LXXXIV. THE CHEMICAL ASPECT OF THE DRYING OF TIMBER.

2. THE DRYING OF A SOFTWOOD.

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(Received April 2nd, 1931.)

IN a previous communication [Campbell and Booth, 1930] an account was given of the chemical changes which accompany the drying of oak wood under various conditions. It was indicated that owing to certain well-defined differences in composition between hardwoods and softwoods these two classes of timber might be expected to react differently to similar conditions of drying. In pursuance of this indication the same experimental procedure which was applied to oak wood has now been applied to a softwood. The material used was the freshly felled mature wood of Silver fir in which there was no differentiation in colour between heartwood and sapwood. After conversion to sawdust the material was ground, as before, to pass an 80 mesh and be retained by a 100 mesh screen. The analytical methods were the same as those used in previous work, and the results throughout are expressed as percentages of the oven-dry weight of the original wood.

EXPERIMENTAL.

The moisture content of the 80–100 mesh material as determined by the standard oven-drying method was 34.58 % and this result was close to that obtained by the xylene method of Schwalbe [Schorger, 1926, pp. 505–506]. The drying experiments were carried out as follows.

(i) *Air-drying.* A weighed sample of the 80–100 mesh wood flour was placed in a glass jar covered with fine linen and left in the laboratory, with occasional mixing, to dry for a period of 200 days. The final moisture content was 13.27 %.

(ii) *Kiln-drying.* A weighed sample of the original wood was placed on a glass dish in a layer $1\frac{1}{2}$ in. deep and the following kiln-drying schedule, which was considered suitable for 2-inch boards, was applied.

The rate of initial warming of the wood flour was 6.7° per hour at a constant humidity of 75 % up to a temperature of 73.9° . The wood was maintained at 73.9° and 75 % relative humidity for 3 hours and then the

Schedule employed in the kiln-seasoning of 80-100 mesh Silver fir.

Temperature ° C.	Relative humidity	Duration of treat- ment (days)	Total time (days)	Assumed moisture content %	Remarks
71.1	75	1	1	35-30	Time includes initial warming
71.1	70	1	2	30-25	
73.9	65	1½	3½	25-20	
73.9	60	1½	5½	20-15	
76.7	55	1½	7	15-10	Time includes final cooling
79.4	50	1	8	10	

temperature was allowed to fall to 71.1°. Final cooling took place at the rate of 6.7° per hour.

As a result of this treatment the moisture content of the wood was reduced to 9.57 %. There was slight darkening in colour and a loss of wood substance amounting to 0.89 % of the oven-dry weight of the original wood was recorded.

(iii) *Oven-drying.* (a) A weighed sample of the original wood was maintained at 105° for 16 hours. The material became darker in colour.

(b) A similar sample of the original wood was maintained at 105° for 9 days. There was pronounced darkening in colour and a loss of wood substance amounting to 0.62 % of the oven-dry weight of the original wood was recorded.

The analysis of the original wood and the analyses of the same material after the several drying treatments are recorded in Table I. The data in Table II were obtained in order to determine the effect of 1 % NaOH on the original wood and on the wood after drying.

Table I. *Analysis of 80-100 mesh Silver fir wood before and after air-, kiln- and oven-drying.*

Material	Dura- tion of treat- ment (days)	Loss due to treat- ment	Cold water- soluble	Hot water- soluble	Cellu- lose	Lignin	Meth- oxyl	Total pento- sanes	Pento- sanes not in cellu- lose	Pento- sanes in cellu- lose
Original wood	—	—	1.34	2.57	57.89	28.09	5.29	10.15	6.89	3.26
Air-dried	200	Nil	1.07	2.06	58.64	28.88	4.89	9.44	6.31	3.13
Kiln-dried	8	0.89	1.36	2.82	57.59	28.24	4.67	9.45	6.35	3.11
Oven-dried (a)	½	Not deter- mined	1.60	2.94	57.41	28.27	4.78	9.49	6.41	3.08
(b)	9	0.62	2.35	4.52	57.23	28.19	4.74	9.29	6.34	2.95

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

Material	Loss due to treatment	Cellulose	Lignin	Methoxyl	Total pentosans	Pentosans not in cellulose	Pentosans in cellulose
Original wood	11.14	55.98	26.52	4.01	8.59	4.97	3.62
Air-dried	12.63	55.64	26.41	3.96	7.88	4.70	3.18
Kiln-dried	10.82	55.96	26.37	4.25	8.18	4.84	3.34
Oven-dried (a)	12.22	54.37	26.12	3.66	7.87	4.99	2.88
(b)	15.07	53.38	25.30	3.93	7.27	4.37	2.90

DISCUSSION.

Having due regard to manifest imperfections in analytical procedure, the data in Table I would, at first sight, suggest that during drying Silver fir wood suffers no radical change in composition. Critical examination reveals, however, that the data are consistent with slight though none the less definite chemical changes. For instance, in the case of air-drying, it can be seen that the yields of Cross and Bevan cellulose and of lignin are higher in dry wood than in green wood. These slight increases are accompanied by depreciations of water-soluble material and furfuraldehyde-yielding complexes respectively. Further, the loss in total pentosans represents a combined loss of pentosans in the cellulose and pentosans not in the cellulose. Since no loss in weight was observed, the depreciation in pentosans must be reflected in the increase in lignin content of the dry wood, and it must follow that the source of the accretions to the cellulose must be some material in green wood which is soluble in water. This contention derives support from the fact that as a result of air-drying, the combined losses of water-soluble material and total pentosans represent 1.49 %, and the combined additions to the cellulose and lignin amount to 1.54 % of the oven-dry weight of the original wood.

Further examination of the data in Table I shows that kiln-drying brings about a loss of wood substance which amounts to 0.89 % of the oven-dry weight of the original wood. It is significant that while no additions have been made to the cellulose, the kiln-dried wood contains approximately the same amount of water-soluble material as the original wood. The observed increase in lignin content during drying is extremely small, but it is consistent with previous work. It is interesting to note that the percentage increase in lignin content is exactly equal to the decrease in the pentosan content of the cellulose, and the suggestion thus presents itself that the drying treatment has been responsible for the decomposition of a portion of the furfuraldehyde-yielding complexes which was not associated with the cellulose in the original wood, and which under other conditions of drying might also have become associated with the lignin. This loss in furfuraldehyde-yielding material calculated as pentosans by means of Kröber's table amounts to 0.55 % of the oven-dry weight of the original wood, and thus accounts in large measure for the observed loss in weight.

For obvious reasons it has been impossible to determine directly whether the oven-drying of wood for a comparatively short period results in a loss of wood substance, but indirect evidence on this important question is afforded by the data in Table I. Oven-drying of green Silver fir wood at 105° for 16 hours results in slight, though perceptible, increases in water-soluble material and in lignin content, which are practically offset by corresponding losses in cellulose and furfuraldehyde-yielding complexes. The combined increases amount to 0.81 % and the combined losses to 0.97 % of the oven-dry weight of the original wood. The loss in weight during drying has thus been

exceedingly small. It is significant that here again the slight increase in lignin content is exactly equal to the decrease in the pentosan content of the cellulose. It would thus appear that the drying treatment has again precluded the permanent addition to the lignin of a further portion of the furfuraldehyde-yielding complexes which in the green wood was not associated with the cellulose.

The experimental data do not reveal the effect of oven-drying at 105° on wood which has already been air-dried, but if it is assumed that on oven-drying for the period commonly adopted in moisture content determinations air-dried wood would attain the same composition as green wood heated under the same conditions, it can be seen from Table I that the loss of wood substance during drying would not exceed 0.43 % of the oven-dry weight of the original wood.

When Silver fir wood is oven-dried for 9 days it is obvious from the data in Table I that incipient decomposition takes place. In the first place there is a loss of wood substance, and secondly, the dry wood contains a much higher proportion of water-soluble material than the original wood. There is a slight depreciation of cellulose and the lignin and pentosan contents are lower in the oven-dried wood than in any of the other samples.

Turning now to the data in Table II it can be seen that an interesting comparison is afforded between the alkali-solubility of the original wood and the alkali-solubility of the same material after the various drying treatments. Further, a comparison of the data in Tables I and II shows the effect of 1 % NaOH at 100° on the major wood components both before and after drying. The most striking fact illustrated by Table II is that after alkali-extraction the original, air-dried, and kiln-dried wood are approximately of the same composition, despite the fact that the alkali-solubility of the air-dried wood is greater than that of either the original or the kiln-dried wood. While alkali attacks the pentosans not in the cellulose of all the samples, the pentosan content of the cellulose exhibits a slight though perceptible increase in amount in each case. The cellulose and lignin aggregates in air-dried wood are more soluble in alkali than the corresponding aggregates in either green or kiln-dried wood. The only explanation of this fact would appear to be that the material added to these aggregates during air-drying is readily soluble in alkali. Since addition to the cellulose does not take place during kiln-drying the alkali-solubility of this component is not increased, but the alkali-solubility of the lignin is slightly increased because in this case material is added during drying. The increase in alkali-solubility of the lignin is offset by a decrease in the alkali-solubility of the pentosans not in the cellulose.

The relatively high alkali-solubility of the oven-dried wood can only be explained by the fact that incipient hydrolysis has taken place as a direct result of the high temperature treatment. This was indicated in Table I by the higher water-solubility of oven-dried wood, but the results in Table II reveal that, irrespective of the fact that after 16 hours' drying at 105° no

additions were made to the cellulose, the alkali-solubility of this component has increased. The incipient hydrolysis has apparently been confined to the carbohydrate components of the wood substance.

Prolonged oven-drying of green wood results in a pronounced increase in the alkali-solubility of the wood as a whole, which is reflected in the greater susceptibility to the reagent of the lignin as well as the carbohydrate components. In the light of previous work [Hawley and Campbell, 1927] the effect of prolonged oven-drying can only be described as a partial hydrolysis.

CONCLUSIONS.

From a comparison of the foregoing data with those obtained in the study of the drying of oak wood [Campbell and Booth, 1930] it is to be concluded that although hardwood and softwood react somewhat differently to similar drying conditions, they have one feature in common. As moisture leaves the wood, changes take place in the furfuraldehyde-yielding complexes of the wood substance. Under suitable conditions of drying the hardwood cellulose and lignin respectively are enhanced at the expense of the furfuraldehyde-yielding complexes, whereas under similar conditions only the lignin of the softwood is enhanced from this source. It is to be concluded that the material added to the cellulose of the softwood during air-drying is probably of an unstable nature, unlike true cellulose in composition, since it is recruited from water-soluble material in the green wood, and can readily be split off by dilute alkali from the air-dried wood.

In general, for both types of wood the effect of moderate heat during drying is to reduce the amount of the additions to the cellulose and lignin, while high temperatures definitely cause hydrolysis. It has become apparent from the results of research at present in progress that even the incipient hydrolysis of wood substance caused by fungi of the brown rot type has such marked effects on the physical properties of timber as the decrease of mechanical strength and a tendency to cause brittleness. Thus it becomes obvious that the woods which are chemically best suited to withstand high temperatures during drying are those which are least susceptible to hydrolysis. It has been shown in previous work that the pentosans, or rather the furfuraldehyde-yielding complexes of wood substance, are the most susceptible to hydrolysis of all the principal wood components and the suggestion has been made [Campbell and Booth, 1930] that a wood of high pentosan content would be more susceptible to heat than a wood of low pentosan content. The results of the present investigation would appear to bear this out.

In the first place, by comparison with previous data [Campbell and Booth, 1930] it can be seen that the extent of the depletion of the pentosans *per se* during drying is approximately of the same order of magnitude in the hardwood and softwood, although depletion in the hardwood takes place only in the pentosans not in the cellulose. Since, however, the softwood contains less than half the percentage of pentosans present in the hardwood, the net effect

of drying on the former is correspondingly less pronounced than it is on the latter.

Purely physical considerations render it difficult in practice to remove the greater part of the moisture from green wood without at the same time producing some of the defects commonly described in technical literature, but since rapid drying is so frequently effected by employing heat and high relative humidities, the question arises as to whether some defects may, in part, be due to chemical changes induced by unsuitable conditions of drying. For instance, it has been pointed out by Stillwell [1928] that all species of wood are not equally tolerant of heat, and the suggestion is further made that there may be a temperature for all species above which seasoning cannot proceed without damage. At the same time it is eminently feasible that there may be critical temperatures for individual species above which drying cannot proceed without causing a degree of hydrolysis which will be reflected in decreased strength of the dry wood. In this connection it should be borne in mind that apparently small changes in composition detected by current methods of analysis may cause marked changes in physical properties, and the results of the present series of investigations suggest that, since the chemical changes due to the drying of timber originate in small changes in the furfuraldehyde-yielding complexes of the wood substance, the so-called pentosans of wood substance play an important part in the determination of physical characteristics of the material as a whole.

Note on the determination of moisture by the standard oven-drying method.

The present investigation throws a new light on the question of moisture determination by the oven-drying method. It is clear that oven-dried wood is not exactly of the same composition as green wood. After drying for 16 hours at 105° the error in moisture content in the case of green Silver fir wood can amount to 0.16 %. For air-dried wood the error might be appreciably greater, and it is conceivable that the degree of error might vary from species to species. The degree of error estimated above cannot in itself be regarded as serious, but, at the same time, it would appear to be advisable in determining moisture by the oven-drying method not to prolong the drying time longer than is absolutely necessary for the samples to attain constant weight. In this way error due to incipient hydrolysis would be minimised.

The effect of 1 % NaOH at 100° on wood substance.

It was reported in a previous paper [Campbell and Booth, 1930] that after oak wood had been heated at 100° with 1 % NaOH the pentosan content of the cellulose was higher than that of the untreated wood. A similar result was later obtained with beech wood [Campbell, 1930]. This was thought to be a characteristic reaction of hardwoods as it had never been reported for a softwood. The same phenomenon has been observed, however, in the present investigation in the wood of Silver fir, although the increase in the pentosan

content of the cellulose here is by no means so great as in the hardwoods examined. These results suggest a possible difference in composition between the furfuraldehyde-yielding complexes which are associated with the cellulose of wood on the one hand and those which are not associated with the cellulose on the other. The matter will receive more detailed investigation.

SUMMARY.

1. The chemical effects of air-, kiln- and oven-drying on the wood of Silver fir have been examined in detail.
2. Air-drying is shown to result in depreciation of pentosans and water-soluble material. Lignin is enhanced at the expense of the furfuraldehyde-yielding complexes, and cellulose is enhanced at the expense of the water-soluble material of the green wood.
3. Kiln-drying precludes the additions to cellulose and part of the additions to lignin.
4. Oven-drying of green wood induces incipient hydrolysis of the wood substance.
5. An attempt has been made to confirm a previous suggestion that softwoods withstand high temperatures during drying better than hardwoods on account of their relatively low pentosan content.
6. The oven-drying method of moisture determination is subject to a slight error due to incipient hydrolysis of wood substance.

The authors wish to express their indebtedness to Mr R. A. G. Knight of the Seasoning Section, Forest Products Research Laboratory, for carrying out the kiln-drying treatment, to Prof. F. Soddy for facilities afforded in the Old Chemistry Department, Oxford University, to Sir James Irvine for criticising the manuscript, and to R. S. Pearson, Esq., Director of Forest Products Research, for permission to publish these results.

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