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Thermal Instability of Fats Relative to Surface Wettability of Yellow Birchwood (Betula lutea)

R. W. HEMINGWAY

The surface wettability and fats of yellow birchwood were examined in an attempt to illustrate how heat-induced changes in wood fats might be related to changes in surface wettability. A marked reduction of surface wettability accompanied heating of yellow birchwood. The degree of water repellency imparted to the wood was highly dependent upon heating temperature and time. Acetone extraction of wood prior to heating to 105°C prevented a change in wettability and increased the surface wettability of wood heated at higher temperatures. Examination of the fats after heating indicated little hydrolysis and considerable oxidation of the unsaturated fatty acids and esters. The amounts of free fatty acids present in fresh, air-dried, or heated wood were far too low to approach amounts considered necessary to influence surface wettability. The preponderance of linoleic acid ester and its rapid oxidation suggest that oxidation products from this ester might be responsible for the observed changes in wettability.

Keywords *Betula lutea* · Cell structure · Esters · Fats · Fatty acids · Fibers · Hardwoods · Heat · Hydrolysis · Oxidation · Surface properties · Surface wettability tests · Thermal stability · Wettability

MANY problems encountered in the manufacture and use of wood products center around the nature of their interactions with water. A reduction of surface wettability of wood and paper after heating has been well documented (*1–5*). Studies of wood wettability after heating have shown that at least some of the change is attributed to acetone- or ether-soluble wood components (*1–5*). The mechanism involved has, however, not been well established. Swanson and co-workers and Hancock have emphasized the adsorption of long chain length saturated fatty acids on wood and paper surfaces (*2–4*). Buchanan *et al.*, however, have suggested that glyceride esters play a significant role in the self-sizing of paper (*1*).

Since fatty acids in fresh wood are present primarily as triglycerides (*6*) and are highly localized in ray and longitudinal parenchyma (*5*), changes in the location and possibly the chemistry of the fats must occur prior to their influencing wood wettability. If saturated fatty acids of long chain length are responsible for changes in wettability after heating, it would appear that hydrolysis of glyceride esters must take place during heating. Mutton has shown that considerable hydrolysis occurs during long-term air drying of wood bolts (*7*). Investigation of birchwood fats during air seasoning of logs by Assarsson and Croon showed that, besides hydrolysis, autoxidation of unsaturated fatty acids and esters was considerable after 1 month under summer conditions (*8*).

There is little literature on the quantities of individual fatty acids and esters present in wood, and none dealing with the responses of fatty acids and esters to heat treatments associated with changes in surface wettability. It would be helpful to know the responses of wood fats to these conditions before predicting a self-sizing mechanism. This study explores some of the properties of heat-induced loss of wettability and shows the response of fatty acids and esters to heat conditions which produce self-sizing of yellow birchwood.

R. W. HEMINGWAY, Research Scientist, Division of Forest Products, CSIRO, South Melbourne, Australia.

EXPERIMENTAL

Wood Source and Storage

Yellow birchwood bolts approximately 12 in. long and 8–14 in. in diameter were cut from the lower stems of three trees felled during the course of the study to insure that the wood was fresh. The first tree was cut in March 1966, near Ann Arbor, Mich.; the second in December 1966, near Pellston, Mich.; and the third in July 1967, near Ann Arbor. Particular care was taken to freeze the bolts as soon as possible after felling the trees. Blocks 1 in. tangentially, 1½ in. radially, and 5–6 in. long were cut from the periphery of the frozen bolts and were stored at −4°C until prepared further for analysis.

Sample Preparation

Wood strips 0.10 in. thick, 1 in. wide and 5–6 in. long were prepared on a band saw from frozen blocks. With the bark against the fence, two strips 0.10 in. thick were cut and discarded. Three additional strips were cut from the frozen blocks and used as samples. The sawdust on the faces was scraped away and then rinsed off with distilled water. The strips were then dried at room temperature under vacuum for 8–10 hr, at which point they reached a moisture content of 6–8%. Care was taken to insure the strips presented a tangential face.

Preparation of Extracted Wood Strips

The vacuum-dried wood strips were acetone extracted for 48 hr in a large soxhlet. After air drying for 1 hr, the strips were soaked for 3 hr in distilled water and then dried under vacuum overnight at room temperature. Ninety percent of the diethyl ether solubles were removed from the strips by the 48-hr acetone extraction, as determined by grinding and extracting the previously acetone-extracted strips.

Air Drying

One set of six strips was randomly selected and was further subdivided into two sets of three strips to represent two samples of fresh wood. These sample blocks had been stored, frozen, about 1 month prior to sampling. The strips were vacuum-dried for 10 hr and then ground on a Wiley mill to pass a 40-mesh screen. Ground wood from each sample was divided into three parts, extracted, and the amounts of individual free and esterified fatty acids present were determined. A similar set of strips was allowed to air dry at room temperature (68–70°F) for 1 month. The air-dried strips were subdivided into two sets of three strips and three samples of groundwood obtained for each set as described above.

Heat Treatments

The heating chamber was a Pyrex glass

tube 5 cm in diameter and 59 cm long. Six iron-constantan thermocouples were placed opposite each other at three positions along the length of the tube, about 1/4 in. from the tube wall. The heating tube was wrapped with a 384-w heating tape, glass wool, and two layers of asbestos tape. Water-pumped dry air was set at a flow rate of 500 ml/min, thus exchanging the air about every 2 min. The air passed through the heating tube to a cold trap in ice water which also served as a reference for the pyrometer. After temperature calibration, thermocouples were removed to insure that volatiles from the thermocouples were not influencing wettability.

There was a time lag for the temperature at the wood surface to equilibrate with the heating temperature. Thermocouples were stapled to the surface of the wood strips, insuring that the junction was against the wood surface. Forty minutes at 105°C, 12 at 160°C, and 7 min at 220°C were required for reaching equilibrium temperatures.

Wood strips were held in position with holders fashioned from wire screen such that three strips were held parallel to and about 1/4 in. from each other in the center of the tube. No systematic difference in the change of surface wettability with respect to position in the sample holder was observed. After each set of three heat treatments, the interior of the heating tube and sample holders were swabbed thoroughly with ethanol and then baked at 250°C for 2 hr.

Measurement of Wettability

A most sensitive method of measurement of changes in wettability was found to be timing the interval from placement of a 5-μl water droplet on the wood surface until the droplet disappeared. The applicator was a 10-μl Hamilton gas chromatography syringe with the needle surface coated with silicon grease to limit wetting of the needle and to help maintain an intact droplet when removing the syringe. With the needle just touching the surface, the plunger was slowly depressed and then carefully lifted away, with care taken not to displace the droplet. The droplet was judged to have disappeared when light reflection was no longer visible. A total of six observations (three along the length of each face) was made on each strip. Fresh, unheated wood required only about 5 sec to lose gloss, while the upper limits of no wetting required about 20 min. The intact water droplet could be moved on the wood surface by gentle teasing with the syringe needle when more than 20 min were required to lose gloss, suggesting no wetting. Care was necessary to obtain tangential surfaces, as grain angle resulted in more rapid water absorption.

Extraction

After the appropriate heat treatment six wood strips were ground to pass a 40-mesh screen and 8 g of ground wood were weighed into each of two thimbles and extracted for 10 hr with acetone. About 2 g were used to determine the moisture content. The acetone extract was evaporated, covered with diethyl ether, and 1 g of sodium sulfate was added to it; it was then allowed to stand overnight. The ether solution was filtered, evaporated under vacuum, and stored under nitrogen not more than 3 hr prior to separation of acidic from neutral components.

Separation of Free Fatty Acids

Free fatty acids were separated from the ether-soluble extract on a DEAE Sephadex A-25 anion exchange column prepared as described by Zinkle and Rowe (*9*). Three grams of DEAE Sephadex were packed in an 11 × 300 mm chromatography tube, and the neutrals were eluted with 150 ml of a solvent containing 89 parts by volume of diethyl ether, 10 parts of methanol, and 1 part of water. The acidic fraction was eluted with 200 ml of a solvent containing 90 parts of diethyl ether, 10 parts of methanol, and 4 parts of formic acid by volume.

Separation of Esterified Fatty Acids

Neutrals were evaporated to about 30 ml and refluxed for 4 hr with 100 ml of 2*N* methanolic KOH with 10% water added. The solvent was evaporated and then diluted to 250 ml with distilled water and acidified with sulfuric acid. After extracting twice into diethyl ether, the ether solubles were washed three times with distilled water, combined, and dried overnight with sodium sulfate. The saponified extract was concentrated and stored under nitrogen not more than 3 hr prior to separation of saponifiables from neutrals on DEAE Sephadex as described above (*9*).

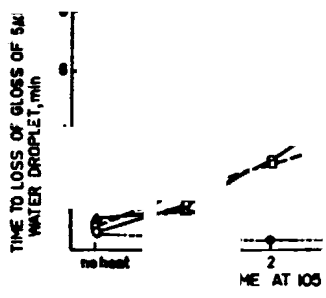


Fig. 1. Change in surface wettability of thin yellow birchwood strips after heating at 105°C, effect of overnight equilibration and sanding surfaces. ○ Surface wettability measured after specimens cooled; □ Specimens allowed to equilibrate with room atmosphere overnight prior to measuring surface wettability; △ Specimens sanded with fine sandpaper prior to measuring surface wettability; ● Specimens sanded with coarse sandpaper prior to measuring surface wettability.

Methyl Esterification

The free fatty acid and saponifiable fractions were collected and methylated with 5 ml of BF_3-methanol for 3 min on a hot water bath (*10*). After cooling, the methylated extracts were separated from water with diethyl ether, and the diethyl ether solubles were dried overnight with sodium sulfate. The ether solubles were evaporated to about 10 ml, and 30 ml of purified hexane was added. The extract was again evaporated to 10 ml and the extract diluted to 40 ml. A yellow to brown precipitate was filtered from the hexane solubles and discarded. The hexane solubles were evaporated under vacuum and the sample diluted to 2 ml prior to gas chromatography.

Gas–Liquid Chromatography

The fatty acid methyl esters were chromatographed on a 6-ft 4-mm ID glass column packed with 7.1 g of a 6% Lac 728 diethylene glycolsuccinate liquid phase on 80–100-mesh Diatoport S. The column temperature was 170°C and the helium carrier gas flow rate was 40 ml/min. Injection port and detector temperatures were 250 and 275°C respectively.

Standard solutions of individual methyl esters in concentrations from 0.5 to 0.001 g per 100 ml of hexane were prepared from pure compounds obtained from Applied Science Laboratory, State College, Pa. Measurement of standard peak heights for each methyl ester gave linear calibration curves whose variability was insignificant, compared to the variation of individual wood samples.

RESULTS

Change of Wettability Induced by Heating

After heating the wood strips at 105°C for 6 hr, there is a 14-fold increase in the time required for absorption of a 5-μl water droplet (Fig. 1). If the surfaces are allowed to stand overnight to equilibrate with the room atmosphere, there is no further change in wettability. Sanding the surface with both fine and coarse sandpaper after heating restores it to its original wettability. The changes in surface roughness of the sample do not appear to be significant because the penetration time returns to nearly the same level whether the wood is sanded with fine or coarse sandpaper. These results suggest that the change in wettability induced by heating is appreciable, is a permanent change, and is a surface effect.

Acetone extraction of the wood strips prior to heating markedly reduces the change in surface wettability induced by the heat treatments (Figs. 2–4).

Some acetone-extracted samples that had been soaked in distilled water and vacuum dried had a surface coating that became yellow after heating. This material was especially prevalent in samples used for 105 and 220°C heat treatments and

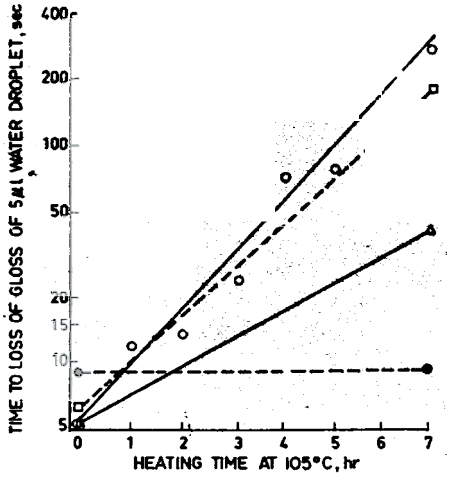


Fig. 2. Change in surface wettability of thin yellow birchwood strips after heating at 105°C, effect of prior acetone extraction and sanding treatment. ○ Specimens not extracted or sanded prior to heating; □ Specimens not extracted but sanded prior to heating; △ Specimens extracted but not sanded prior to heating; ● Specimens both extracted and sanded prior to heating.

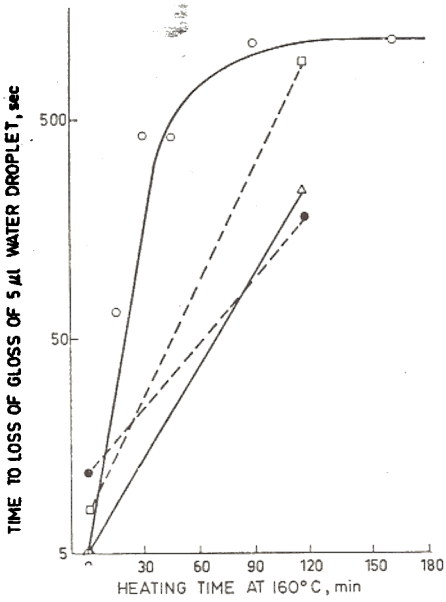


Fig. 3. Change in surface wettability of thin yellow birchwood strips after heating at 160°C, effect of prior acetone extraction and sanding treatment. ○ Specimens not extracted or sanded prior to heating; □ Specimens not extracted but sanded prior to heating; △ Specimens extracted but not sanded prior to heating; ● Specimens both extracted and sanded prior to heating.

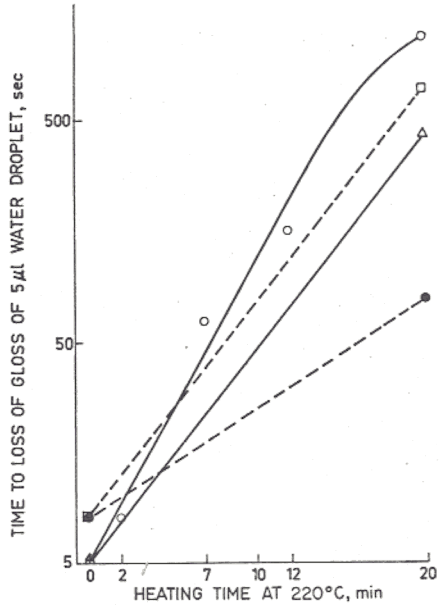


Fig. 4. Change in surface wettability of thin yellow birchwood strips after heating at 220°C, effect of prior acetone and sanding treatment. ○ Specimens not extracted or sanded prior to heating; □ Specimens not extracted but sanded prior to heating; △ Specimens extracted but not sanded prior to heating; ● Specimens both extracted and sanded prior to heating.

was related to the duration of water soaking. Strips were heated both with and without prior sanding in an attempt to isolate the effect of the yellow substance and acetone-soluble wood components on the surface wettability of heated wood. The surface wettability of acetone-extracted wood was significantly greater for wood strips sanded prior to heating at 105 and 220°C than those heated directly after drying (Figs. 2, 4). Sanding unextracted wood strips prior to heating did not increase the wettability of wood after heating. The yellow substance appears to be related to water soaking, to which unextracted wood was not subjected, and the yellow material does decrease surface wettability after heating.

The change of wettability attributable to fatty materials is more accurately evidenced by comparing the effect of acetone extraction on the wettability of wood that is sanded prior to heating (Figs. 2–4). Acetone-extracted wood retains its unheated wettability after 6 hr of heating at 105°C, while there is a marked reduction of wettability in the corresponding unextracted wood. When wood is heated at 160 and 220°C, there is a reduction in the wettability of acetone-extracted wood, but it is significantly less than that of the unextracted wood (Figs. 3, 4). Changes in wettability at these higher temperatures may be caused, in part, by the modification of pentosans, since they are unstable at these temperatures (*11*). Oxidized hemicelluloses retain a high affinity for water (*9*) and even if polymerization does reduce water absorbency, it should result in an overall decrease in wettability rather than a surface effect. It is evident from the above results that acetone-soluble components of yellow birchwood are responsible for changes in wettability of this wood, particularly at the lower temperatures studied.

Free Fatty Acids of Fresh Yellow Birchwood

The average amounts of free fatty acids in wood from the three trees sampled are shown in Table I. The individual free fatty acids are present at about one tenth their concentration as esters for each fatty acid studied. The unsaponifiables amount to approximately 40% of the lipid extract. Thus, the individual free fatty acids are uniformly distributed in proportion to their amounts present as esters, and the total free fatty acid fraction amounts to about 5% of the lipid extract. Wood which was obtained at three vastly different physiological times (December, March, and July) contains a remarkably similar free fatty acid composition. The total amount of saturated free fatty acid in the three samples studied amounted to only 20–40 ppm of the ovendry wood weight.

Response of Yellow Birchwood Free Fatty Acid to 1 Month of Air Drying

One month of air drying of thin strips of yellow birchwood does not result in a significant increase in the concentration of free fatty acids (Table II). The differences shown could be due to variations in the wood supply. The saturated fatty acids both increase (stearic acid) and decrease (palmitic acid). The decrease in the amounts of unsaturated fatty acids suggests oxidation of the linoleic and linolenic acids.

Effect of Heating in Air on the Fats of Yellow Birchwood Saturated Free Fatty Acids

The concentration of saturated free fatty acids generally increases with increasing heating periods at the three temperatures studied (Table III). The longer chain length saturated fatty acids increase in concentration during heating more rapidly than the shorter fatty acids. After 1 hr and 30 min of heating at 160°C, palmitic acid increases from 14 to 20 ppm, stearic acid from 4.8 to 12.6 ppm, and arachic acid from 0.4 to 6.4 ppm. An increase in saturated free fatty acid concentration is not observed between 1½ and 3 hr of heating at 160°C. The increase in saturated free fatty acid that occurred after heating at 105°C also appears to approach a plateau.

Wood which could be sampled from a small area, thus minimizing the sample variation, was heated at 160°C for 1, 2, and 4 hr. The results from these samples verified that further increases in saturated free fatty acids are not developed after 1 hr at 160°C (Fig. 5). The heat treatments at 220°C also show an increase in the saturated free fatty acid concentrations after heating.

Table IV. Effect of Heating in Air on the Amounts of Esterified Fatty Acids in Thin Yellow Birchwood Strips

(ppm methyl ester on ovendry wood weight)

	C_{16}	C_{18}	C_{20}	C_{22}	C_{18}^1	C_{18}^2	C_{18}^3
			105°C				
No heat avg.	112	71	35	24	47	1197	203
30 min	105	72	40	25	48	1166	233
1 hr	114	71	30	25	47	1080	159
2 hr	104	72	39	26	45	1079	182
3 hr	100	62	32	22	33	623	61
4 hr	100	65	34	25	39	674	85
7 hr	114	54	23	16	24	126	6
			160°C				
No heat avg	112	71	35	24	47	1197	203
15 min	138	95	50	32	61	1531	264
45 min	129	74	32	15	46	817	101
1 hr 30 min	102	70	39	26	31	313	22
3 hr	97	47	24	17	22	68	7
			220°C				
No heat avg	112	71	35	24	47	1197	203
2 min	120	102	56	39	46	1040	147
7 min	118	83	44	31	34	708	94
12 min	137	72	32	31	47	930	110
20 min	113	87	46	42	25	494	50

Saturated Fatty Acid Esters

The saturated fatty acid esters show little response to the heat treatments studied (Table IV). There is a decrease in the concentration of the esters after 3 hr of heating at 105°C and 1 hr at 160°C, which corresponds to the heating times where increases in free fatty acids were evident. Palmitate decreases from 112 to 97 ppm, stearate from 71 to 47 ppm, arachidate from 35 to 24 ppm, and behenate from 24 to 17 ppm after 3 hr of heating at 160°C. The decreases of esterified fatty acids are higher than the observed increase in the free fatty acids discussed above. Approximately half of the decrease in saturated ester appears as an increase in the corresponding free fatty acid.

Unsaturated Fatty Acid Esters

The unsaturated fatty acid esters are extensively oxidized under the heat treatments studied (Table IV). After 7 hr of heating at 105°C, 3 hr at 160°C, and 20 min at 220°C, the amount of oleate in the wood is reduced by about 50% (47 to 24 ppm). The oleic acid was postulated to increase by 9 ppm through hydrolysis, which would account for a portion of the loss, and about 35% reduction of oleate would then be attributed to oxidation.

Linoleate is severely oxidized since only 11% of the unheated concentration remains after 7 hr at 105°C, 6% after 3 hr at 160°C, and 42% after 20 min at 220°C. This corresponds to decreases from 1197 ppm to about 100 ppm, by far the most important reaction from the standpoint of quantities of material altered. It is postulated that about 200 ppm of the loss of linoleate corresponds to hydrolysis at a maximum; thus about 900 ppm or 80% of the linoleate is lost through oxidation after 7 hr of heating at 105°C and 3 hr at 160°C. Only 3% of the original linolenate remains after 7 hr at 105°C and 3 hr at 160°C. Twenty-five percent of the linolenate is present after 20 min at 220°C.

DISCUSSION

Although small amounts of free fatty acids have been found in the middle lamella (*13*), the majority of the fats in wood are located in the ray and longitudinal parenchyma (*5*) and are largely triglycerides (*6*). If these fats are to influence the surface wettability of wood, it would appear that they must be dispersed from the rays to the fibers at the surface of the wood. The structure of the simple and half-bordered pit membranes thus becomes extremely important to a consideration of the relevant pool of fats that contribute the changes in surface wettability. The few studies that have been made of these pit membranes show a relatively thick (from 0.5 to 1 μ) and imperforate structure (*14, 15*). Krahmer states that while these dense imperforate membranes may readily allow liquid transport by diffusion, the rate of gas phase transfer must be greatly restricted (*15*). The low permeability to gas transfer coupled with the low vapor pressure of the free fatty acids under the conditions studied (5.5×10^{-3} mm Hg for stearic acid at 105°C) must mean that fatty acid transfer from ray cells in the interior of the wood in the vapor state to the external surface of the wood is highly unlikely. If vaporized fatty acids did penetrate the pit membranes, data obtained by Stamm and Millett on selective adsorption of stearic acid from benzene by lumen surfaces would indicate that internal adsorption would not allow concentration at the wood surface (*16*). Although Huffman observed a concentration of resins on the surface of kiln-dried pine wood, a similar concentration of fats to the surface of birchwood would not be expected because the resins of pine are apparently forced through the resin canals (*17*).

A similar exudation of fats from ray cells would not appear to be effective due to the void space in the ray cells and restraint of the pit membranes. A transfer of the fatty acids with water would be unlikely because of low solubility and the minimal time that liquid water is at the surface, as evidenced by the rapid initiation of the falling rate drying curve. It would appear, then, that only those fats located near the surface of the piece can contribute to changes in wettability observed after heating.

Swanson and Cordingly showed that the surface wettability of paper changed when from 0.14 to 0.3 g of stearic acid per 100 g of paper was adsorbed from the vapor state (*3*), while there was no further change above this level of stearic acid. Assuming that an oriented stearic acid molecule has an area of 21 A^2 per molecule, this would correspond to a monomolecular layer on 150 m^2 of surface area. A surface area of 1.5 m^2/g of paper is very similar to actually measured areas and it would appear, then, that the limit of wettability change per gram of stearic acid adsorbed does correspond to the completion of a monomolecular layer. Projecting from the results of Swanson and Cordingly, it would appear that adsorption of stearic acid would alter the wettability of wood when from one third to a complete monomolecular layer was developed.

To estimate the amount of surface area accessible to fatty acids in birchwood it is necessary to make an approximation from the data of Stamm and Millett (*16*). These authors determined the unswollen surface area of sugar pine wood (*P. lambertiana*) by selective adsorption of stearic acid from a benzene solution. They found a surface area of 2500 cm^2/g using this method, which has been confirmed by other methods of measurement. The surface area per gram of birchwood was approximated from this data by adjusting the data according to the average specific gravity by the ratio

$$\frac{\Sigma_1}{g - S_1} = \frac{\Sigma_2}{g - S_2}$$

where

Σ_2 = effective surface area of yellow birchwood
Σ_1 = effective surface area of white pine (2500 cm^2/g)
g = specific gravity of cell wall substance (1.53)
S_1 = specific gravity of white pine wood (0.35)
S_2 = specific gravity of yellow birchwood (0.63)

A surface area of about 1900 cm^2/g is thus obtained. The amount of stearic acid

Table I. Free Fatty Acids of Fresh Yellow Birchwood
(ppm methyl ester on ovendry wood weight)

Fatty acid	Source and date of sampling: Ann Arbor March 1966	Pellston December 1966	Ann Arbor July 1967
Palmitic C16	12	34	14
Stearic C18	2.7	2.7	3.3
Oleic C18[1]	5.7	5.6	3.4
Linoleic C18[2]	83	99	109
Linoleic C18[3]	15	15	24
Arachic C20	7.4	...	0.44
Behenic C22	3.7	3.3	...
Total	130	160	
Total saturated	26	40	

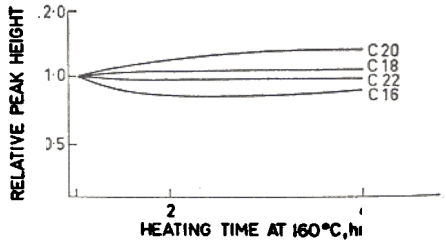


Fig. 5. Effect of heating at 160°C on the amounts of saturated free fatty acids in thin yellow birch strips.

Table II. Response of Individual Free Fatty Acids in Thin Yellow Birchwood Strips to 1 Month of Air Drying
(ppm methyl ester on ovendry wood weight)

	C_{16}	C_{18}	C_{18}^1	C_{18}^2	C_{18}^3	C_{20}
Refrigerated 1						3.1
						3.1
						3.1
2						3.1
						3.8
						3.8
Avg.						3.3
Air-dried 1 month 1						4.1
						4.4
						4.3
						3.8
						...
Avg.						4.1

Table III. Effect of Heating in Air on the Amounts of Free Fatty Acids in Thin Yellow Birchwood Strips
(ppm methyl ester on ovendry wood weight)

	C_{16}	C_{18}	C_{20}	C_{18}^1	C_{18}^2	C_{18}^3
			105°C			
Unheated avg.	14	3.3	0.44	3.4	109	24
30 min	16	4.4	0.35	5.2	170	42
1 hr	14	3.1	0.37	3.5	114	20
2 hr	17	5.3	0.73	4.8	128	15
3 hr	18	7.3	2.6	3.3	38	5
4 hr	18	7.2	2.1	3.6	53	10
7 hr	25	9.2	3.9	3.3	34	7
			160°C			
Unheated avg.	14	3.3	0.44	3.4	109	24
15 min	24	4.8	0.41	5.6	150	33
45 min	23	7.7	2.5	5.3	85	15
90 min	20	13	6.4	4.0	31	4.5
3 hr	22	11	4.5	3.3	33	7.2
			220°C			
Unheated avg.	14	3.3	0.44	3.4	109	24
2 min	19	3.8	0.37	4.1	76	15
7 min	19	3.9	0.50	4.0	67	12
20 min	16	6.2	2.0	2.8	23	4

It is evident from all three temperature treatments that there is an induction period when little change in the saturated free fatty acids occurs. This time period corresponds well to the time period necessary for the wood to reach equilibrium in heating temperature, and rapid loss of water is apparent.

Unsaturated Free Fatty Acid

As would be expected from studies of relative oxidation rates on model fatty acids and esters, the oxidation of the C18 unsaturated fatty acids is highly dependent on the degree of unsaturation (Table III). The amounts of oleic acid in the heated wood do not change markedly in the three temperatures studied. There is a general increase in oleic acid early in the heating period and a decrease to the original level. Although it is not known if the amount of oleic acid generated by hydrolysis is proportional to stearic acid, the assumption is made to obtain an estimation of the amount of oleic acid oxidation. Considering the amount of oxidation of the free fatty acid in this way yields an oxidation rate for oleic acid which is somewhat greater than the oxidation of the oleic acid ester. Swern states that the oxidation rates of free fatty acids exceed those of their glycerides (*12*).

It appears, then, that the two responses of hydrolysis and oxidation of oleic acid result in a nearly constant concentration of oleic acid in the heated wood. Accepting the difference between the relative response of stearic acid and the unsaturated acid as oxidation, the oleic acid is 64% oxidized after 7 hr at 105°C, 71% oxidized after 3 hr at 160°C, and 56% oxidized after 20 min at 220°C.

Linoleic acid is 90% oxidized after 7 hr at 105°C, 94% after 2 hr at 160°C, and 90% oxidized after 20 min at 220°C. In terms of actual quantities of linoleic acid, the unheated average of seven samples was 109 ppm, which increases to as high as 170 ppm after 30 min and then decreases to 34 ppm after 7 hr of heating at 105°C. Similar responses are found for the heat treatments at 160°C, where linoleic acid concentration decreases to 31 ppm after 1½ hr, and at 220°C, where the concentration is reduced to 23 ppm after 20 min of heating.

Linolenic acid is rapidly oxidized under the heat treatments studied. Because of the small amount of linolenic acid remaining after short heating periods, and due to the presence of a small contaminating peak which showed a shoulder on the back side of the methyl linolenate peak, the linolenic acid in wood is probably more extensively oxidized than is shown. With these limitations in mind, linolenic acid is 93% oxidized after 7 hr at 105°C, 95% oxidized after 2 hr at 160°C, and 93% oxidized after 20 min at 220°C, assuming that linolenic acid is generated similarly to stearic acid during the heat treatments.

necessary to coat this surface with a monomolecular layer can then be approximated as

$$\Sigma \quad aNWm/M$$

where

Σ = effective area of absorbent
a = effective cross-sectional area of adsorbate molecule
N = Avogadro's number (6.02×10^{23})
Wm = weight of adsorbate
M = molecular weight of adsorbate

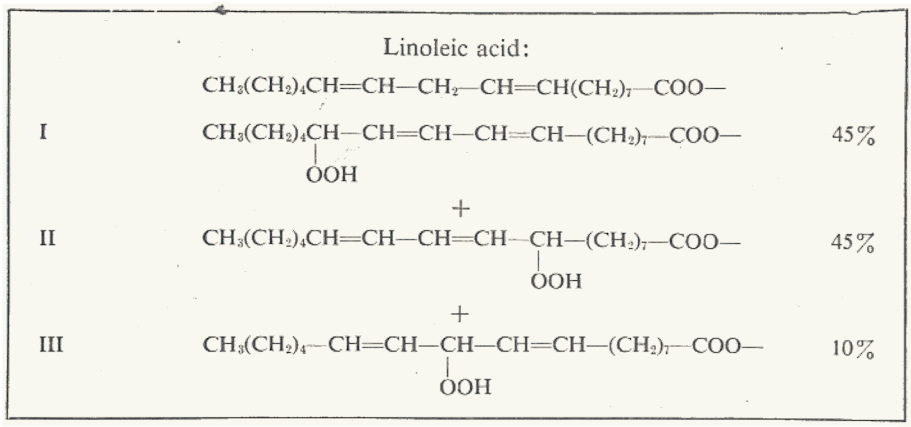
or about 400 ppm. It should be noted that the surface area per gram of wood is not appreciably dependent on the geometry of the specimen. Assuming smooth surface preparation, the effect of changing from a cube to a sheet is that cut cell walls assume a greater proportion of the total surface area with a corresponding decrease in the lumen surface area. Surface roughness is more important as the geometry approaches a thinner sheet, and the estimate of 1900 cm^2/g is a minimum surface area. Accepting 1900 cm^2/g as the surface area and the previously discussed restriction against movement of fatty acids from the center of the sample to the external surface, it is necessary to have a fatty acid concentration of about 400 ppm to achieve a monomolecular layer and about 130 ppm to begin to influence the surface wettability of the wood.

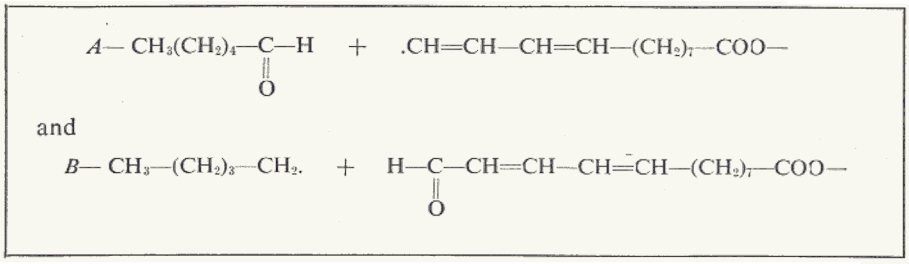
The amount of saturated free fatty acid did not exceed 40 ppm during any of the three heat treatments studied. The discrepancy between 40 and 400 ppm with the accompanying large change in surface wettability does not appear to allow an explanation of reduced wettability as adsorption of long chain length free fatty acids.

If the fatty constituents of wood do play a role in the heat-induced loss of water absorbancy, as would appear from the data obtained in this study, and if saturated long chain length free fatty acids are not present in sufficient quantities to explain this observed reduction in wettability, it would appear that the reduced wettability might be associated with the severe oxidation of the unsaturated fatty acids and esters. In terms of quantities of materials altered, the oxidation of linoleic acid and its ester are by far the most significant.

Although purely speculative, an examination of the oxidation products of these compounds might provide an answer to where to look for a reason for the observed changes in wettability. Heating paper at 105°C for 8 hr reduced the critical surface tension of wetting from a value of more than 60 dynes/cm for unheated paper to between 25–30 dynes/cm (*2*). A critical surface tension of wetting as low as 25–30 dynes/cm places definite restrictions on the chemical nature of the components responsible, and from data collected by Zisman, dictates an aliphatic nature (*24*).

The oxidation of linoleic acid and





linoleic acid esters would proceed along the same routes, except that the free acid should be more rapidly oxidized than the ester. The first step in the oxidation route should be formation of hydroperoxide derivatives under the conditions studied. (See reaction illustrated in top box above.) The hydroperoxides are 90% conjugated and there is isomerization from the cis-cis configuration to cis-trans under the milder conditions below 150°C and a shift to the trans-trans configuration under the more extreme oxidation conditions (*19*). The hydroperoxides are somewhat stable below 100°C and they tend to accumulate without significant chain cleavage (*12*). If the fats are then subjected to higher temperatures (150°C), chain cleavage initiates a geometric increase in the oxidation rate and the hydroperoxide concentration rapidly decreases (*22*).

Chain cleavage of hydroperoxide I shown above leads to four products shown in bottom box above. At temperatures below 100°C, Crossley and co-workers obtained the aldehyde cleavage products, while above 100°C the aldehydes were rapidly oxidized to their corresponding mono and dibasic acids (*23*). Free radicals such as $CH_3(CH_2)_3CH_2$. readily adsorb more oxygen to form a series of aldehydes and/or acids (*21*). A polar end group is necessary to have the compound act as an efficient adhesive (*18*). The above compounds satisfy requirements for a polar adsorption site to the substrate, while exposing an aliphatic structure to the air interface. The chain length of these products is short, however, and Brockway and Jones have demonstrated the importance of long chain length on rough surfaces to form a continuous film (*25*). Hancock observed a similar effect when examining the effect of chain length of adsorbed fatty acid on the percent wood failure of strip shear specimens (*4*). Buchanan found linoleic acid to be more effective in reducing the wettability of paper than either stearic or oleic acid (*1*). Glycerol esters were also highly effective water repellents. Although pure glycerides were not available for analysis, fractions of the neutral lipids from paper birch containing mixed glycerides with the major acid linoleic were very effective. The data obtained in this work substantiate this proposition. The role of oxidation in this process seems to be significant. Attention should be focused on the interaction of free radicals of the glycerides, formed by chain cleavages of unsaturated fatty acid esters, especially linoleate.

CONCLUSIONS

There is a marked reduction of surface wettability of yellow birchwood after heating in air. The change in wettability is a surface effect and related to the acetone-soluble constituents of wood, especially at the lower heating temperatures.

The fresh wood contains only about 40 ppm saturated free fatty acids, which is too small an amount to cause changes in surface wettability. Air drying for 1 month does not significantly increase the concentration of free fatty acids. Heating wood strips in air at temperatures between 105 and 220°C does not increase the concentration of free fatty acids sufficiently to allow an explanation of the reduced surface wettability. The unsaturated fatty acids and esters undergo considerable oxidation under heat conditions which produce water repellency. It would appear that the reduced wettability might be related to the oxidation of the linoleic acids and esters.

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