LXXIII. THE CHEMICAL ASPECT OF THE DRYING OF TIMBER.

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INTRODUCTION.

It is common knowledge that timber does not in general find its way into commercial usage until it has attained a moisture content approaching that which will be in equilibrium with the moisture of the atmosphere in which it will be used after conversion. In view of the high moisture content of freshly felled timber, the progress of drying under natural conditions must necessarily take considerable time, but despite this fact, and the economic issues which it involves, the question often arises as to whether air-drying of timber is to be preferred to the methods of kiln-drying which are now finding widespread application in the timber-using industry. In view of the belief existing in some quarters that certain beneficial chemical changes are associated with air-drying, prejudice has arisen from time to time against the practice of drying timber in kilns.

So far as it is known, no detailed chemical investigation of the effects of the drying of wood at moderate temperatures has hitherto been carried out, although throughout the literature of wood chemistry many references are to be found regarding the effect of high temperatures. It is pointed out by Hawley and Wise [1926, p. 197] that even at temperatures far below the destructive distillation point (approximately 280°) decomposition is indicated by the formation of small traces of acetic acid and methanol, probably as a result of hydrolysis. Under the conditions obtaining in a well regulated kiln-drying treatment of timber, however, there has been some doubt as to whether chemical changes of even a minor character are to be expected, in view of the fact that Hawley [1925] has stated that no chemical difference can be detected between the results of natural air-seasoning and artificial kiln-seasoning.

Since the value of wood as a structural material is dependent largely, if not entirely, on the nature of its skeletal substance, the composition of which varies but little from species to species, and since only such physical properties as colour, odour, taste, etc., are traceable to extractives, any chemical investigation on the effect of drying must in the first instance be confined to the effects produced on the major constituents of wood substance. The presence in wood, however, of substances characterised as extractives which may play a part in the seasoning process by acting on the major constituents in some way must not be overlooked. It is for this reason, for example, that woods containing extractives of a notably acidic nature may react differently when dried under different conditions of temperature, as a certain amount of hydrolysis may be possible when high temperatures are employed. The wood of oak is known to contain small percentages of weak acids such as tannic acid, and it is conceivable that although small acid concentrations might only have a negligible effect on the major constituents of wood during air-drying, they might, none the less, have some effect when wood is dried at relatively high temperatures. As the amount of extractives in oak heartwood is invariably greater than that in the sapwood, it is conceivable that these might react differently to the same drying conditions. In the light of previous work [Hawley and Campbell, 1927] any increase in the alkali-solubility of wood after drying at relatively high temperatures would be indicative of chemical change of a hydrolytic nature. At the same time, however, there may be other chemical changes attendant on the drying of wood, which hitherto have escaped observation.

The present investigation has been undertaken therefore with a view to determining *de novo* whether any chemical changes accompany the drying of timber, and if so, whether any relationship exists between the changes attendant upon air-drying on the one hand, and artificial drying on the other.

The wood used was cut from coppice shoots of English oak of approximately 40 years' growth. After separation of the heartwood and sapwood, the material was quickly converted to sawdust and finally ground to pass an 80-mesh and be retained by a 100-mesh screen, the grinding parts of the mill being of acid-resistant steel. The analytical methods used were those recommended by Schorger [1926, p. 505] and Hawley and Wise [1926, p. 123] and the results throughout are expressed as percentages of the oven-dry weight of the original wood.

EXPERIMENTAL.

During conversion to sawdust the wood used in this investigation had undoubtedly dried to a considerable extent, but the 80–100 mesh sapwood and heartwood still retained 25·4 % and 27·2 % of moisture respectively. Moisture contents were determined both by the standard oven-drying method and the xylene method of Schwalbe [Schorger, 1926, pp. 505–506] with closely comparable results. These materials were analysed as soon as possible following conversion (Table I).

Table I. *Analysis of original wood.*

	Sapwood	Heartwood
Cold water-soluble	1·76	4·63
Hot water-soluble	4·16	9·79
Cellulose	56·46	53·01
Lignin	19·98	20·94
Methoxyl	6·36	6·92
Total pentosans	24·75	24·88
Pentosans not in cellulose	11·23	11·07
Pentosans in cellulose	13·52	13·81

Samples of both sapwood and heartwood were then extracted with 1 % NaOH solution, under the conditions laid down by Schorger [1926, p. 506] for the standard alkali-solubility determination of wood, and, after removal of the alkali by thorough washing with hot water, the residues were dried at 105° and analysed (Table II).

Table II. *Analysis of original wood after extraction with NaOH.*

	Sapwood	Heartwood
Loss on alkali extraction	19·0	22·92
Cellulose	56·96	53·87
Lignin	18·55	18·42
Methoxyl	4·70	4·23
Total pentosans	19·67	19·27
Pentosans not in cellulose	2·91	2·79
Pentosans in cellulose	16·76	16·48

The drying experiments were carried out as follows.

(i) *Air-drying.* Weighed samples of both sapwood and heartwood were placed in jars, covered with fine linen to prevent access to dust, and left in the laboratory with occasional mixing to dry for a period of 126 days. At the end of this time the moisture content of the sapwood had fallen to 13·0 % and that of the heartwood to 12·8 %.

No loss in dry weight due to air-drying was observed.

(ii) *Kiln-drying.* Weighed samples of sapwood and heartwood were subjected to a kiln-drying treatment as follows. The wood flour was in each case spread on a glass dish in a layer 1 inch deep and the following kiln-seasoning schedule, which was considered suitable for 1 inch oak boards, was applied.

Schedule employed in the kiln-seasoning of 80–100 mesh oak.

Temperature ° F.	Humidity %	Duration of treatment (days)	Total time (days)	Assumed moisture content %
115	75	2	2	30
120	65	4	6	25
125	55	5	11	20
130	45	5	16	15–10

The rate of initial warming of the sawdust was 9° F. per hour at a constant humidity of 75 %.

As a result of this treatment the moisture content of both the sapwood and heartwood fell to 7·5 %. Further, a loss of 0·2 % and 0·33 % of the dry weight of the original wood was observed in sapwood and heartwood respectively, and a decided darkening in colour was noted in each case.

(iii) *Oven-drying.* Weighed samples of sapwood and heartwood were placed in weighing bottles in a drying oven, and maintained at 105° for 200 hours. Pronounced darkening in colour took place in both sapwood and heartwood and the respective losses in weight of wood substance were 0·41 % and 1·12 %.

Analyses were now carried out on each of the residues remaining after the several drying treatments (Table III). Further, each residue was analysed after alkali extraction under the same conditions as the extractions applied to the original wood (Table IV).

Table III. *Analysis of 80–100 mesh English oak wood after kiln- and oven-drying.*

Samples		Duration of treatment (days)	Loss due to treatment	Cold water-sol.	Hot water-sol.	Cellulose	Lignin	Methoxyl	Total pentosans	Pentosans not in cellulose	Pentosans in cellulose
Air-dried	Sap	126	Nil	1·52	3·59	57·57	21·22	7·06	23·76	8·90	14·86
	Heart		Nil	4·95	9·05	54·26	22·03	7·91	23·42	8·82	14·60
Kiln-dried	Sap	16	0·20	1·81	3·65	57·27	21·98	5·81	23·74	9·44	14·31
	Heart		0·33	4·37	9·17	52·53	22·47	5·49	23·11	8·89	14·22
Oven-dried	Sap	9	0·41	2·23	4·11	55·47	21·70	5·50	23·61	11·53	12·08
	Heart		0·12	3·94	9·84	52·00	23·60	4·76	23·78	11·62	12·17

Table IV. *Analysis of air-, kiln- and oven-dried wood after alkali extraction.*

Samples		Loss due to treatment	Cellulose	Lignin	Methoxyl	Total pentosans	Pentosans not in cellulose	Pentosans in cellulose
Air-dried	Sap	18·78	57·09	18·33	4·79	20·15	4·43	15·72
	Heart	23·41	53·70	17·95	4·38	19·73	4·79	14·94
Kiln-dried	Sap	18·88	56·32	19·48	4·74	19·36	3·73	15·63
	Heart	24·62	51·94	18·51	4·10	18·62	3·04	15·58
Oven-dried	Sap	19·41	54·52	17·62	4·35	18·94	3·82	15·12
	Heart	28·93	49·30	19·60	4·10	16·52	3·42	13·10

The effect of mild hydrolysis on the original wood.

A sample of the original heartwood was subjected to a hydrolytic treatment as follows. 100 g. of the material was incorporated with 2 litres of 1 % aqueous hydrochloric acid and maintained at 100° for 6 hours. After removal of the acid, thorough washing with hot water and drying at 105°, the residue was analysed (Table V).

Table V. *Analysis of 80–100 mesh English oak wood (heart) after hydrolysis with 1 % HCl for 6 hours at 100°.*

Loss on hydrolysis	33·43
Cellulose	42·44
Lignin	18·98
Methoxyl	4·06
Total pentosans	7·28
Pentosans not in cellulose	2·47
Pentosans in cellulose	4·81

DISCUSSION.

Comparison of Tables I and III shows that, irrespective of the method of drying, the percentage amount of water-soluble material in the wood under investigation does not vary except within the limits of experimental error. Changes during drying, however, are apparent in the cellulose, lignin and pentosans.

So far as the cellulose is concerned this constituent exhibits a slight increase in amount in the passage from the green to the air-dried condition in both sapwood and heartwood. A similar though not quite so pronounced increase is noted in the cellulose content of kiln-dried sapwood, while the cellulose content of kiln-dried heartwood is slightly lower than that of the original wood. In the case of the oven-dried material depreciation of the cellulose content is observed to take place in both sapwood and heartwood. These slight variations in cellulose content are further seen to be accompanied by concomitant variations in the percentage amounts of furfuraldehyde-yielding complexes in the wood, for, while the total pentosan content exhibits a constant decrease in amount as a result of all three drying processes, the pentosan content of the cellulose increases on air- and kiln-drying, and decreases on oven-drying. The variations in the pentosan content of the cellulose agree very closely with the variations in the cellulose content itself, except in the case of oven-drying where the loss of pentosans in the cellulose is greater than that of the cellulose, and in kiln-dried heartwood where a slight increase in the pentosan content of the cellulose is accompanied by a decrease in cellulose content. Coupled with the fact that only slight losses in weight have been observed as a result of kiln- and oven-drying, the depreciations of cellulose and of pentosans in the cellulose indicate that kiln-dried heartwood and oven-dried heartwood and sapwood have undergone a certain amount of incipient hydrolysis, decomposition being most pronounced in oven-dried heartwood.

From the analytical data it is impossible to deduce to the fullest extent the true nature of the changes which take place in the furfuraldehyde-yielding complexes during drying. It is none the less evident, however, that definite changes take place in that portion of such bodies which in green wood is not associated with the cellulose, since, whether an increase or decrease in the pentosan content of the cellulose be observed, depreciation of the total pentosan content is a consistent result of drying by all three processes. The results therefore indicate that, of that portion of the furfuraldehyde-yielding complexes which is not associated with the cellulose in the original wood, part becomes associated with the cellulose during drying, and remains associated with it provided the drying conditions are not too severe, and part is transformed into something which ceases to yield furfuraldehyde on distillation with 12 % hydrochloric acid. It is probable that this latter portion becomes associated with lignin during drying, as this constituent exhibits a consistent increase in amount as a result of all three drying processes studied. Thus the question of the relationship between the lignin and pentosans of wood is again revived. From the conflicting experimental evidence available on this subject up till 1926, Hawley and Wise [1926, pp. 70–71] are unable to draw definite conclusions, but Jonas [1928] has recently discussed numerous theories of lignin constitution, and arrives at the conclusion that lignin is a condensed furfuran product containing the stable tetrahydrofurfuran ring.

Further light on the nature of the chemical changes attendant on the drying of wood is obtained only by a comparative study of the effect of alkali on green and dried woods respectively. Comparison of Tables I and II shows the effect of 1 % sodium hydroxide at 100° on the original green wood.

It can be seen that the pentosans and lignin are the components most susceptible to alkali attack, but the outstanding fact is that cellulose appears to be but little affected by alkali until it is observed that the pentosan content of the cellulose in alkali-extracted wood is higher than that of the cellulose isolated from the original wood. The explanation of this fact is not yet apparent, but from the results of research at present in progress it would appear that an increase in the pentosan content of the cellulose after alkali-extraction is characteristic of hardwoods.

Comparison of Tables II and IV shows that the total respective alkali-solubilities of green and air-dried wood are approximately the same, but closer examination of the data reveals that, while the alkali-solubility of the pentosans not in the cellulose is much less in air-dried wood than it is in the original wood, an increase in the alkali-solubility of lignin is noted as a result of drying. This points to the conclusion that the increase in the alkali-solubility of the lignin is attributable not so much to any effect of drying on the lignin nucleus as to the original susceptibility to attack by alkali of those bodies derived from the furfuraldehyde-yielding complexes which have become associated with it during drying. This is further borne out by the analytical data, which show that after air-drying the increase in alkali-solubility of the lignin is approximately equal to the increase in the percentage of that constituent which results from the drying treatment.

As a result of kiln-drying, the pentosans not in the cellulose are slightly more susceptible to alkali attack than the corresponding components of air-dried wood. In this case also it seems probable that the increased alkali-solubility of lignin is accounted for by the additions made to it during drying.

So far as oven-drying is concerned, the low cellulose yields recorded, coupled with the depreciation of the pentosan content of the cellulose, suggest that the severity of the treatment has induced a certain amount of hydrolysis. This is borne out by the data in Tables II and IV, which indicate that the pentosans in oven-dried wood are more susceptible to attack by alkali than the corresponding components in kiln- and air-dried wood. In conjunction with the fact that the cellulose in oven-dried sapwood is more resistant to alkali than the corresponding components in oven-dried heartwood, the experimental evidence favours the conclusion that prolonged heating of green wood at 105° has the effect of inducing hydrolysis, the results of which are more marked in heartwood than in sapwood.

The ease with which green oak heartwood can be hydrolysed is demonstrated by the data in Table V. Comparison of these with the data in Table I shows that the pentosans are by far the most susceptible to hydrolysis of all the principal wood components.

CONCLUSIONS.

From the foregoing considerations it is to be concluded that the drying of oak timber is associated with definite chemical changes in the furfuraldehyde-yielding complexes of the wood substance, which are responsible in their turn for alterations in the cellulose and lignin aggregates, as determined by standard analytical methods. In this respect close agreement has been proved between the nature of the chemical changes attendant on the processes of air- and kiln-drying, although the analytical data suggest that kiln-drying may induce very slight decomposition in heartwood. The effects of drying by continuous heating of wood at 105° for 200 hours are marked by a certain amount of decomposition which has been shown to be of a hydrolytic nature. It must further be concluded that the greater amount of hydrolysis noted in the heartwood is due to its higher content of extractives of an acidic nature. In this connection it is probable that the reason why it is found in practice that softwoods are much easier to dry at elevated temperatures than hardwoods, is that softwoods invariably contain less pentosans than hardwoods. The susceptibility of the pentosans of wood to hydrolysis has been amply demonstrated in previous work, but having regard to the evidence cited above it is conceivable that conditions which would be severe enough to cause marked depletion in the pentosans of a hardwood—with possible influence on the other major constituents, and probably the physical properties of the wood as a whole—might produce no marked detectable difference on a softwood, solely on account of the low pentosan content of the latter. While it is admitted that the effects of drying on the wood flour used in this investigation cannot implicitly be claimed for wood in its natural form, owing to purely structural considerations, the results show that in so far as its effect on wood substance is concerned, a well-regulated and suitable kiln-drying treatment should have no detectable deleterious effect. It is indicated, however, that if the conditions obtaining in the interior of a piece of wood in the process of kiln-drying should by any chance become so drastic as to approach the conditions obtaining in an oven-drying treatment, deleterious effects might reasonably ensue. This is all the more probable for the reason that if volatile acids cause the hydrolysis, their action would be of a more serious nature than that detected in the present investigation, in view of the fact that they could not volatilise so readily from the interior of a piece of wood as they could from the more discrete particles of a wood flour.

SUMMARY.

1. The effects of air-, kiln- and oven-drying on both sapwood and heartwood of English oak have been examined in detail.

2. It is shown that air- and kiln-drying of wood are associated with chemical changes in the furfuraldehyde-yielding complexes of wood substance, to the extent that total pentosans are depreciated while the pentosan content of the cellulose is enhanced, and an increase in lignin is noted.

3. Oven-drying of wood is shown to result in an increase of lignin and a slight amount of hydrolysis of the carbohydrate components, which is more marked in the heartwood.

4. Reasons are given for concluding that well-regulated kiln-drying treatment of timber is strictly comparable in effect to ordinary air-drying. On the other hand, it is shown that if conditions in a kiln should become so drastic as to approach those obtaining in an oven-drying treatment, decomposition of the wood substance would be imminent.

5. It is suggested that the reason why softwoods can be kiln-dried with greater ease than hardwoods, is to be found in the fact that these invariably contain less pentosans than hardwoods, so that drying conditions which might be severe enough to hydrolyse the pentosans of wood would always affect hardwoods more than softwoods.

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