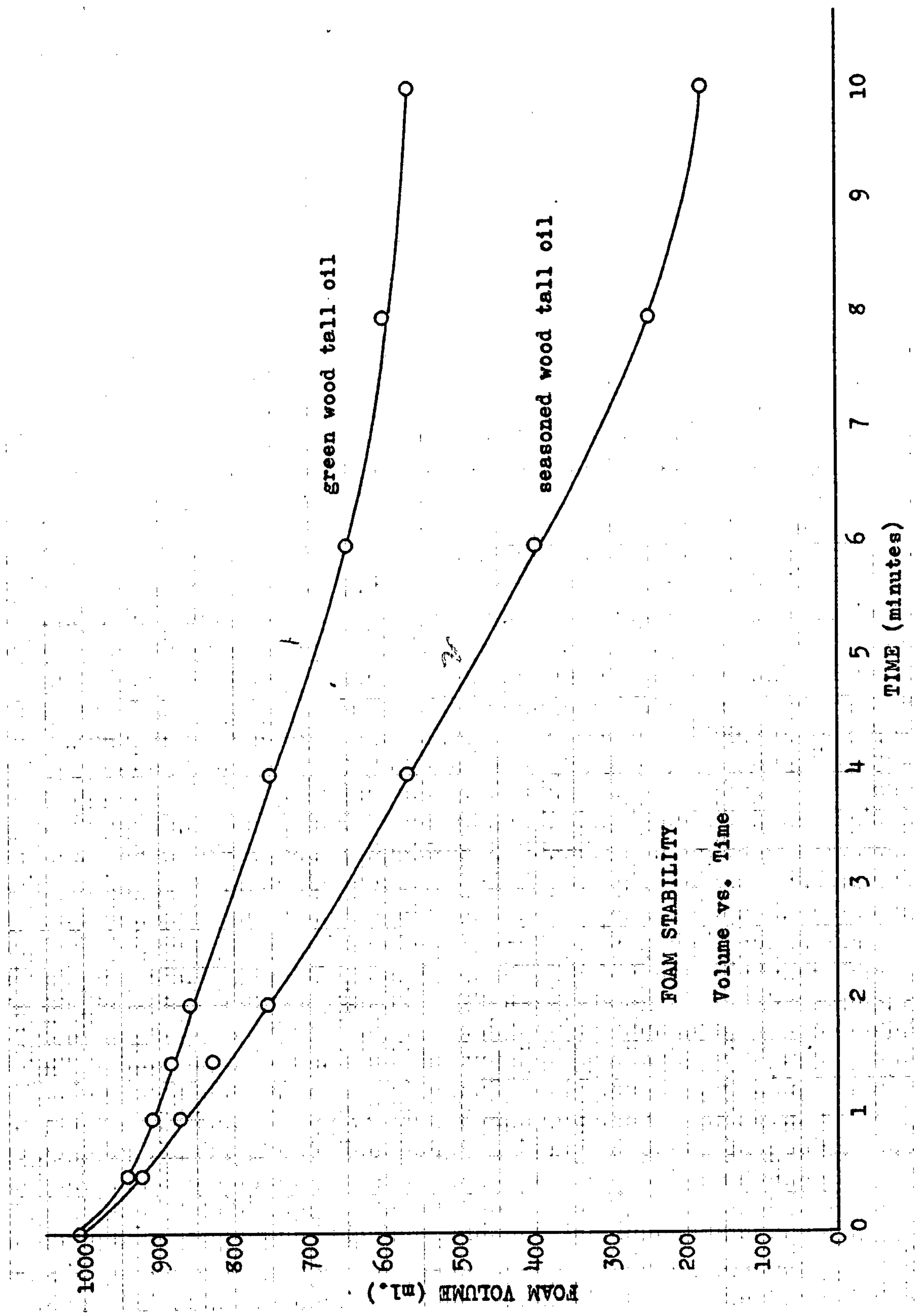
FOAM STABILITY
Volume vs. Time
green wood tall oil
seasoned wood tall oil
FOAM VOLUME (ml.)
1000
900
800
700
600
500
400
300
200
100
0
TIME (minutes)
0
1
2
3
4
5
6
7
8
9
10

FIGURE 4

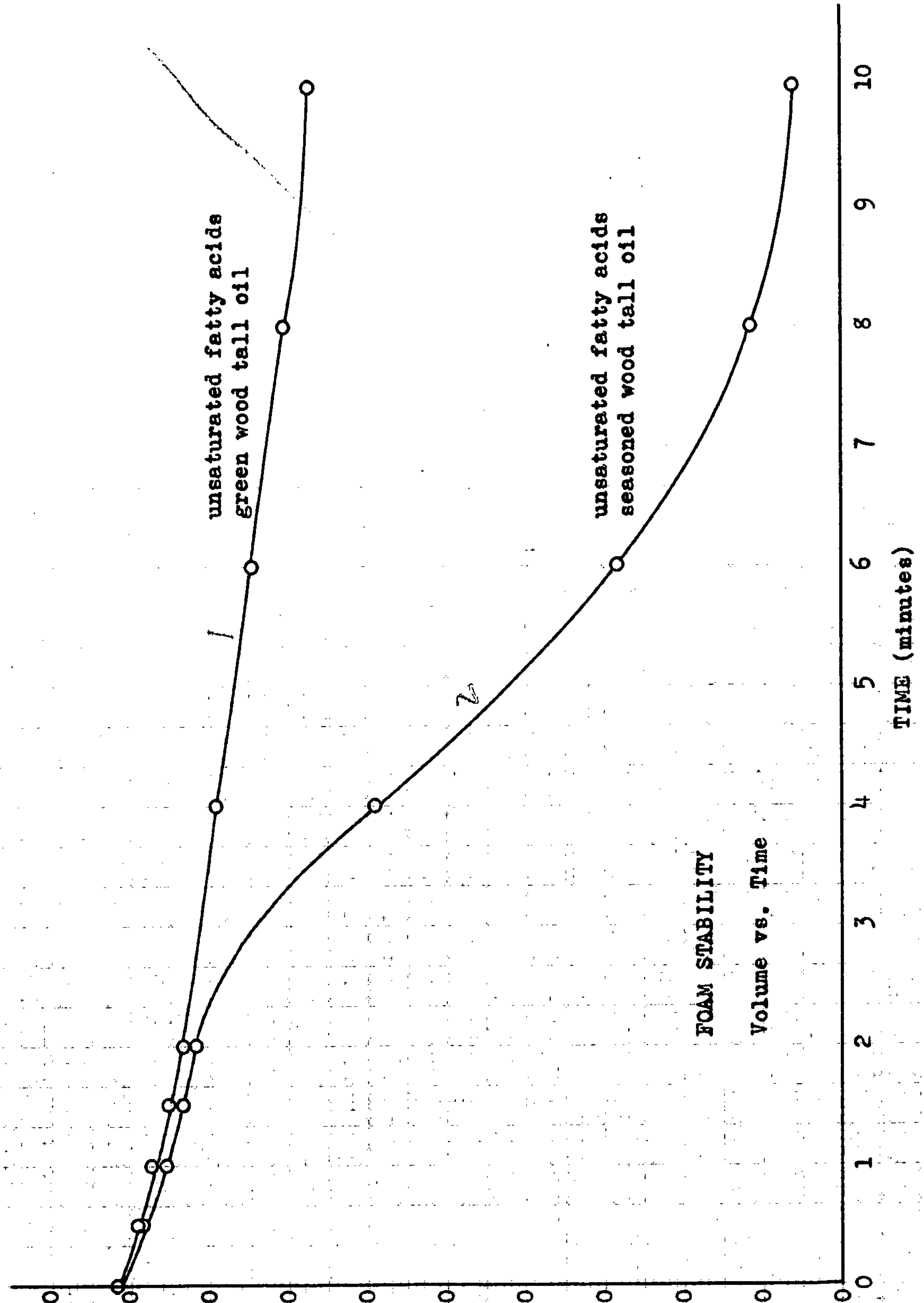
FOAM STABILITY
Volume vs. Time
unsaturated fatty acids
green wood tall oil
unsaturated fatty acids
seasoned wood tall oil
1
2
FOAM VOLUME (ml.)
1000
900
800
700
600
500
400
300
200
100
0
TIME (minutes)
0
1
2
3
4
5
6
7
8
9
10

FIGURE 5

TABLE ~~II~~ V

SURFACE TENSION DATA

	Surface Tension dynes per cm.
Green wood tall oil	40.10
Seasoned wood tall oil	42.06
Unsaturated fatty acids from green wood tall oil	38.08
Unsaturated fatty acids from seasoned wood tall oil	40.42

Both the whole tall oil and the unsaturated fatty acids from the green wood show lower surface tension values by approximately 2 dynes per centimeter. This difference is not great, but yet it may be sufficient to have some effect on foam stability.

The essential difference between green and seasoned wood acids ~~was shown~~ to be a result of oxidation at double bonds of the fatty acids, probably to hydroxy acids. The question of foam stability may depend upon such a change. In a soap film the molecules have some degree of orientation, which probably depends upon their lyophilic and lyophobic groups, or more specifically on the polar groups (66, 67). The sodium salt formed from the carboxyl group is more compatible with water and probably is attracted to the inner water layer of a soap film. However, other functional groups in the fatty acid chain, such as double bonds, hydroxyl groups, carbonyl groups, etc., may be of great influence in governing the position and arrangement of the lyophobic chain. For example, the double bonds present in soaps probably are attracted to the water layer of the film, whereas a less hydrophilic group would allow the whole chain to protrude away from the water layer. On the other hand, it seems likely that hydroxyl groups would increase the hydrophilic nature of the whole soap molecule, perhaps to such an extent that the arrangement of soap molecules at the film interface would be somewhat random.

In theory, such a random orientation could reduce the strength of the soap film. Because the proportion of oxidized fatty acids in the seasoned wood tall oil is considerably increased and the degree of unsaturation decreased over that of green wood tall oil, a cause for decreased foaming may be found in the more hydrophilic nature of the functional groups of the fatty acids. There is no assurance that such a mechanism is the sole cause for the reduced foaming of seasoned wood black liquor, for other components in the tall oil soaps, as well as substances in the black liquor which are not present in tall oil, may have some effect.

In addition to the decreased foam stability per unit weight of seasoned wood tall oil soap, the amount of tall oil and thus the concentration of sulfate soap in seasoned wood black liquor (Table V) are decreased markedly. It appears, therefore, that the decrease in foam troubles in seasoned wood black liquors is a result of a combination of these two factors.

Some further work was carried out on the unsaponifiable fractions of both extractives and tall oil from both green and seasoned wood. A phytosterol ~~material~~ was isolated by the digitonin method described in the preceding section. After the formation and purification of phytosteryl acetate, the melting point was determined. It was found that the phytosteryl acetates from all four of the unsaponifiable fractions ~~had a~~ melting point of 120° C. This is in agreement with data reported by Kurth (28) for phytosteryl acetate from yellow pine extractives.

The phytosterols, although they were not studied quantitatively, seem to remain unaltered during wood seasoning and cooking.

Because some authors have denied the presence of solid fatty acids in tall oil, it was interesting to note that all four materials--green wood extractives and tall oil and seasoned wood extractives and tall oil--contained small amounts of saturated fatty acids. An attempt to identify the solid acid from green extractives was made. Recrystallization of this product from 80 per cent ethyl alcohol produced an acid which melted at 66-68° C. Further recrystallization did not change the yellowish color or improve the sharpness of the melting point, but it is possible that a well purified product might prove to be stearic acid. Kurth (28) has reported stearic acid in the ether extractives of longleaf pine.

EXTRACTIVES OF LOBLOLLY PINE

In addition to the data presented in the main body of this thesis, a partial analysis of green loblolly pine wood (*Pinus taeda* L.)

and the ether extractives therefrom is here appended. These data were determined in the same manner as described for slash pine. Because the yield of extractives was exceedingly low and since a loss of tall oil from this wood occurred accidentally, the investigation was abandoned in favor of slash pine. However, the data in Table X show a striking contrast to those for slash pine presented in Tables II, III, and IV.

TABLE X

DATA ON GREEN LOBLOLLY PINE

Average specific gravity	0.53
Average growth rate, rings per inch	4.93
Average age, years	18.0
Wood analysis (oven-dry unextracted wood basis)	
Pentosans, %	8.83
Cross and Bevan cellulose, %	59.00
Lignin, %	27.10
Uronic acids, %	0.79
Extractions (oven-dry unextracted wood basis)	
Alcohol-benzene, %	2.76
Ether, %	1.83
Hot water (on alcohol-benzene extracted wood), %	1.24
Ether (on steam-distilled wood), %	1.35
Alcohol (on steam-distilled and ether-extracted wood), %	0.21
Volatile (calculated), %	0.48
Ether extractives analysis (on the basis of the oil)	
Unsaponifiable, %	15.80
Rosin acids, %	37.20
Fatty acids, %	43.60
Total, %	96.60
Saturated fatty acids, %	2.28
Unsaturated fatty acids, %	41.32
Hanus iodine number	113.5

Although these data do not fit in the problem as it was proposed, a comparison with the corresponding data for slash pine gives emphasis to the dependency of tall oil on the species of wood used as a source.

SUMMARY

Green slash pine wood bolts directly from the stump were cut in half; one set of halves was stored for 4 months to season, whereas the other set was used immediately for green wood studies.

In order to build up a historical background for the wood, its physical and chemical properties were determined. The age, growth rate, density, chemical composition, etc. were recorded so that the tall oil and its precursors in the extraneous portion would also have a definite history. The nature of the extractives from both green and seasoned wood was determined by various extractions. The ether, alcohol, alcohol-benzene, and hot water solubilities, as well as the volatile matter, of the wood meal were measured.

After this preliminary information had been assembled, a study was made of the effect of wood seasoning on the ether extractives and the tall oil.

The precursors of tall oil (the ether extractives) were isolated from both green and seasoned wood in sufficient quantity by large-scale extraction in a Soxhlet apparatus.

Tall oil was also prepared from both green and seasoned wood by sulfate pulping under well-defined conditions, concentration of the black liquor, separation of the sulfate soaps, and acidification. This

crude tall oil was mechanically purified and dried, and then subjected to further study.

The four fractions--green wood extractives and tall oil and seasoned wood extractives and tall oil--were examined. Each was separated into component groups of unsaponifiables, rosin acids, and fatty acids (both saturated and unsaturated), and the percentage of each group was determined.

The chemical properties of the unsaturated fatty acids were then studied, because this fraction was of primary interest. Saponification, acid, ester, iodine, and thiocyanogen numbers and petroleum ether-insoluble material gave good indications as to the differences between the fractions.

A comparison of the whole crude tall oils from green and seasoned wood was also made. Yield saponification, acid, ester, and iodine numbers, index of refraction, specific gravity, and optical rotation were determined. These results showed striking differences--with trends toward reduced unsaturation.

In order to ascertain the foam stability of tall oil soaps and soaps of the unsaturated fatty acids therefrom, the rate of foam volume decrease of 1 per cent solutions was measured. This information, together with surface tension measurements on 1 per cent soap solutions, gave data showing considerable differences between green and seasoned wood products.

Phytosterols (as acetates) were isolated from each of the four unsaponifiable fractions. The melting points were found to be identical.

In the discussion of the results of the experimental work, comparisons are made between green and seasoned wood products, between extractives and tall oil, and between fatty acids and other components.

Several theories are advanced which attempt to explain some of the results of the experimental determinations.

A complete analysis of the wood and extractives of green loblolly pine is given.

CONCLUSIONS

In the seasoning of slash pine wood, several important changes occur in the extraneous matter. The most outstanding of these is the decrease in ether solubility. This decrease is not confined to a loss of volatile matter. On the contrary, very substantial decreases in the percentages of fatty acids and rosin acids are noted. The loss of fatty acids is most prominent.

The yield and properties of the tall oil are largely dependent on the degree of seasoning of the wood. The yield of tall oil from the seasoned slash pine is less than one-fourth that from green slash. Seasoned wood tall oil shows decreased unsaturation, increased average molecular weight, accentuated physical properties, and increased color. These changes appear to be a result of oxidation and perhaps polymerization.

There is some relation between the composition of tall oil and the nature of the ether extractives of the wood; however, some of the components are not recovered in the form of tall oil as efficiently as are others. Tall oil from both green and seasoned wood is comparatively richer in fatty acids and poorer in rosin acids than the ether extractives.

The fatty acids in green wood undergo a decrease in unsaturation on seasoning. Considerable amounts of what may be hydroxy fatty acids are formed from the unsaturated fatty acids through oxidation by air during the seasoning period.

The effect of the cooking conditions on green and seasoned extractives is very different. Green wood extractives are not lost during cooking and isolation of tall oil to as great an extent as are seasoned wood extractives. The oxidized acids appear to be partially destroyed during cooking.

In the pulping and isolation operations, green wood fatty acids undergo a decrease in unsaturation. It appears that this decrease is chiefly a result of the oxidation of one double bond in linoleic acid. On the other hand, the fatty acids in seasoned wood are already in a highly oxidized state, and these oxidized acids are either destroyed or lost during the pulping operation. Consequently, the resulting tall oil contains fatty acids of apparently higher unsaturation than do the seasoned extractives.

Although this point requires further chemical proof, a hypothesis explaining an ester number in tall oil is the presence of hydroxy acids which ~~esterify~~ with themselves or with carboxyl groups of adjacent molecules.

Tall oil from slash pine contains solid fatty acids, of which stearic acid may be a constituent.

A phytosterol ~~material~~ (acetate, melting at 120° C.) was found in each of the tall oils; the products were identical with those isolated from the green and seasoned extractives.

The soaps of tall oil in black liquors ~~are related~~ to the problem of foaming. The soaps from seasoned wood tall oil show considerably lower foam stability than those from green wood. Furthermore, the soaps of fatty acids from seasoned wood tall oil are much less stable than those from green wood tall oil. The oxidation of double bonds appears to be one cause for this reduced stability. This effect, in combination with the decreased concentration of soaps, seems to be the reason for reduced foaming troubles with seasoned wood black liquor during evaporation.

It should be pointed out that there are numerous variables affecting the yield and quality of tall oil. Not only do the age, proportion of heart- and sapwood, species, degree of seasoning, etc. of the wood exert a direct influence on the resulting tall oil, but the conditions of pulping also have a direct effect. Therefore, a complete history of the wood and its treatment is necessary for an accurate evaluation of tall oil.

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