AN ABSTRACT OF THE THESIS OF

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Various methods of determining moisture content (oven-drying at 65°C, 85°C, 105°C, and 125°C; drying over the desiccant phosphorus pentoxide; Cenco Moisture Meter, and Karl Fischer Titration) were evaluated to determine which method was most accurate in determining Douglas-fir bark moisture content. Extractive content, cork vs. fiber composition, and particle size were examined to determine their influence on moisture content determination and moisture sorption by Douglas-fir bark.

Sample composition, extractive content, and particle size did not significantly influence the methods of moisture content determination for Douglas-fir bark. There were, however, significant differences among the methods of moisture content determination ($P \leq .01$). The most accurate way to determine bark moisture was deduced to be by drying over the desiccant phosphorus pentoxide (P_2O_5) and then

titrating the samples by the Karl Fischer method to determine any remaining moisture. Methods which gave statistically similar results ($P \leq .01$) were oven-drying at 85°C and the Cenco Moisture Meter.

Sample composition and extractive content exerted significant influence ($P \leq .05$) on the equilibrium moisture contents at which the samples equilibrated. Bark fiber had a significantly higher equilibrium moisture content than cork material. Extraction increased the equilibrium moisture content of both fiber and cork, but only the fiber fraction exhibited an increase in the amount of moisture sorbed.

For wood, differences resulting from oven-drying at different temperatures were attributed to the equilibrium moisture content established in the oven at these temperatures.

Determining Moisture Content and Moisture Sorption in Douglas-fir Bark

by

John D. Litvay

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DETERMINING MOISTURE CONTENT AND MOISTURE SORPTION IN DOUGLAS-FIR BARK

INTRODUCTION

There has been mounting concern recently regarding the problem of utilizing bark residue generated at log breakdown plants in the Pacific Northwest. The reason for this interest is due primarily to new environmental laws and regulations governing water and air pollution. Governmental agencies and the public are demanding that forest industries more fully utilize forest resources so that (1) air and water pollution can be reduced, and (2) the growing demand for timber resources, both physical (i. e., wood and wood products) and recreational can be balanced with the limited supply of land and trees.

Before making an intelligent decision regarding bark utilization, a thorough knowledge of the subject must be available. Unfortunately, at this time the forest products industry has insufficient knowledge about various bark properties to permit proper decisions regarding its utilization.

The ability to accurately measure the moisture content of bark is a necessary prerequisite for some possible applications involved in the utilization of bark. It has been shown that many wood properties and processing operations are affected by the moisture content of the wood (12). Due to this knowledge certain methods of accurately

determining the moisture content of wood have evolved. However, the amount of work done on methods of determining moisture content of bark is very limited. There is at this time no common or standard method of determining the moisture content of bark.

The moisture content of bark has usually been estimated by applying knowledge and techniques used for wood, namely, oven-drying at 105°C (2, 8, 11, 15, 16, 18, 19). Smith and Kozak (19) pointed out that there is some doubt as to the reliability of this method for moisture content determination of bark because the extractive content of bark is very high and volatilization could cause large inaccuracies to develop in any method utilizing heat.

This experiment was designed to help define the moisture content of bark and some of the factors affecting it--extractive content, sample particle size, and sample composition. The objective was to find a method or methods of determining moisture content that would be accurate and practical within the limits set by ASTM (1) for determining moisture content.

DESIGN OF EXPERIMENT

Seven methods of moisture content determination were studied and classified into three groups according to inherent errors assumed to be present. A short description of these methods and associated errors follow.

Heat methods used were oven-drying at 65 °C, 85 °C, 105 °C, and 125 °C and the Cenco Moisture Meter. All oven-drying procedures complied with ASTM standard D1348 (1), except the entering air was not pre-dried. The Cenco Moisture Meter utilized an infra-red heat lamp and a suspended sample pan. The moisture content of a sample was determined by placing a sample on the pan and turning on the lamp. As weight was lost, the amount the pan rose was reset by turning a dial calibrated to give the moisture content. This moisture content value was based on green weight and was converted to a dry weight basis for comparison to the other methods by the following equation.

$$\text{Moisture content}_{dry} = \left(\frac{100}{100 - \text{moisture content}_{green}} - 1\right) \times 100$$

The Cenco used in this study was also connected to a transformer which reduced the line voltage from 120 V to 92 V. All sample determinations were for 15 minutes at this setting.

Any method of moisture content determination using heat will possibly involve two sources of error. First, volatilization of extractives could give erroneously high moisture content values, and second,

the oven temperatures used might allow moisture to remain in the samples (residual moisture), thus giving a low moisture content value. Therefore, the actual error associated with the heat methods of moisture content determination may be a combination of the above two factors and might lead to high (+), accurate (o) or low (-) values depending upon the magnitude of each error involved.

Only one desiccant, phosphorus pentoxide (P_2O_5) was used in the experiment. Samples were placed in a desiccator containing phosphorus pentoxide until no further weight losses were observed--approximately 11 days.

Drying over a desiccant has basically one source of error caused by not achieving an absolute relative humidity of zero. Thus an equilibrium moisture content condition may be set up within the desiccator and the samples may retain some moisture (residual moisture) resulting in low (-) moisture content values.

In the Karl Fischer titration method, samples were immersed in methanol for 18 hours after which they were titrated by stabilized Karl Fischer reagent to an electrical end point. The procedure followed was in accordance with ASTM standard D1348 (1). Kollman and Côté (12) and Resch (17) have recommended this method as the best method of determining moisture in small samples, especially those containing volatile substituents.

The Karl Fischer method, however, is limited by an equilibrium

condition set up in the reaction flask between the solvent (methanol) and undetected water. A dilution error further compounds the error in this method. A brief explanation of these errors follows.

As titrating reagent is added the volume of liquid in the flask becomes greater. Since the solvent and undetected water are at equilibrium at the end point, the amount of undetected water will be greater in a flask containing a larger volume of liquid. Samples with higher moisture contents require larger volumes of titrating reagent; thus, their final volumes are greater, their undetected water volumes are greater, and consequently their inherent errors are greater. This assumes that the sample size is not altered to reduce the amount of titration reagent needed to reach an end point. Therefore, the error connected with the Karl Fischer method will give low (-) moisture content values. The magnitude of this discrepancy will increase with an increase in moisture content if sample size remains constant.

Table 1 is a summary of the above assumptions. It should be noted that if a correction is made for residual moisture the error connected with the P_2O_5 method goes to zero as the reliability of the correction increases.

From the above assumptions came the design of this experiment.

Table 1. Sources of error in methods of moisture content determination.

Method	Error
Heat (error)	(+ or -)[a] = volatilization (+) plus R. M. C.[b] (-)
P_2O_5 (error)	(-) = R. M. C. (-)
Titration (error)	(-) = Dilution (-)

[a] Error due to heat is a combination of two factors.

[b] R. M. C. = residual moisture content

Study I - Evaluation of Different Methods Used To Determine the Moisture Content of Douglas-fir Bark

Samples of 10 material fractions (eight bark, two wood) were equilized in two conditioning rooms designated L and H (L for low moisture content, dry bulb temperature 70°F, wet bulb depression 10°F; H for high moisture content, dry bulb temperature 90°F, wet bulb depression 4°F). The moisture content of the samples was then determined by the seven different methods. After an initial determination of moisture content, two of the three replications in this study were titrated by the Karl Fischer method. This was done to determine any residual moisture in the sample.

The third replication of the P_2O_5 technique, however, was used to help estimate the relative accuracy of the Karl Fischer method in determining the residual moisture content of the wood and bark

samples. This replication, after being dried over P_2O_5, was divided into two groups of 10 samples each. One group of samples was placed in an oven equilibrated at 65 °C for 24 hours. The other group was placed in an oven equilibrated at 105 °C for 24 hours. The samples were then reweighed and any change in weight of the samples noted. The weight differences between the equilized P_2O_5 samples and the same samples after re-equilibrating at 65 °C and 105 °C were an indication of the change in their respective residual moisture contents and served as a check on the Karl Fischer titration method.

Factorial analyses were conducted on the moisture content values obtained by (1) the different methods of moisture content determination cited above, and (2) corrected moisture content values which consisted of the moisture content values in (1) plus the residual moisture contents obtained by the Karl Fischer technique.

These analyses determined what factor or factors (extractive content, particle size, composition, or methods of determining moisture content) had a significant influence on the determination of Douglas-fir bark moisture content, and established if residual moisture (as determined by Karl Fischer titration) was present in significant amounts. These data also established that the assumptions made regarding the methods of moisture content determination were correct.

The uncorrected moisture content values obtained for the samples by the various methods were then statistically compared to a

base moisture content to determine which methods of moisture content determination were accurate in predicting bark moisture content. The base moisture content was determined to be the P_2O_5 method corrected for residual moisture by the Karl Fischer method. To further study some of the results obtained from Study I, Study II was undertaken.

Study II - Adsorption-Desorption Isotherms for Various Fractions of Douglas-fir Bark and the Effect of Sample Condition on Equilibrium Moisture Content

This study consisted of subjecting comparable samples of the 10 material fractions to gradually increasing and then gradually decreasing relative humidities in an Aminco Climate Laboratory. The samples were removed from the Aminco after being equilibrated at the last condition tested and their moisture contents were determined by the Karl Fischer method. Thus, an adsorption-desorption isotherm for each of the various fractions was obtained. Statistical tests then determined whether or not significant differences in equilibrium moisture content existed among the various fractions at each specific relative humidity. The bark fractions tested represented the same factors analyzed in Study I and were tested to determine their influence on equilibrium moisture content. The wood samples were used as reference samples. This study had three replications.

Justification of Factors Studied

The factors selected for study (extractive content, sample composition, and particle size) came from considering the anatomy of Douglas-fir bark.

Anatomy of Douglas-fir Bark

Douglas-fir bark is a variable and complex composite because of its anatomical nature. Such bark is composed of two distinct parts; namely, the inner and the outer bark (Figure 1). In the living tree the inner bark is composed of live phloem tissue. The outer bark, however, is dead and is composed of two distinct and repeatedly alternating tissues, (1) the once live inner bark or phloem, and (2) cork tissue.

The boundary between the inner and outer bark is delineated by the cork cambium (phellogen), which forms new cork cells. In the cork cambial zone there are three types of cells; namely, the phellogen, the actual cork cambial initials; the phellem, newly formed cork cells which lie towards the outer bark; and the phelloderm, the newly formed cork cells which lie toward the inner bark side of the phellogen (5, 6).

There are large amounts of extractives in bark. The specific amount of extractives present varies and they are not yet completely

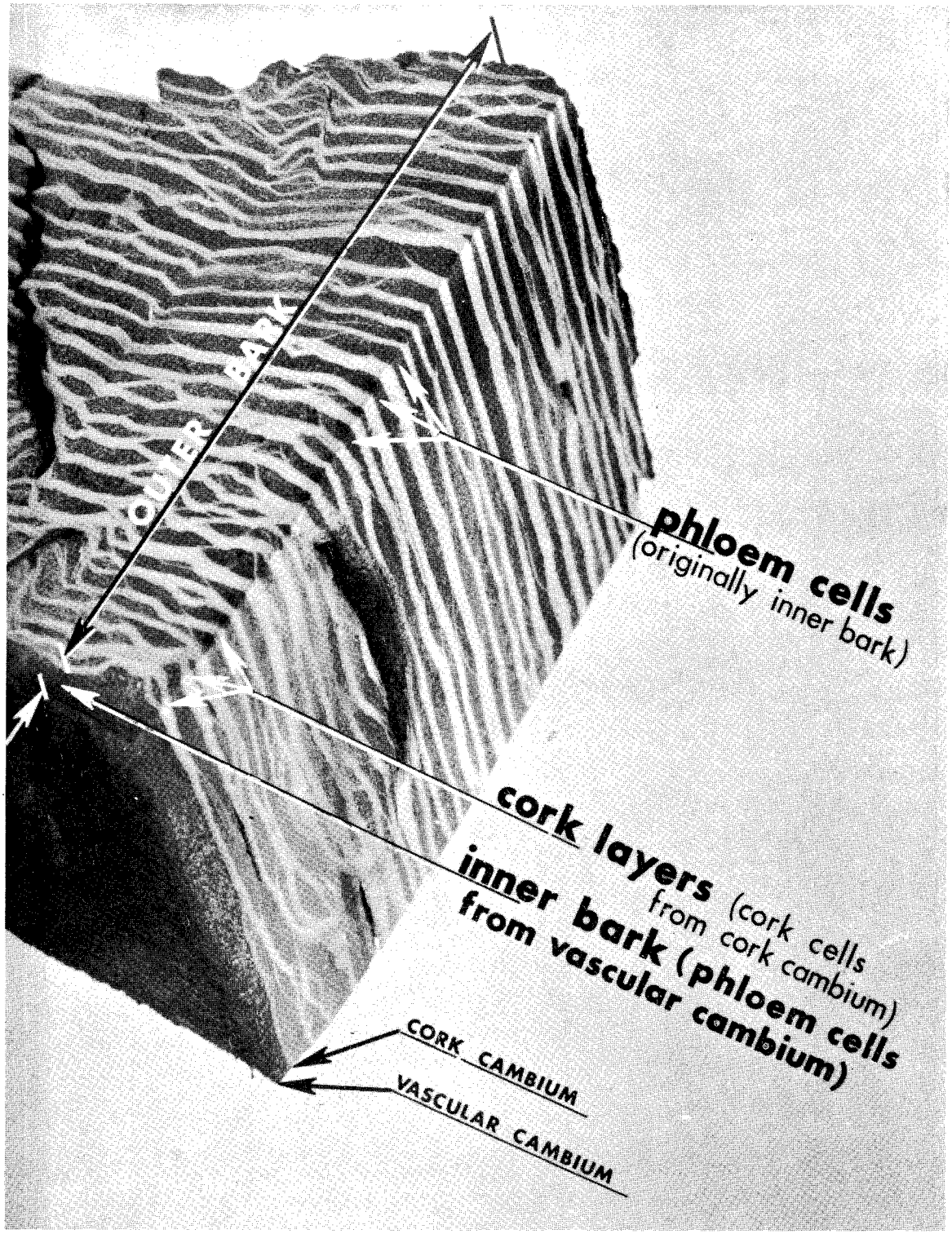

Figure 1. Photograph showing major anatomical features of Douglas-fir bark.

known. Different yields of extractives have been reported depending upon the extraction sequence, condition of sample material and material used (time of year samples collected, position of sample in tree with respect to height, etc.) (7, 10, 13). In general, more extractives are present in the cork than in the phloem tissue. The approximate amounts of extractives present are shown in Table 2, the phloem fraction being represented by bark fiber.

Table 2. Percent extractives from Douglas-fir bark components[a] (values based on oven dry weight of materials).

Solvent	Cork[b]	Fiber[c]
Hexane soluble	7.19	3.07
Benzene soluble	2.64	1.12
Ether soluble	15.62	1.38
Ethanol soluble	9.81	10.72
Hot water soluble	1.22	1.64
Total	36.48	17.93

[a]Reproduction of part of table from Hergert and Kurth (7).

[b]Sample number 9, Hergert and Kurth (7).

[c]Sample number 1b, Hergert and Kurth (7).

Douglas-fir cork cells are thin-walled, spherical (isodiametric) cells with a diameter of approximately 50-90 micrometers (6). The extractive free chemical composition of Douglas-fir cork cells can be divided into two fractions. One fraction comprising 82-85%[1] is

[1]Based on dry weight of extractive free cork.

composed of non-carbohydrate materials (saturated and unsaturated hydroxy acids, glycerols and phenolic acid materials). The other fraction which comprises approximately 15% (see footnote number 1) is carbohydrate material (13).

The phloem fraction of Douglas-fir bark is composed of several different fiber types. One type, the bast fiber, represents how greatly different the phloem fraction is from the cork fraction.

Bast fibers are thick-walled and have dimensions of approximately 50 micrometers in diameter and 600 micrometers to 1500 micrometers (1.5 mm) in length (6). The chemical composition of extractive free bast fibers closely parallels that of wood and representative values are shown in Table 3.

Table 3. Percentage analysis of bast fibers and Douglas-fir wood[a] (values based on oven dry extracted material).

	Fiber	Wood
Ash	0.60	0.17
Lignin	44.80	30.15
Holocellulose	54.58	71.40
Pentosans	8.62	10.11
Methoxy groups	3.89	4.75
Acetyl groups	2.39	0.59
Uronic acid anhydrins	4.62	2.80
Methoxy lignin	7.16	15.20

[a]From Kiefer (10).

In summary, bark is a complex material and is composed of two tissue types, cork and phloem, which are radically different in both physical appearance and chemical composition. Because of this, any method of determining moisture content in bark must be able to accommodate these differences and the variability they introduce and still produce accurate results. Bark fiber, or "fiber" in this paper, will refer to all cell types found in the moisture content samples from the phloem tissue and not necessarily to just bast fibers.

Degree of Extraction

It has been previously stated that the extractive content of bark is high and probably exhibits a strong influence on moisture content determination due to the volatilization of certain extractives. Extracted and unextracted bark should permit the evaluation of the effect of extractives on moisture content determination of Douglas-fir bark.

Size of Particles

Generally, the inability to get bark to equilize in oven-drying techniques has been attributed to high extractive contents and the inability of moisture to diffuse through the bark material rapidly, thus prolonging the time to equilibrate. Thus, two particle sizes were prepared. One size was composed mainly of single cells or fibers which would allow maximum external surface exposure and require

minimum diffusion. The other sized particles were composed mainly of fiber or cork cell bundles which might require more diffusion and cause longer drying times resulting in more time to equilibrate.

Sample Composition

Cork and fiber are radically different tissues, both in cell size and chemical composition, and because they contain widely different amounts of extractives their individual contribution to moisture content determination may differ significantly. Consequently, this factor was studied.

Selection of Levels to be Studied

Only two levels for each factor (except methods of determining moisture content, which had seven) were used primarily due to economics. The two level method of analysis helped establish evidence regarding which factor or factors tend to control or influence moisture content determination in bark. Once gross overall governing factors were found, more definitive studies could be undertaken to further explain the precise mechanisms involved. Consequently, it was decided to include more factors with fewer levels rather than examine only a few factors at a greater number of levels.

The large number of methods selected were needed to help prove the validity of the assumptions concerning the methods of moisture content determination.

In order to check the dilution effect inherent in the Karl Fischer method, all methods used to determine bark moisture content in Study I were tested at two moisture content conditions.

Inclusion of Douglas-fir Wood

Because it could not be accurately predicted how the bark would behave during this experiment, a reference material was included in both studies. This reference material, Douglas-fir wood, was treated, where applicable, the same as the bark samples, and gave a frame of reference to the experiment based on the long history of developed knowledge concerning wood moisture content determination. The only factor relevant to the wood samples was particle size. The factor of extraction was not applicable because Douglas-fir wood usually contains such a small amount of extractives that their removal would not result in any substantially different results. The factor of sample composition was not applicable because Douglas-fir wood can be considered homogeneous in regard to cell composition. Therefore, only two wood sample fractions based on particle size were generated.

The factors, with their respective levels, are shown in Table 4. The material fractions needed to represent the factors analyzed are shown in Table 5.

Table 4. Levels of factors analyzed in Study I and Study II.

Factors and levels	Bark	Wood
Factor I - Degree of extraction	X	
level 1--extracted		
level 2--unextracted		
Factor II - Sample composition	X	
level 1--high ratio of cork to phloem (cork fraction)		
level 2--low ratio of cork to phloem (fiber fraction)		
Factor III - Size of sample particles	X	X
level 1-- $\leq$ 1 mm (small particle size)		
level 2-- $\geq$ 2 mm (large particle size)		
Factor IV[a] - Methods of determining moisture content	X	X
level 1--oven-dry at 65°C		
level 2--oven-dry at 85°C		
level 3--oven-dry at 105°C		
level 4--oven-dry at 125°C		
level 5--Cenco Moisture Meter		
level 6--Phosphorus pentoxide (P_2O_5) desiccant		
level 7--Karl Fischer Titration		

[a]Pertains only to Study I.

Table 5. Material fractions generated for Study I and Study II.

		Bark	
1.	Extracted	Cork	Large particle size
2.	Extracted	Cork	Small particle size
3.	Extracted	Fiber	Large particle size
4.	Extracted	Fiber	Small particle size
5.	Unextracted	Cork	Large particle size
6.	Unextracted	Cork	Small particle size
7.	Unextracted	Fiber	Large particle size
8.	Unextracted	Fiber	Small particle size
		Wood	
9.	Wood		Large particle size
10.	Wood		Small particle size

SAMPLE PREPARATION

Listed below are the five steps in preparation of bark and wood material used in Study I and Study II. These were:

1. Collection of sample material
2. Processing into desired conditions
3. Equilization of processed material
4. Randomization into individual samples
5. Sample composition study

Collection of Sample Material

Bark

Criteria for selecting bark material for this study were: (1) no pond stored material should be used, thus eliminating the possibility of leaching out any water soluble extractives from the sample material, and (2) the bark should be representative of the population as a whole, thereby necessitating collection from old-growth and young-growth trees.

Approximately equal volumes of peeler log and saw log bark were taken. No specific information on time of cutting, length of storage, etc., was collected. However, all logs came from the Cascade Mountains.

The bark samples collected varied in length from one to four

feet, from one to two feet wide, and contained both inner and outer bark. At the time of collection the bark was labeled and sealed in plastic garbage can liners. At the laboratory, the bark samples were stored in a cold room (3°C) until used for further study.

Wood

A random sample of approximately 14 pounds (green weight basis) of Douglas-fir chips was collected from a chip storage silo. These wood chips were placed in plastic bags, sealed, labeled, and stored in a cold room (3°C) until needed for further study.

Processing of Sample Material

Bark

Shortly after collection, the bark material was processed into what would eventually be the various fractions needed for the study. The bark material was processed through sequences of sawing, chipping, disc refining, Wiley milling, screening, and extracting (detailed information on processing can be found in Appendix A). Once the bark material had been processed, the various fractions were placed on compartmentalized trays in the conditioning rooms.

Wood

The wood was processed in a manner similar to that of the bark

material (detailed information on wood processing can be found in Appendix B). Once processed, the wood was placed in the conditioning rooms in two of the compartments of the same tray that contained the bark material.

Equilibration of Processed Material

Representative samples of bark and wood in each of the moisture conditioning rooms were used to check for undue moisture content variation due to the different position the fractions occupied on the trays in the conditioning rooms (local variation). These wood samples when equilibrated were removed and oven-dried at 105 ^{o}C for 24 hours. The equilibrium moisture content of the wood was calculated and the variation among samples with respect to location noted. It was decided that the moisture content variation caused by sample location was not unduly large.

Randomization into Individual Samples

Once the samples were equilized in the conditioning rooms, the material was randomized into individual samples for Study I (detailed information can be found in Appendix C). These individual samples were contained in labeled plastic sandwich bags which were hung on a rack. The bags were left open so that the samples would remain exposed to the conditioning room atmosphere to prevent unwanted

equilibrium moisture content changes. The samples remained on the rack 4 weeks before any were removed for Study I. During these 4 weeks, sample composition data were taken.

Sample Composition Study

The composition study was undertaken to determine the approximate purity or percent of cork and fiber material in the two bark material groups represented by cork- and fiber-rich material. To determine the approximate composition of the samples, a sampling grid method, much like that used in forest photogrametry, was used (detailed procedures found in Appendix D). The average values obtained from this study are shown in Table 6. Representative photographs of the material generated can be found in Figure 2.

Table 6. Percent of cork and fiber in cork- and fiber-rich large sized Douglas-fir bark particles.

	Percent cork	Percent fiber
Cork-rich material (cork)	63.61	36.39
Fiber-rich material (fiber)	34.17	65.83

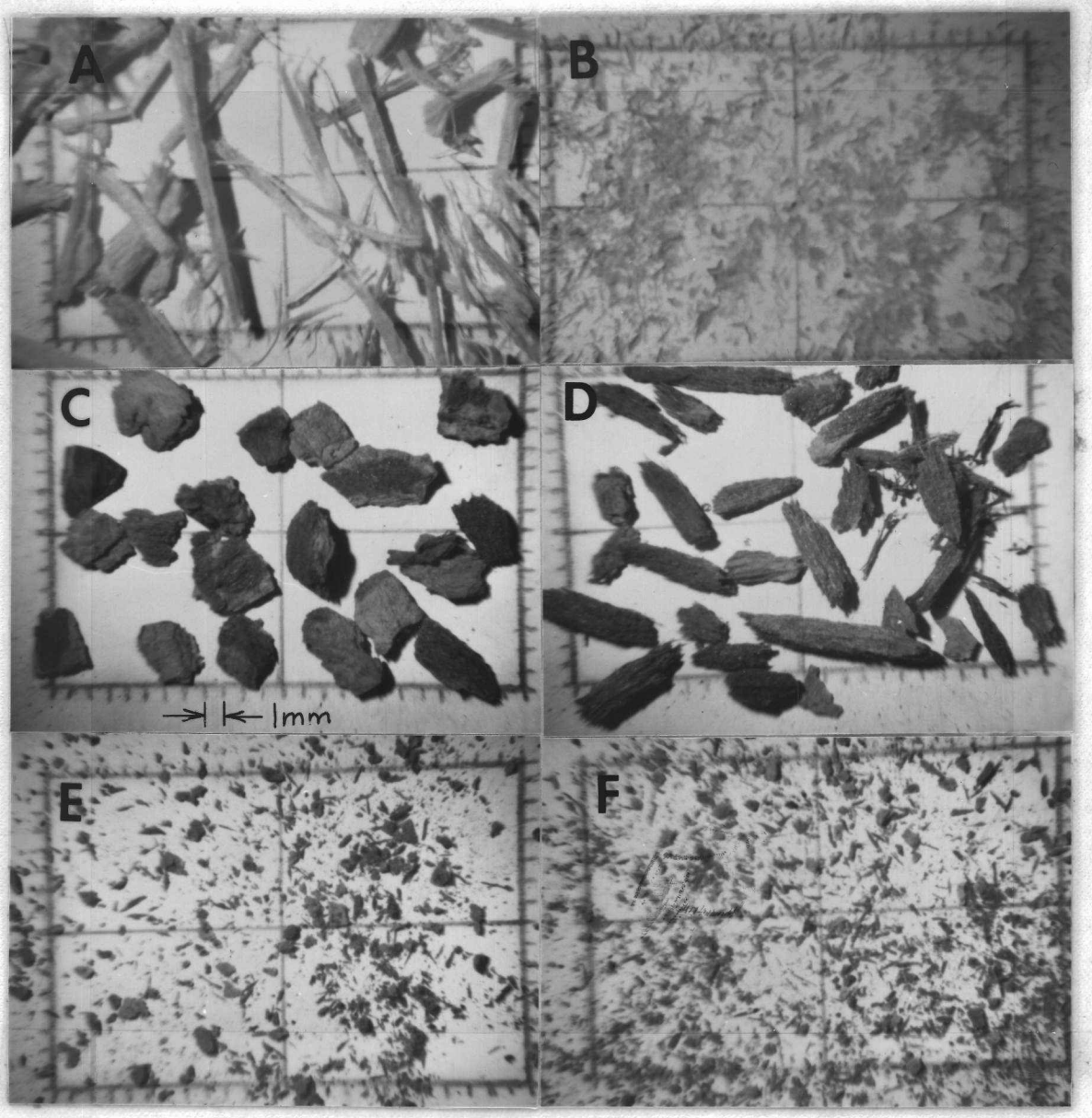

Figure 2. Photographs of representative samples. (Magnification of all photographs is approximately 2X.)

a) Douglas-fir wood, large particle size
b) Douglas-fir wood, small particle size
c) Douglas-fir cork, large particle size
d) Douglas-fir bark fiber, large particle size
e) Douglas-fir bark, cork-rich, small particle size
f) Douglas-fir bark, fiber-rich, small particle size

LABORATORY PROCEDURE

Study I - Evaluation of Different Methods Used to Determine Moisture Content of Douglas-fir Bark

Equipment shortages caused by the large number of samples in each replication (140 samples) prevented all samples in a replication from being removed simultaneously from the conditioning rooms. Therefore, the oven-drying methods were randomized within a replication to determine the order in which samples were removed from the conditioning rooms. The samples for one method of determining moisture content were removed from both conditioning rooms and their moisture contents determined. Once a method was completed the samples for the next method of determining moisture content were removed and their moisture contents determined. This technique was continued according to the procedure presented in Table 7 until all replicates were measured.

Note that Table 7 shows there was a malfunction in the conditioning rooms between replication 1 and replications 2 and 3. This malfunction caused the equilibrium moisture content of the samples in both rooms to change for the remainder of the study (replicates 2 and 3). Although this event was unfortunate, it happened at a most convenient point because all of replication 1 had been removed but none of replication 2 had been studied. The full implication of this situation will become evident in the analysis of data.

Table 7. Random order in which samples were removed for the various methods of determining moisture content.

	Order of sample removal[a]		
Replication 1	1	85°C	
	2	65°C	Simultaneous removal of samples for Cenco, P_2O_5, Karl Fischer titration
	3	105°C	
	4	125°C	
Two-week delay caused by malfunction of conditioning rooms.			
Replication 2	5	85°C	
	6	105°C	Simultaneous removal of samples for P_2O_5, Karl Fischer titration, Cenco
	7	65°C	
	8	125°C	
Replication 3	9	105°C	
	10	125°C	Simultaneous removal of samples for Karl Fischer titration, Cenco, P_2O_5
	11	65°C	
	12	85°C	

[a]For both conditioning rooms

Once the samples had re-equilibrated after the malfunction, the study was continued (detailed information of the procedure used for the methods of Karl Fischer titration, oven-drying, P_2O_5, and Cenco can be found in Appendices E, F, G, and H, respectively).

Study II - Adsorption-Desorption Isotherms for Various Fractions of Douglas-fir Bark and the Effect of Sample Condition on Equilibrium Moisture Content

The remaining material from Study I was used for Study II. All large particle bark fractions were further purified by hand sorting. This hand sorting process consisted of dumping a bark fraction on a sheet of white paper and separating the cork particles from the phloem particles with a spatula. This was done so that adsorption-desorption isotherms for the large particles would more realistically represent pure cork and pure fiber and would not be the product of a cork-fiber interaction. The small particles were not separated, therefore their sorption isotherms were the result of a certain percentage of cork influence and a certain percentage of fiber influence.

Once the bark fractions were separated, three replicates of approximately 2-gram samples were weighed into tared aluminum weighing pans. These pans containing the sample material were then dried over P_2O_5 for approximately 11 days. The samples were weighed periodically and when no more weight was lost (weighings 2

days apart) the samples were considered "dry." The samples were then taken from the desiccator and placed in an Aminco Climate Laboratory which was used for this part of the study. A Mettler pan balance (Model no. 160) was placed inside the Aminco and used to weigh the samples as equilibrium moisture content conditions changed. The individual samples were randomly placed on a rack next to the balance in a gridlike pattern (6 x 5). The Aminco was sealed and the samples subjected to the first equilibrium moisture content condition of the experiment (relative humidities of 20, 23, 30, 63, 79, 95, 79, 63, 30, 23, and 20% were used for the adsorption and desorption conditions in this experiment). The methods used to determine the relative humidity values are given in Appendix I. To achieve these relative humidities the dry bulb temperature was held constant (35^{o}C) and only the wet bulb depression changed. The samples were weighed when they reached equilibrium. The time required for the samples to reach equilibrium when a new relative humidity condition was introduced was approximately 24 hours (Figure 3).

Weighing of the samples was accomplished without changing the conditions in the Aminco chamber by the use of a glove-box like constructed door. As the samples were weighed, the weights were recorded by voice on a tape recorder; a procedure which allowed the samples to be weighed quickly. The conditions in the Aminco chamber were not changed after the weighing until the tape was replayed and the weights of the samples properly recorded.

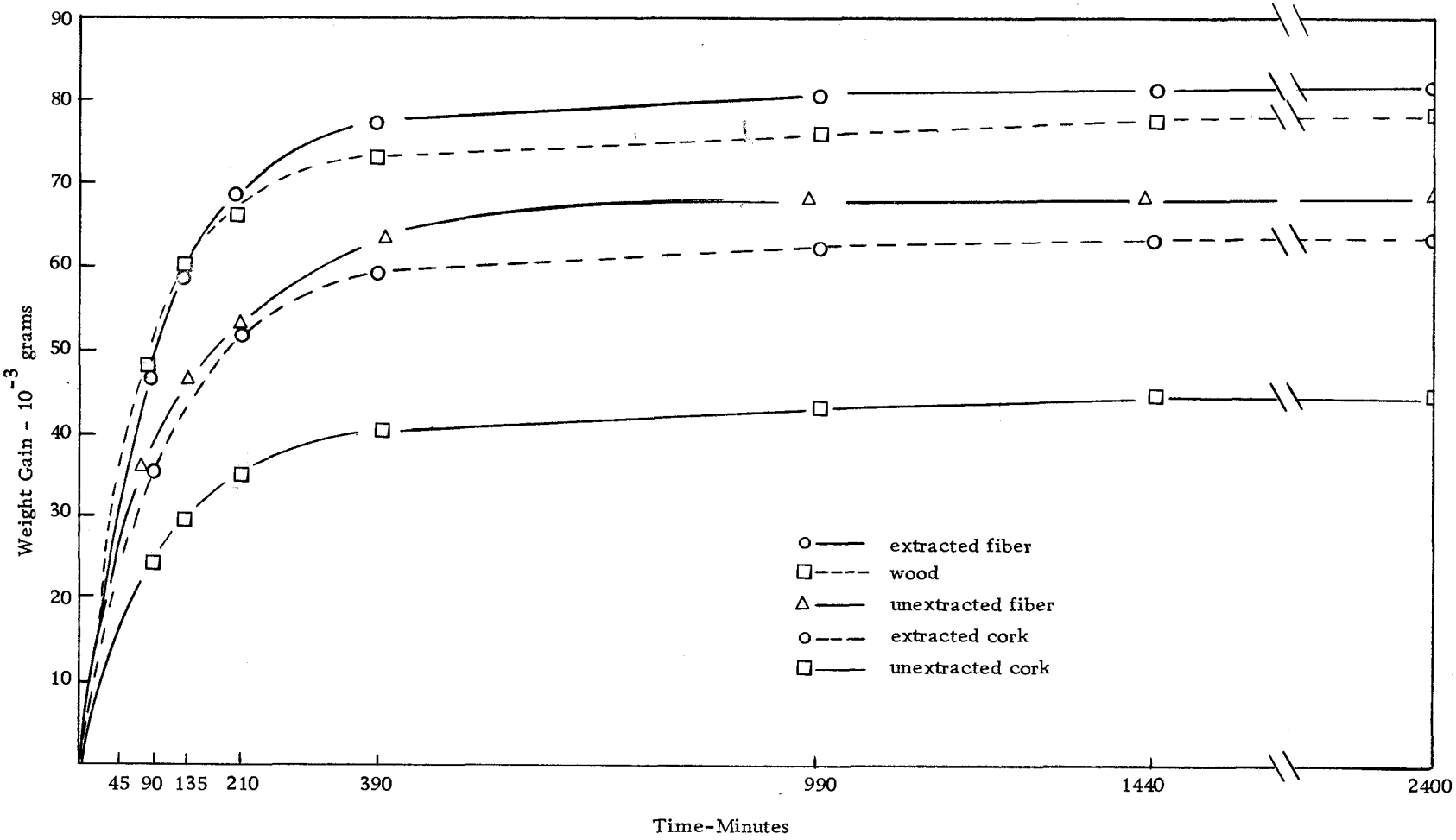

Figure 3. Weight Gain with Time for Douglas-fir Wood and Bark Fractions when Relative Humidity was Changed from 63% to 79%.

Once the weights were recorded, the wet bulb temperature was altered to produce the next relative humidity. This sequence of events, weighing samples and then changing the relative humidity conditions, was repeated for all the relative humidities used in this study. Once the weights of the samples at the final relative humidity condition (20%) were recorded, the samples were prepared for moisture content determination by the Karl Fischer titration method (the technique used for preparation and titration of the samples is described in Appendix E).

From the moisture content data collected by titration (green weight of sample and weight of water in sample at the last condition) and similar data collected during the experiment (green weight of samples at each condition), it was possible to construct an adsorption-desorption isotherm for each of the samples.

The equations used for moisture content calculation at each relative humidity were:

$$\text{o. d. wt or dry wt} = \text{green sample wt at last condition} - \text{wt water determined by Karl Fischer titration}$$

$$\text{M. C.}_{(RH)} = \left(\frac{\text{green sample wt}_{RH} - \text{o. d. wt}}{\text{o. d. wt}} \right) \times 100$$

RESULTS AND DISCUSSION

Study I. Evaluation of Different Methods Used to Determine Moisture Content of Douglas-fir Bark

Factorial Analysis of Initial Moisture Content Values

The data obtained from this study was analyzed at the Oregon State University Computer Center using standard statistical programs for factorial analysis (6, 30). The bark data were considered as a five factor experiment (extractive content, sample composition, particle size, methods of moisture content determination, and replications). The wood data were considered as a three factor experiment (particle size, methods of moisture content determination, and replications) (see analysis of variance tables 4, 5, 6, and 7, Appendix J).

The replication factor was found to be significant in the wood and bark data ($P \leq .01$), with significant differences existing between replication 1 and replications 2 and 3. An explanation for this fact follows.

It was stated earlier that the relative humidity conditions in the conditioning rooms were inadvertently changed during the experiment. The L room was accidently saturated with steam for approximately 24 hours (higher dry bulb temperature, lower wet bulb depression). The H room

was slightly changed (higher dry bulb temperature, slightly greater wet bulb depression) by high outside temperatures. When these changes in relative humidity conditions were corrected, the moisture contents of the samples did not return to the same moisture contents as before the changes occurred. The difference in moisture content of the samples was approximately equal to the hysteresis loop differences of the various fractions at their respective relative humidities. Therefore, significant differences in equilibrium moisture contents between the replications were expected and could be accounted for.

Partitioning of the moisture content data with respect to the time when the changes in the conditioning rooms occurred yields the same statistical results that will be presented. The only difference is that in the partitioned data the replication factor would be non-significant. Because of the simplicity and reduced space involved, the unpartitioned data were used in this presentation.

All replication interactions were pooled for a more reliable estimate of error. This was done to support the objectives of this study set forth earlier and not as a result of the inadvertent change in conditioning room relative humidities. The pooling of the replication interaction terms was acceptable since no replication interactions were found to be significant.

Significant differences in moisture content were consistently found in the bark data for the factors of extractive content, sample

composition, and methods of moisture content determination ($P \leq .01$). Significant differences in the moisture contents of extracted vs. unextracted material and fiber- vs. cork-rich material were expected due to Spalt's work (21) and the chemical composition of the bark components reported by Hergert and Kurth (7). Significant differences among the methods of moisture content determination for bark were also expected from the assumptions made concerning the errors inherent in the various methods.

The factor of particle size was statistically significant in the bark samples from only the H conditioning room, indicating a reliance on relative humidity. The cause of this factor being significant probably lies in the processing of the sample material. The small particle sized samples were generated from the large particle sized samples. The composition of the small sized samples could have been altered by the additional milling. Moderate differences in composition could create a situation such that only at high relative humidities would significant differences be found. Study II will help clarify and substantiate the above.

The most important result of these data was the lack of significant differences among the interaction terms (methods x extractive content, methods x sample size, methods x particle size, etc.). No first order interactions were found to be significant, thus the factors of extractive content, sample composition and particle size did not

influence the methods of moisture content determination (differences among the methods of determining bark moisture content were independent of extractive content, sample composition, and particle size).

The only factor found statistically significant for the wood samples was methods of moisture content determination. Table 8 shows the moisture content means from the data for the methods of moisture content determination, ranked into groups which have non-significant differences. The calculation of all least significant differences (LSD) were based on mean square error terms from the analysis of variance tables found in Appendix J.

Factorial Analysis of Moisture Content Values Corrected for Residual Moisture

Another analysis of variance using new corrected moisture content values obtained from the correction for residual moisture showed that no factors were changed in statistical significance (Appendix Tables 8, 9, 10, and 11 in Appendix J).

The most striking changes occurred in the table (Table 9) which represents the means of the methods of moisture content determination from the new data ranked into non-significantly different groups. In comparing the uncorrected data found in Table 8 and the corrected data in Table 9, the following should be noted regarding the wood data:

Table 8. Moisture content means from the factorial analysis ranked into non-significantly different groups. Methods within a column or group for a conditioning room are non-significantly different. However, some methods between columns or groups will exhibit significant differences.

Material and conditioning room	Groups									
	Group 1		Group 2		Group 3		Group 4		Group 5	
Bark										
Room L[a]	65°	12.49	P_2O_5	13.60	Cenco	14.89	105°	15.57	125°	16.45
			Karl Fischer titration	13.69						
			85°	13.83						
Room H[b]	Karl Fischer titration	20.03	85°	21.06	105°	21.85	125°	23.30		
	65°	20.10			Cenco	21.87				
	P_2O_5	20.35								
Wood										
Room L[c]	65°	13.44	Karl Fischer titration	13.73	Cenco	14.91	105°	15.77		
	Karl Fischer titration	13.73	85°	14.18	105°	15.77	125°	16.72		
	85°	14.18	P_2O_5	14.28						
	P_2O_5	14.28	Cenco	14.91						
Room H[d]	Karl Fischer titration	20.97	P_2O_5	21.60	85°	22.39				
	P_2O_5	21.60	65°	21.75	105°	22.95				
	65°	21.75	85°	22.39	125°	23.41				
					Cenco	23.48				

[a] Least significant difference = .54

[b] Least significant difference = .68

[c] Least significant difference = 1.45

[d] Least significant difference = 1.29

Table 9. Moisture content means from the factorial analysis ranked into non-significantly different groups (values corrected for residual moisture). Methods within a column or group for a conditioning room are non-significantly different. However, some methods between columns or groups will exhibit significant differences.

Material and conditioning room	Groups									
	Group 1		Group 2		Group 3		Group 4		Group 5	
Bark										
Room L[a]	Karl Fischer titration	13.69	65°	14.29	65°	14.29	Cenco	14.89	105°	15.96
					P_2O_5	14.36			125°	16.45
					85°	14.80				
Room H[b]	Karl Fischer titration	20.03	P_2O_5	21.29	Cenco	21.87	125°	23.19		
			Cenco	21.87	65°	21.95				
			65°	21.95	85°	22.14				
					105°	22.21				
Wood										
Room L[c]	Karl Fischer titration	13.73	65°	14.77						
	65°	14.77	Cenco	14.91						
	Cenco	14.91	85°	14.95						
	85°	14.95	P_2O_5	14.98						
	P_2O_5	14.98	105°	15.90						
			125°	16.22						
Room H[d]	Karl Fischer titration	20.97	P_2O_5	22.18						
	P_2O_5	22.18	105°	23.09						
			65°	23.16						
			85°	23.20						
			125°	23.41						
			Cenco	23.48						

[a] Least significant difference = .54 [b] Least significant difference = .68 [c] Least significant difference = 1.49 [d] Least significant difference = 1.34

(1) the large amount of grouping into non-significantly different groups for the methods of moisture content determination, and (2) the methods of moisture content determination fall into place according to the assumptions made concerning the various methods if residual moisture is removed as a source of error (Table 1). The P_2O_5 values are in the center of the moisture content values while the heat method values are high (+) and the Karl Fischer values are low (-).

For the bark data shown in Tables 8 and 9 the following should be noted: (1) the methods of moisture content determination are still dispersed for bark material, and (2) the stated assumptions concerning the various methods of moisture content determination are still supported (Table 1). The P_2O_5 values are in the middle, the methods of moisture content determination using heat have high (+) values (statistically high) while the Karl Fischer technique values are low (-) (statistically low).

From these results it was concluded that the major differences among heat methods of moisture content determination in wood were due to differences in the equilibrium moisture contents caused by the different temperatures. The inclusion of residual moisture content values due to equilibrium moisture content differences in the heat methods for bark samples explained some of the variation observed among the methods, but significant differences still existed which were probably caused by volatilization of some chemical components. The

components volatilized were not necessarily extractives since the extractive content did not influence the methods of moisture content determination. The most important conclusion from these data was that the stated assumptions concerning the inherent errors in the methods of moisture content determination seem to be correct. Further evidence that the assumptions made concerning the Karl Fischer technique were correct came from the following considerations.

1. The residual moisture contents for the samples in the various oven-drying methods found by titration were in agreement with what was expected according to sorption theory. Figure 4 shows the average residual moisture found for all bark fractions at the various oven-drying temperatures. This figure shows that the equilibrium moisture content of the samples was lowered with increasing temperature.

2. Confidence limits were calculated for the residual moisture content data determined by Karl Fischer titration for the following methods--oven-drying at 65 ^{o}C and 105 ^{o}C, and P_2O_5.

As previously stated, one set of P_2O_5 samples (total of 20 samples), after being equilibrated and their moisture contents determined, were divided into two sample groups. One group was placed in an oven equilized at 65 ^{o}C and the other set of samples was placed in an oven equilized at 105 ^{o}C. The weight gain or loss of these samples was then recorded as an indication of how accurate the Karl

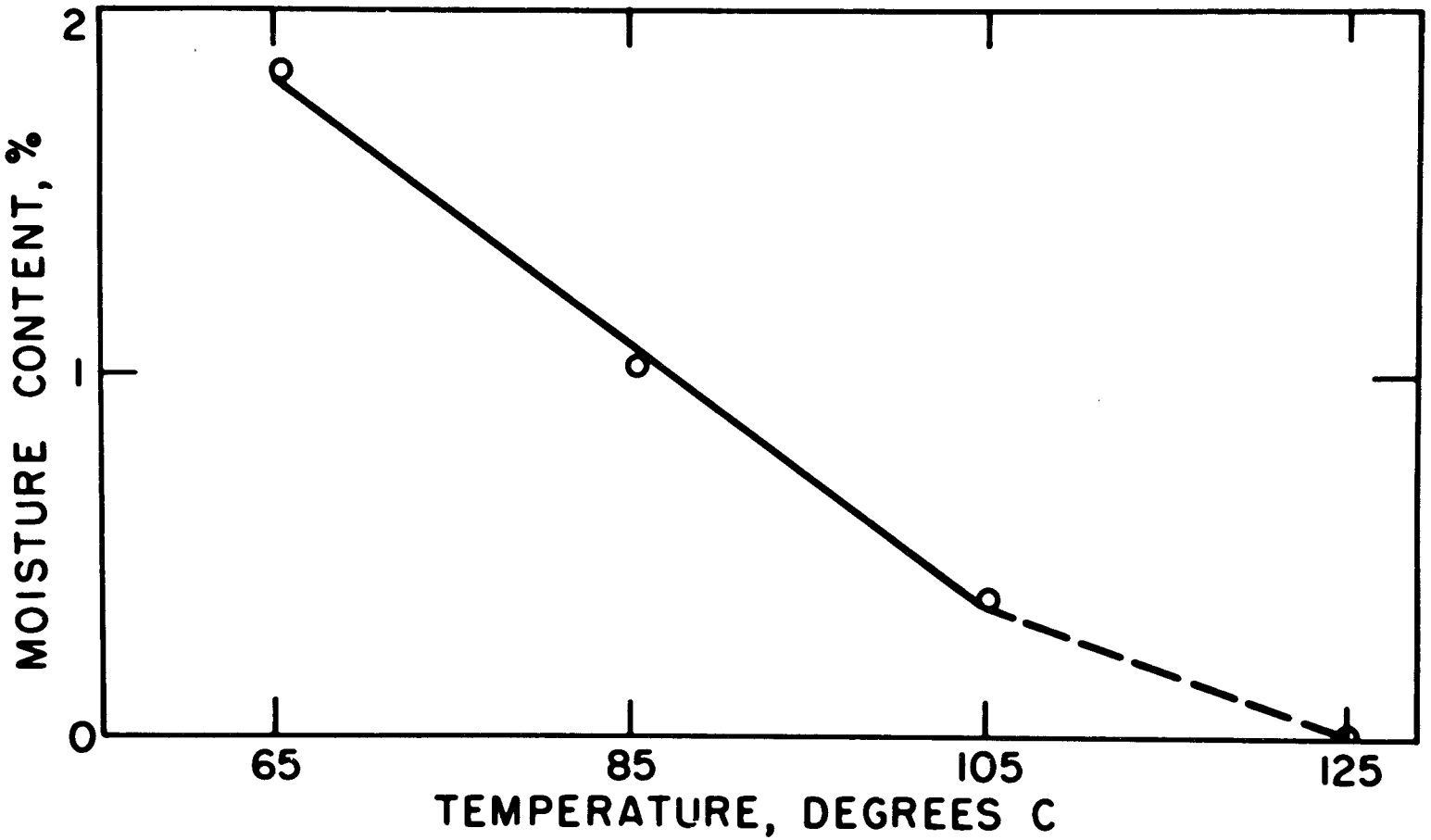

Figure 4. Average equilibrium moisture content values (by Karl Fischer titration) for Douglas-fir bark samples oven-dried at various temperatures.

Fischer technique was in predicting residual moisture content.

The Karl Fischer method predicted that the samples, equilibrated in P_2O_5 and then re-equilibrated in an oven at 65°C, would increase in moisture content an average of .72-1.20%. The average actual change was .74%. The Karl Fischer method predicted that the samples, equilibrated in P_2O_5 and then re-equilibrated in an oven at 105°C would decrease in moisture content an average of .32-.67%. The average actual change was a decrease of 1.42%. The change in equilibrium moisture content from P_2O_5 to the oven-drying at 105°C was more than that predicted by approximately .75-1.10%. This discrepancy could be attributed to some volatilization of extractives which would lessen the amount of moisture gain from P_2O_5 to oven-drying at 65°C, and would increase the recorded amount of moisture lost from P_2O_5 to oven-drying at 105°C.

3. If the moisture content values determined by the P_2O_5 method corrected for residual moisture values are used as a base, the deviations of the Karl Fischer method from this base moisture content show that with increasing moisture content the amount of deviation connected with the Karl Fischer method increased. The deviation from a base moisture content of 14.63% was -.67% and from 21.29% was -1.26%.

From the above considerations it was concluded that the Karl Fischer method was an accurate method of determining low moisture

contents in bark samples. However, the accuracy of this method, if sample size was kept constant, decreased with increasing moisture content.

Thus, from the assumptions which were considered to be correct, the most accurate way to determine bark moisture content was by drying over the desiccant P_2O_5 until the samples equilibrate then titrating the samples for residual moisture content by the Karl Fischer method (base moisture content). This sequence to determine bark moisture content is time consuming and rather expensive if large numbers of samples are used. To help select a more practical method of determining bark moisture content, the values obtained by this sequence (P_2O_5 + Karl Fischer) were compared to the values obtained by the various methods used to determine which methods were not significantly different or were within current ASTM standards of $\pm$ 1%.

Comparison to Base Moisture Content Values

Figures 5, 6, 7, and 8 are comparisons of the moisture content values determined by different methods with the base moisture content values. It should be noticed that for bark, three methods of moisture content determination were consistently within ASTM standards. These methods were oven-drying at 85 °C, Cenco, and P_2O_5. However, the confidence limits based on the study were only .54% for the

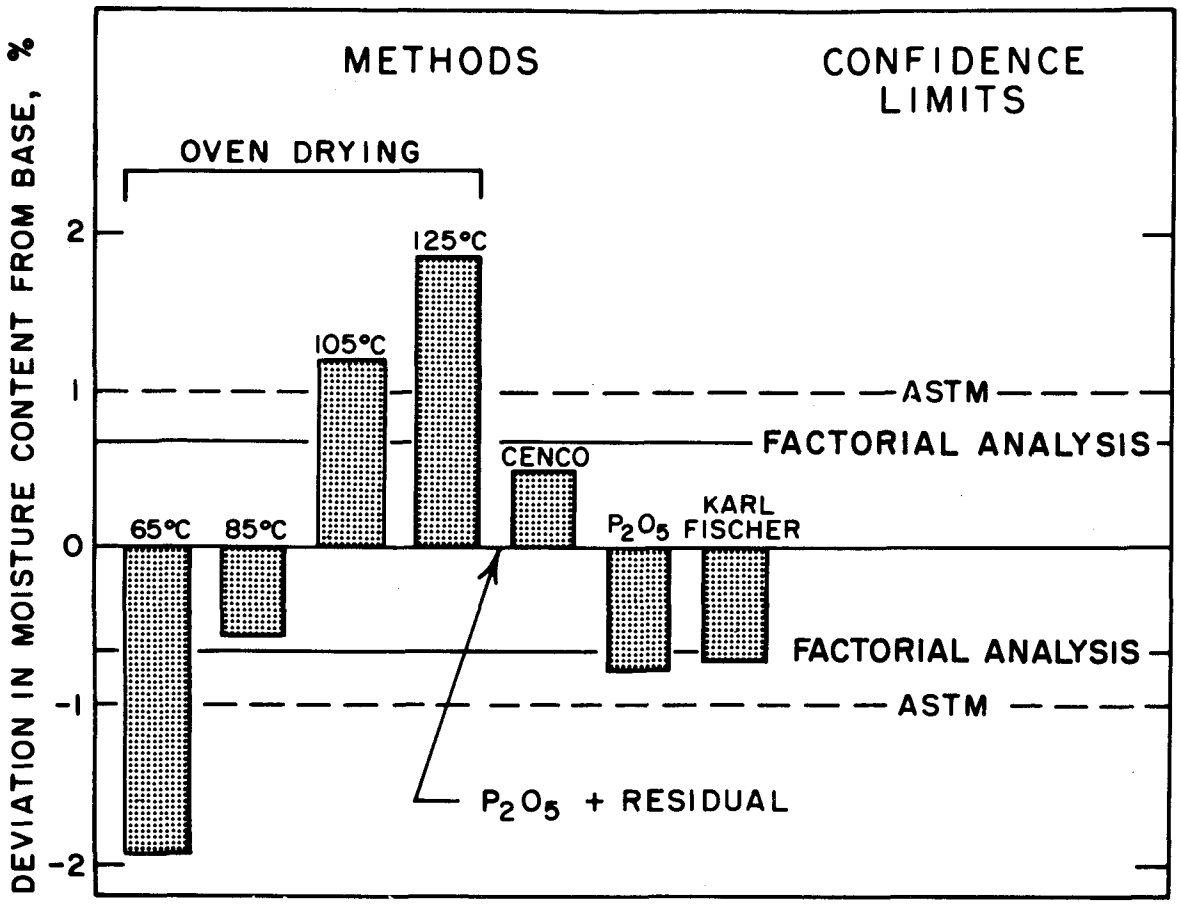

Figure 5. Deviation of various methods of moisture content determination from a base moisture content value (determined by the P_2O_5 method corrected for residual moisture) for Douglas-fir bark samples conditioned in room L (dry bulb temperature 70°F, wet bulb depression 10°F).

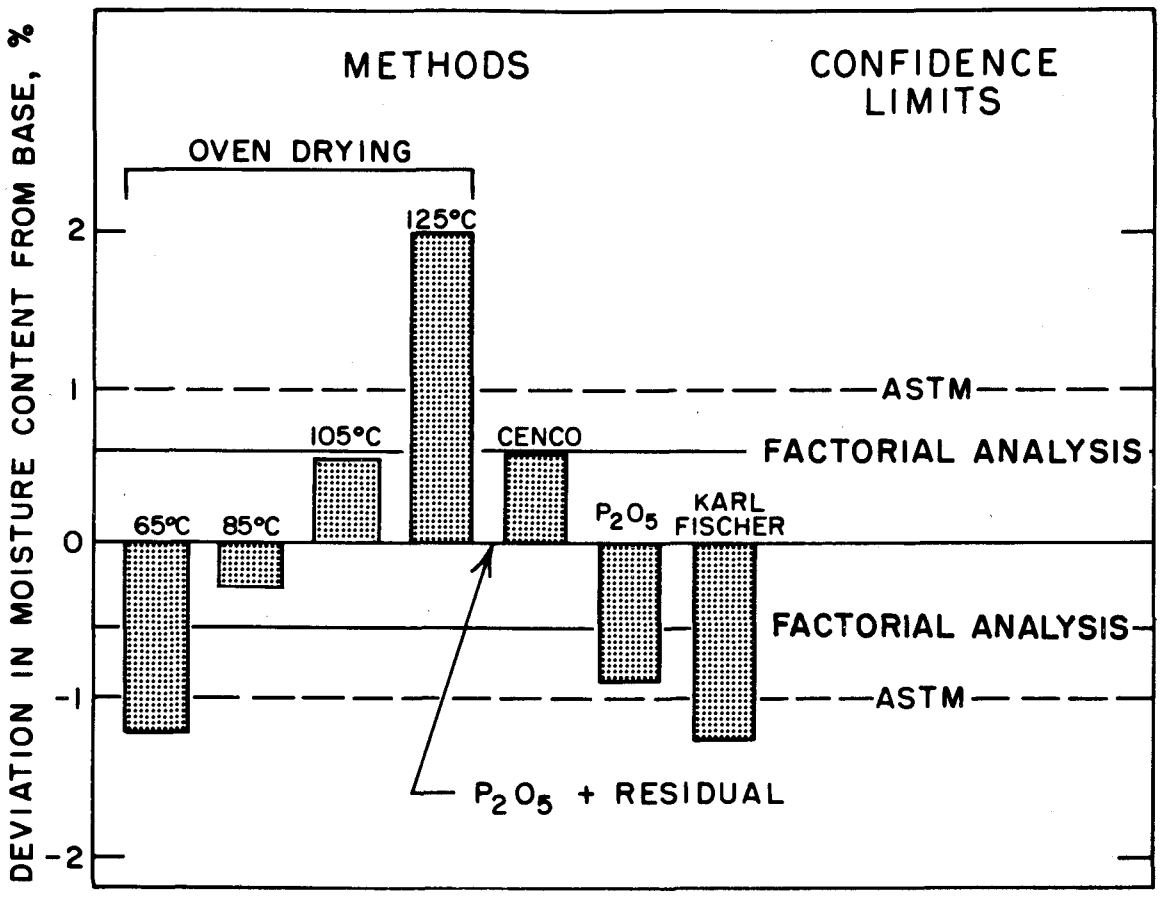

Figure 6. Deviation of various methods of moisture content determination from a base moisture content value (determined by the P_2O_5 method corrected for residual moisture) for Douglas-fir bark samples conditioned in room H (dry bulb temperature 90 ^{o}F, wet bulb depression 4 ^{o}F).

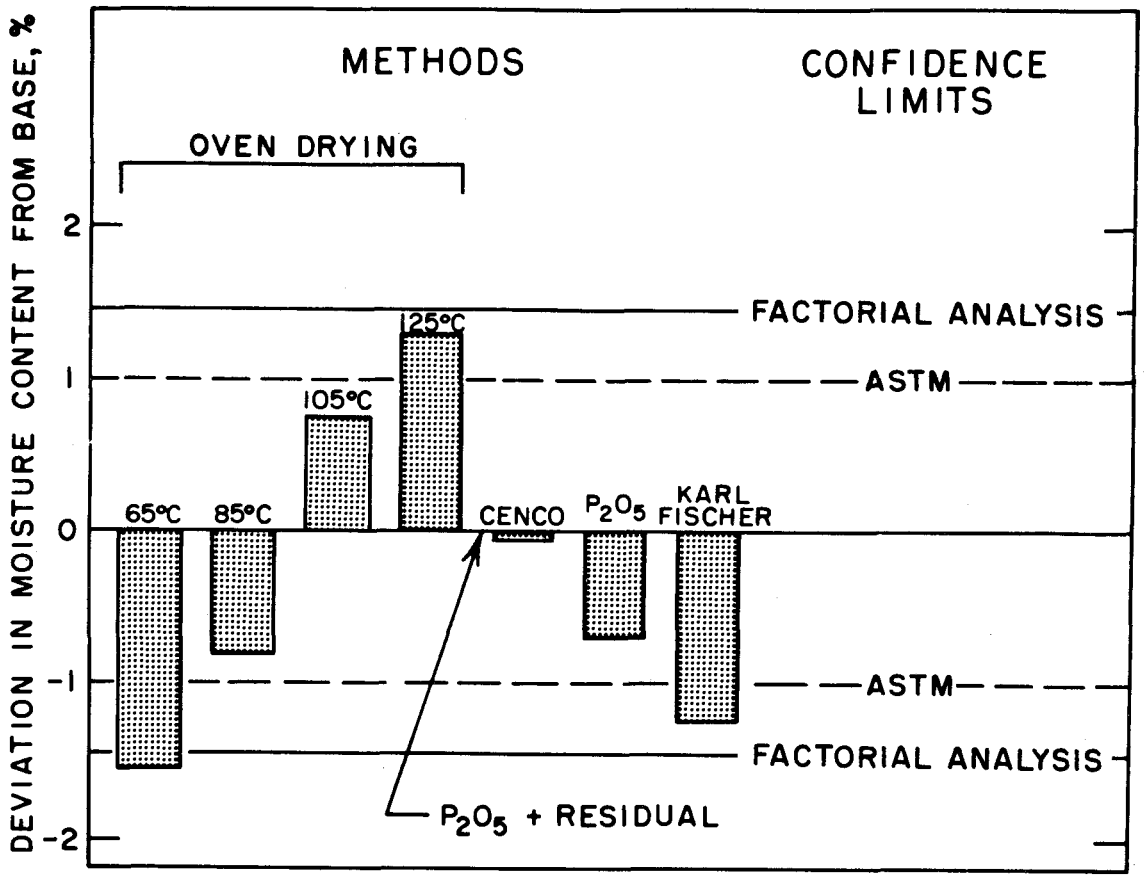

Figure 7. Deviation of various methods of moisture content determination from a base moisture content value (determined by the P_2O_5 method corrected for residual moisture) for Douglas-fir wood samples conditioned in room L (dry bulb temperature 70 °F, wet bulb depression 10 °F).

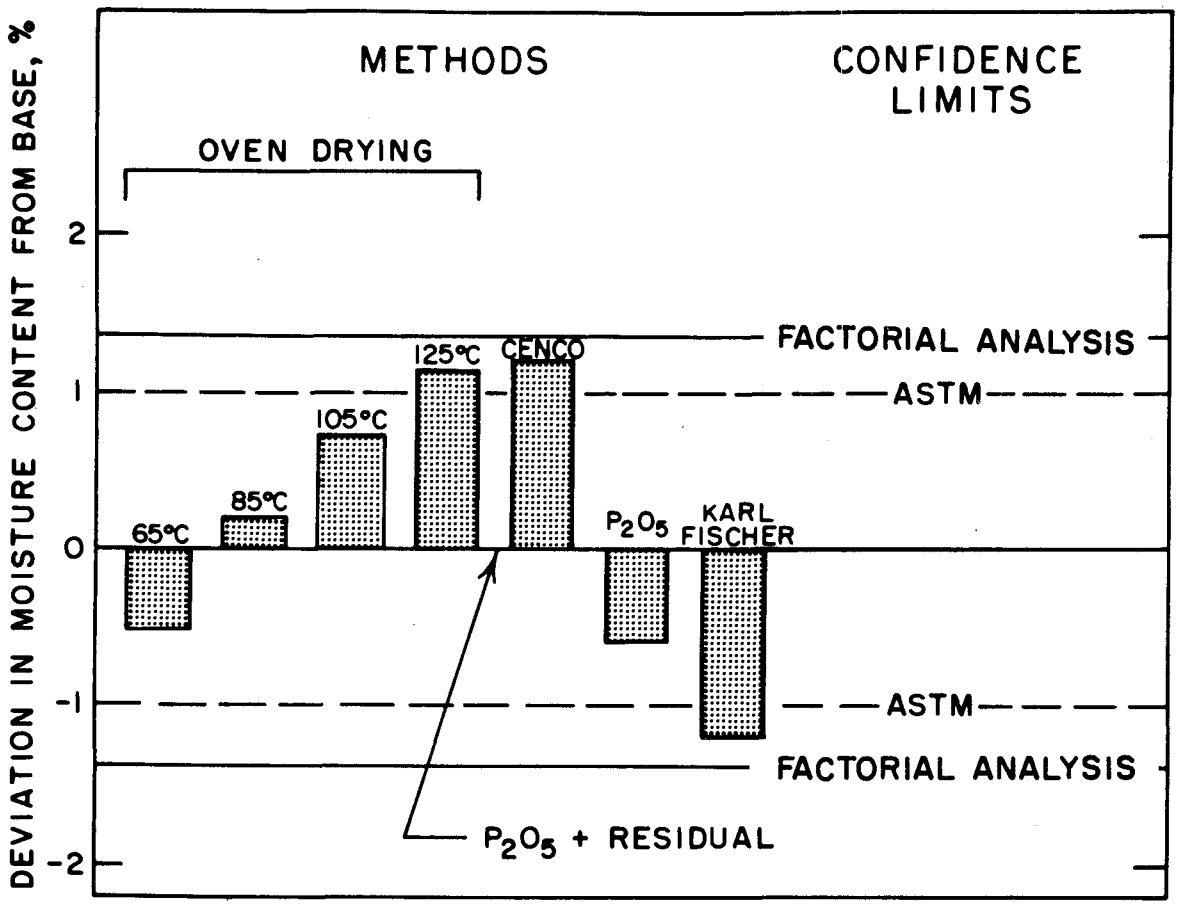

Figure 8. Deviation of various methods of moisture content determination from a base moisture content value (determined by the P_2O_5 method corrected for residual moisture) for Douglas-fir wood samples conditioned in room H (dry bulb temperature 90°F, wet bulb depression 4°F).

L room and .68% for the H room. Only two methods, namely, oven-drying at 85°C and Cenco, were consistently within these limits. These two methods appear to best balance their inherent errors to give statistically accurate moisture content results.

Three methods of moisture content determination were consistently within the ASTM confidence limits (± 1%) for wood. These were oven-drying at 85°C and 105°C and P_2O_5. It was interesting to see that the standard method of determining moisture content in wood was within the ASTM confidence limits. If the confidence limits derived from the study were used, both the Karl Fischer and Cenco methods in addition to the three methods already mentioned were within these confidence limits.

To further study the significant differences in moisture content found for the factors of extractive content and sample composition and particle size, Study II was undertaken.

Study II. Adsorption-Desorption Isotherms for Various Fractions of Douglas-fir Bark and the Effect of Sample Condition on Equilibrium Moisture Content

The data collected from this study are summarized in Table 10. The charts of these data for the large particle sized fractions are shown in Figures 9 and 10. These data show that the factors of sample composition (cork vs. fiber) and extractive content strongly influence

Table 10. Equilibrium moisture content values for the various fractions of Douglas-fir bark and wood at different relative humidities.

Material fractions	P_2O_5	Relative humidity conditions (%)										
		20	23	30	63	79	95	79	63	30	23	20
Wood small	.60[a]	4.14	4.88	5.97	10.41	14.65	21.97	16.49	12.01	7.89	6.02	5.01
Wood large	.57	4.13	4.76	5.93	10.32	14.68	21.61	16.81	11.93	7.76	5.90	4.84
Unextracted fiber large	.61	4.51	5.15	6.31	10.50	14.31	20.10	16.13	12.19	8.41	6.35	5.68
Extracted fiber large	.53	5.34	6.09	7.26	12.12	16.66	24.04	19.13	14.15	9.51	7.52	6.35
Unextracted cork large	1.02	3.12	3.66	4.63	7.56	9.89	13.66	10.77	8.41	6.05	4.86	4.17
Extracted cork large	.75	4.10	4.61	5.51	9.26	12.67	17.95	14.35	10.70	7.30	5.81	4.87
Unextracted fiber small	.57	4.56	5.27	6.40	10.54	14.13	19.89	15.85	12.11	8.45	6.78	5.78
Extracted cork small	.91	4.72	5.32	6.26	10.49	14.36	20.65	16.37	12.28	8.37	6.61	5.77
Unextracted cork small	1.00	4.35	4.83	5.74	9.34	12.57	17.54	14.03	10.62	7.46	5.96	5.09
Extracted fiber small	1.17	5.33	5.94	7.06	11.73	16.04	23.44	19.00	13.59	9.36	7.40	6.47

[a]All values of moisture content in percent.

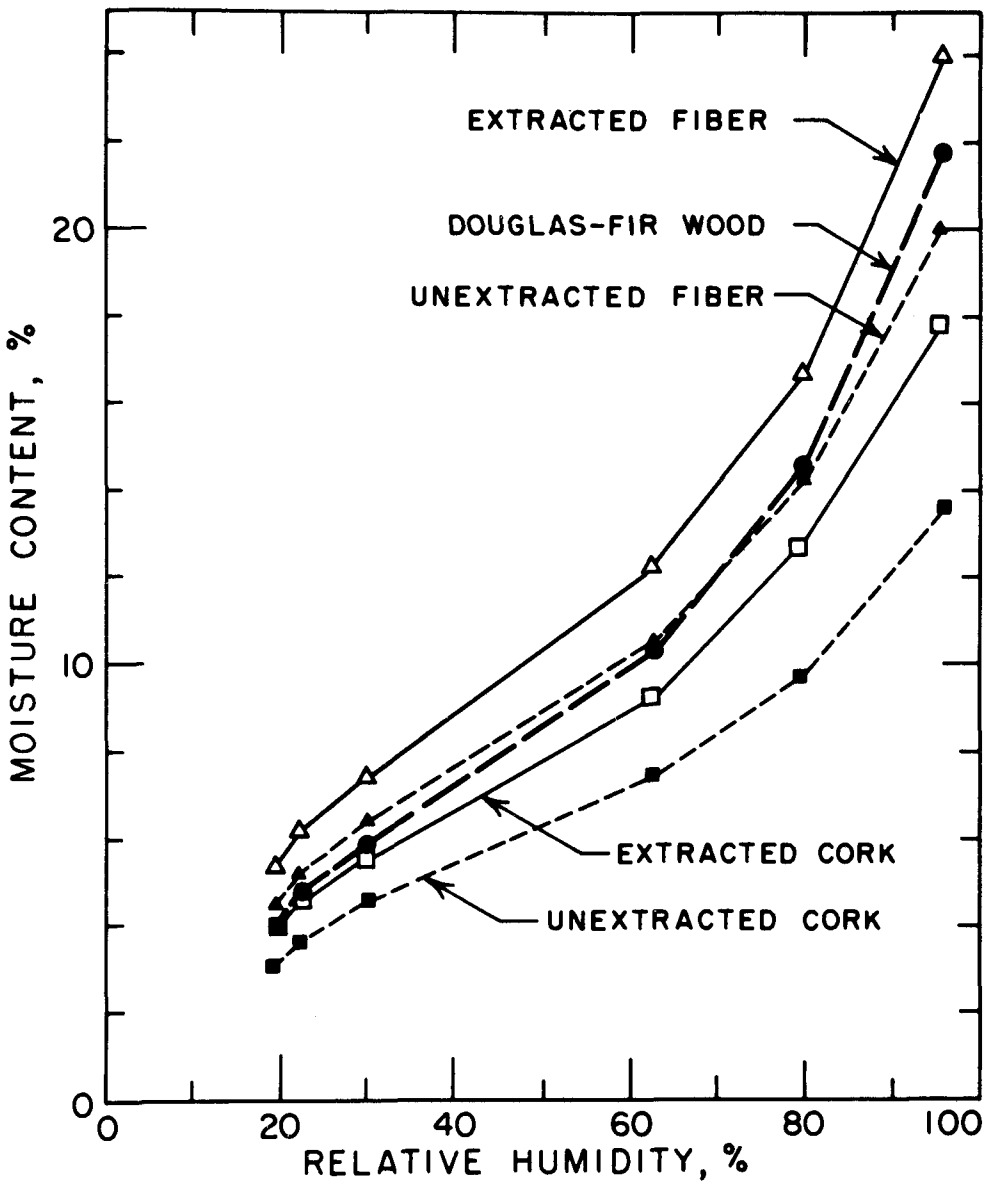

Figure 9. Adsorption isotherms for large particle fractions of Douglas-fir bark and wood.

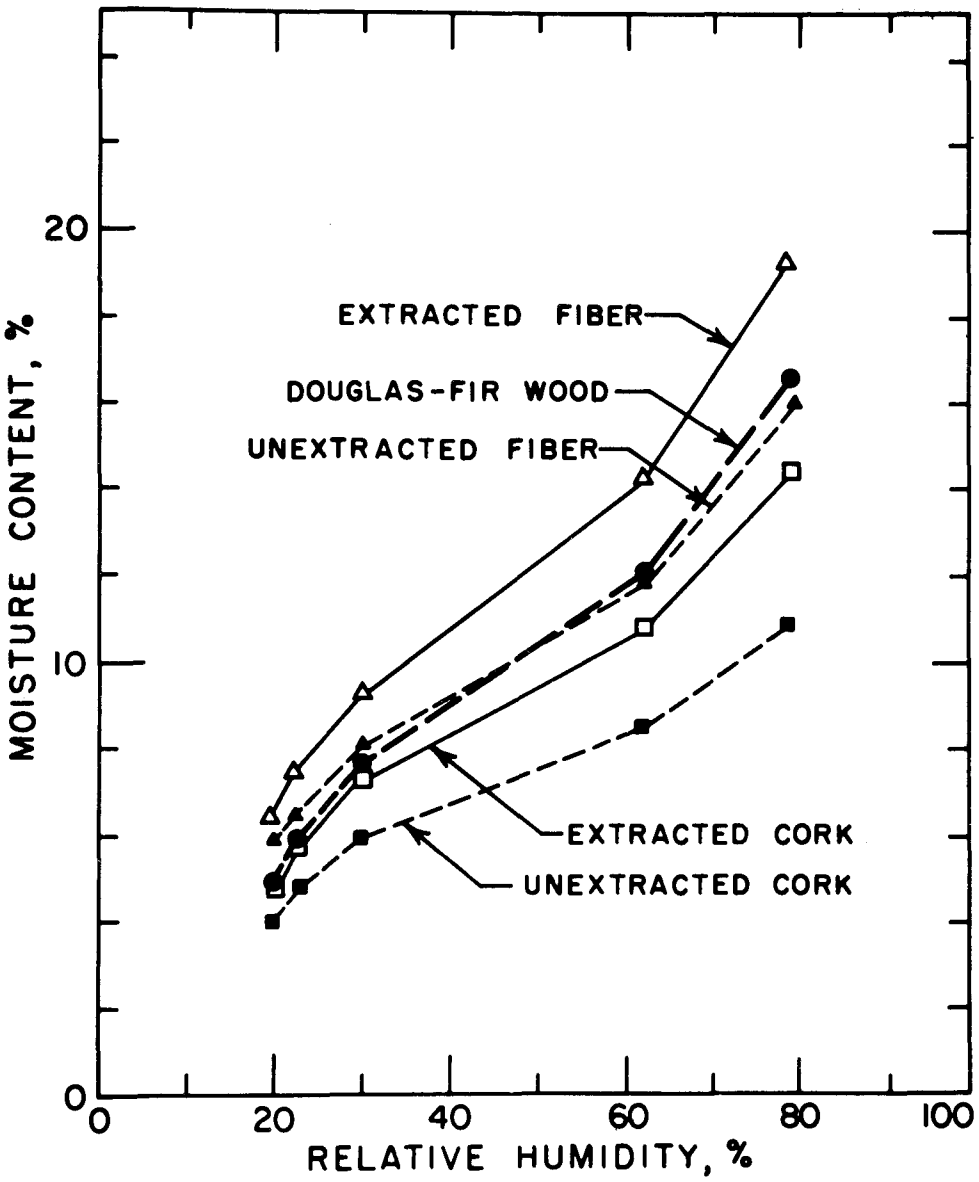

Figure 10. Desorption isotherms for large particle fractions of Douglas-fir bark and wood.

the equilibrium moisture content of Douglas-fir bark. All five of the fractions shown in Figures 9 and 10 came to significantly different equilibrium moisture contents ($P \leq .05$). However, unextracted fiber and Douglas-fir wood exhibited significant differences from each other only at low and high relative humidities ($P \leq .05$).

There are two reasons for an increase in equilibrium moisture content when hydrophobic extractives are removed. The first reason is due to the mathematical formula used to calculate moisture content. The removal of non-moisture adsorbing or less moisture adsorbing extractives from bark results in a lower oven-dry weight for the remaining bark which still adsorbs essentially the same amount of water as before the extraction. The lower oven-dry weight, however, results in an increase in the calculated moisture content. Thus, a mathematical increase in equilibrium moisture content can be caused by the removal of hydrophobic extractives from bark. The more hydrophobic the extractives and the more extractives removed, the greater will be the increase in moisture content.

The second reason for an increase in equilibrium moisture content in extracted bark is due to the ability of the extracted bark to actually sorb more moisture. This greater sorption is of two types. The first type is surface-bound adsorption, which occurs at low relative humidities; the second type is microcapillary condensation which occurs at high relative humidities. The removal of extractives

makes available more sites for surface-bound adsorption and more spaces for microcapillary condensation.

Using extraction data from Hergert and Kurth (7) the mathematical influence of extraction on equilibrium moisture content was calculated for the cork and fiber fractions and plotted in Figure 11. It can be seen that the observed increase in equilibrium moisture content for the cork was significantly lower than the predicted mathematical increase for the removal of extractives; thus, no additional moisture adsorption or microcapillary condensation was observed for cork. The reason for this is that a significant amount of the cork cells' moisture sorbing components are also removed with extraction. From Hergert and Kurth's work (7) one can see that the unextracted cork cell contains only a small percentage of moisture sorbing material (carbohydrates and tannins, etc.). Upon extraction, only small amounts, by weight, of carbohydrates and tannins are lost; however, they represent a large percentage of the cork cells' total moisture sorbing material. Evidently the loss of these moisture sorbing components overshadows any increase in sorption due to extraction.

The fiber fraction, however, showed an increase in equilibrium moisture content above that predicted by the mathematical removal of extractives. These increases above predicted values were observed, however, only at the higher relative humidities. Thus, the main

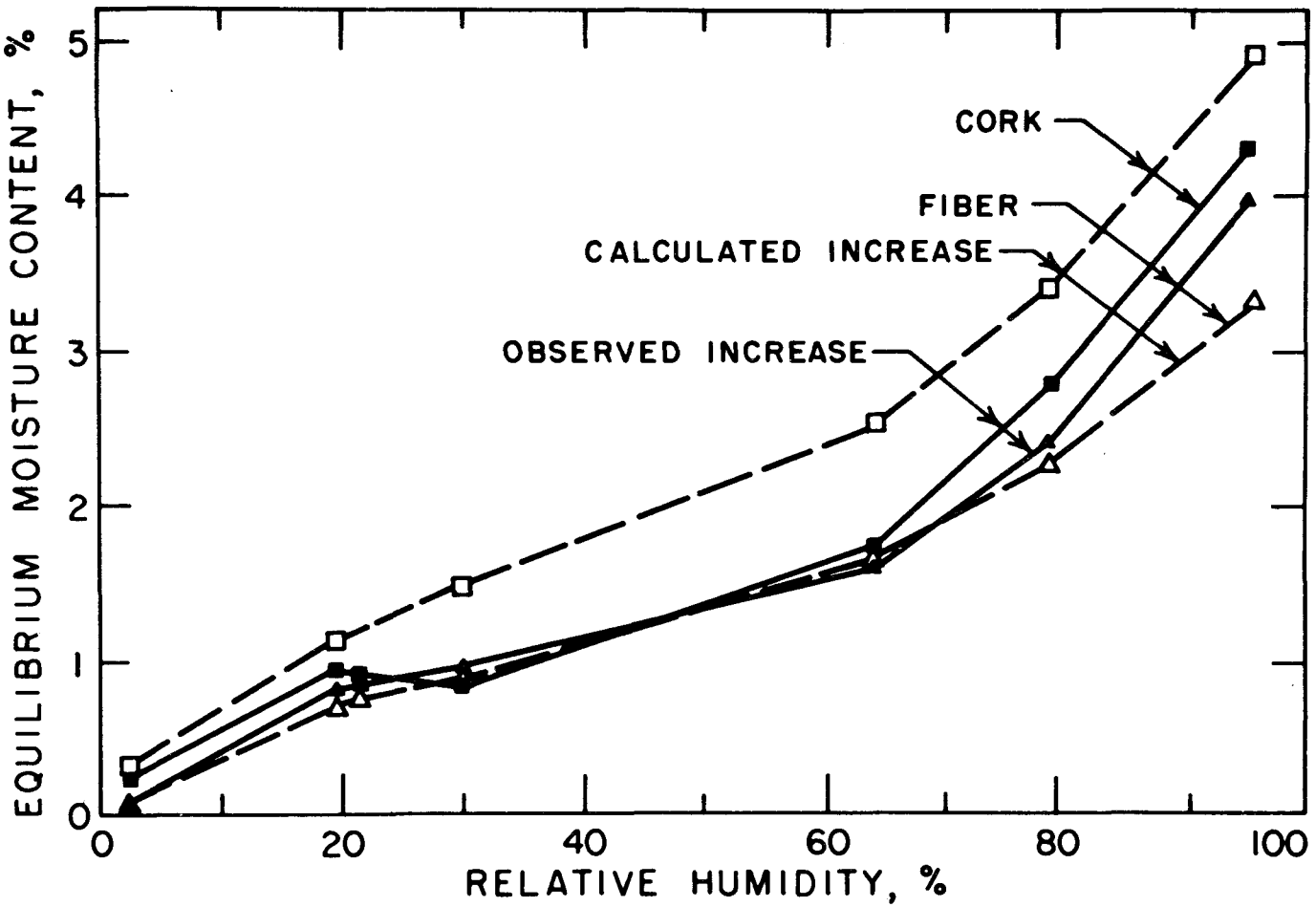

Figure 11. Average equilibrium moisture content differences between extracted and unextracted Douglas-fir bark fiber and cork at various relative humidities.

influence extraction had on the fiber fraction was to act as a debulking agent for microcapillary condensation.

Another finding of Study II was the lack of difference in equilibrium moisture content between large and small sized particles of wood at all relative humidity conditions ($P \leq .01$), which agrees with the definition of an equilibrium condition. No conclusions about the influence of particle size for the bark material could be gained. But with regards to the results of Study I, these data do show that moderate differences in composition could create significant differences in equilibrium moisture content at high relative humidities (Figures 8 and 9).

CONCLUSIONS

On the basis of this study the following conclusions are summarized:

1. Samples of extracted bark (three steps; benzene-ethanol, ethanol, hot water) had a higher equilibrium moisture content than unextracted bark at any relative humidity Most of the increase in equilibrium moisture content for bark fiber and cork was due to the extraction of non-moisture sorbing material which resulted in a lowering of the oven-dry weight for the remaining material which adsorbed approximately the same amount of moisture as when unextracted. This caused an increase in moisture content because the equation used to calculate moisture content was based on oven-dry weight. However, in the cork fraction a large percentage of the moisture sorbing material was also extracted, thus the increase in equilibrium moisture content for the cork fraction was not as high as was expected.

   The fiber fraction exhibited an increase in equilibrium moisture content above that predicted due to an increase in the amount of moisture sorbed. This increase in sorbed moisture was attributed to the extractives acting as a bulking agent.

2. Significant differences in equilibrium moisture content values were found for cork and fiber particles. In general, cork had a

lower equilibrium moisture content than fiber. The ranking of bark fractions and Douglas-fir wood for any relative humidity with regard to equilibrium moisture content were found to be as follows: extracted fiber > unextracted fiber $\lesseqgtr$ Douglas-fir wood > extracted cork > unextracted cork.

3. No significant differences in equilibrium moisture content were found between the large and small particle sizes of Douglas-fir wood. No conclusions can be drawn concerning effect of particle size of bark on equilibrium moisture content because the small-sized bark particle fractions consisted of unknown mixtures of cork and fiber. Probably particle size does not influence the equilibrium moisture content of bark, however, bark particle size may influence some methods of determining moisture content.

4. Differences in moisture content found by oven-drying Douglas-fir wood at the various temperatures were attributed to the different equilibrium moisture content conditions which were established in the oven at the various temperatures. However, differences in moisture content found among the oven-drying methods for Douglas-fir bark were only partially attributed to differences in equilibrium moisture content in the oven. Significant differences among the oven-drying methods were still found after correcting for equilibrium moisture content in the

oven. The remaining differences in moisture content among the methods were attributed to differences in the amount of volatilization which occurred under a respective temperature.

5. The most accurate way to determine bark moisture content was to dry a sample (approximate dry wt. of 2-3 g) over the desiccant Phosphorus Pentoxide (11 days with periodic maintenance of the P_2O_5) and then titrate the sample by the Karl Fischer method. Oven-drying at any low temperature ($\leq 85^{\circ}C$) and then titrating the sample by the Karl Fischer method is also a sequence giving accuracies within the ASTM standards of ± 1% moisture content.

6. Two; fast, easy, and economical methods of moisture content determination which gave accuracies within ± 1% for bark were, oven-drying at $85^{\circ}C$ and the Cenco Moisture Meter.[2] Thus the bark processor interested in accurately determining moisture content is not required to use tedious and costly techniques if an accuracy within ± 1% is allowable.

7. As the moisture content of the samples increases the accuracy of the Karl Fischer method decreases. For determining the moisture content of samples high in moisture content,

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[2]The Cenco Moisture Meter was used with a transformer which reduced the line voltage from 120 V to 92 V, all sample determinations were for 15 minutes at this voltage. Also, all moisture content values were corrected to a dry weight basis.

manipulating the sample weight so that the milliliters of titrating reagent used per sample is reduced (< one buret, 25 ml) probably would help maintain high levels of accuracy.

8. When determining bark moisture content by oven-drying, predrying the entering air or use of a desiccant inside the oven is only recommended for oven temperatures $\leq 85^{\circ}C$. The use of a desiccant at higher oven-drying temperatures will only increase the amount of error associated with the method. This is due to reducing the equilibrium moisture content condition in the oven, thus the balance between material volatilized and the moisture remaining in the sample is upset and significantly higher moisture content readings will be obtained. The same situation applies when a vacuum oven is used to determine bark moisture content. The use of a vacuum oven will be beneficial only if the temperature is $\leq 85^{\circ}C$.

9. Oven-drying at $105^{\circ}C$ was found to be an acceptable method for determining bark moisture content (within ± 1%) if the moisture content of the samples was high (>21%). This method, however, was not acceptable if the initial moisture content of the samples was low (< 12%). Thus the initial moisture content of bark samples can have an effect on the dependability of a heat method of moisture content determination. This is probably caused by the fact that at high temperatures and high moisture contents,

unwanted volatilization of component chemicals is reduced due to a cooling effect caused by the evaporation of the moisture from the surface of the sample particle.

10. The time samples remain at high temperatures is also important in reducing volatilization. The Cenco Moisture Meter was found to be acceptable at both high and low moisture contents even though the Cenco method eventually produced a maximum temperature in this study of 126 ^{o}C. However, unlike the oven drying method of 125 ^{o}C which was found to be unacceptable at any moisture content, the length of time to which the samples in the Cenco method were exposed at a temperature of 125 ^{o}C was less than 2 minutes.

11. It was also found that the extractive content of bark did not influence the methods of moisture content determination or volatilization. Thus, volatilization in bark is mainly a function of temperature, time and initial moisture content, and not of extractive content.

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APPENDICES

APPENDIX A

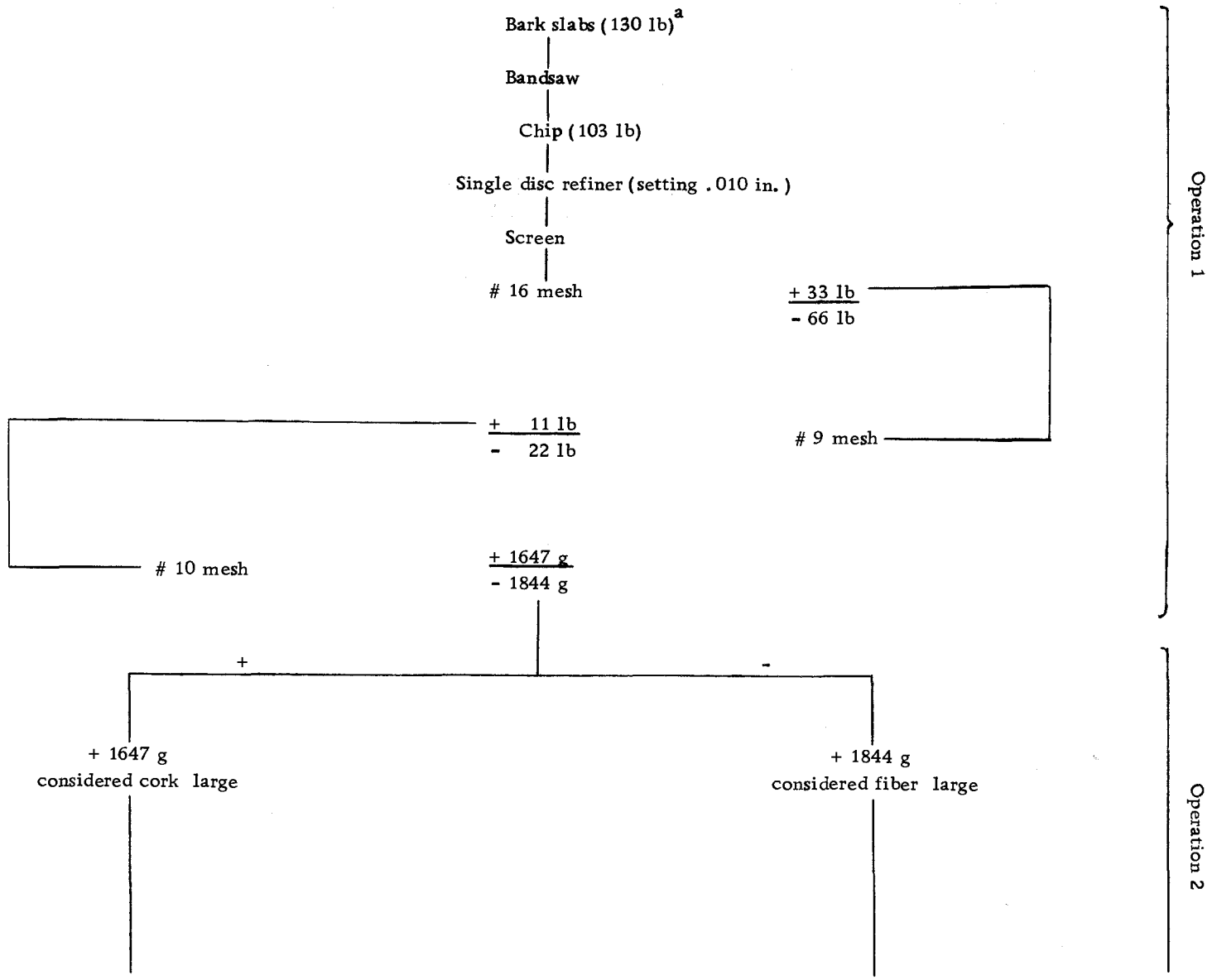
BARK PROCESSING

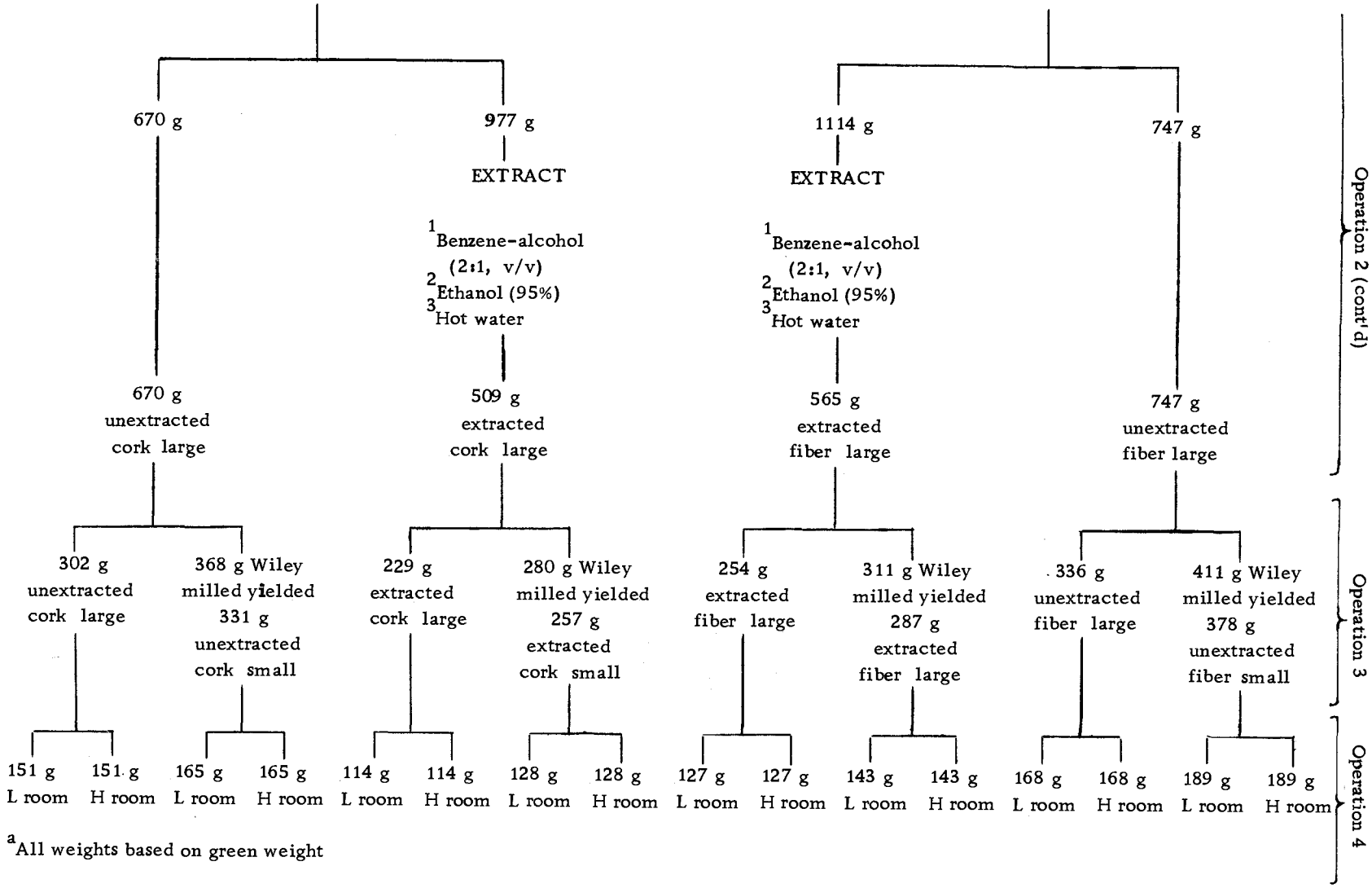
The flow diagram in Appendix Figure 1 shows the four operations required to obtain the needed fractions.

Operation 1 was primarily concerned with converting the large bark samples into large particles ($\geq$ 2 mm) of fiber-rich and cork-rich material. This was done by selective milling (disc refining) and screening techniques. The disc refiner settings and screen sizes used were selected to yield the largest possible particles of pure cork.

Operation 2 was the solvent extraction. A three step extraction sequence (48 hours per step) was used on approximately 60% instead of 50% of each fraction to compensate for weight loss caused by removal of extractive material during the extraction procedure. The three steps were assumed to yield an extractive free product (10, 13). Once the fractions had been extracted, the bark material was placed on trays in a hood to vent any remaining benzene and ethanol fumes that remained after the extraction process. From the hood, the material went to operation 3.

Operation 3 was concerned mainly with reduction of one-half of the large sized bark particles into smaller sized particles. This was accomplished by passing the material through a Wiley mill with a screen size of .047 inches. Slightly more than 50% of the material was passed through the Wiley mill to compensate for losses incurred


Bark slabs (130 lb)[a]
Bandsaw
Chip (103 lb)
Single disc refiner (setting .010 in.)
Screen
16 mesh
+ 33 lb
- 66 lb
9 mesh
+ 11 lb
- 22 lb
10 mesh
+ 1647 g
- 1844 g
+
-
+ 1647 g
considered cork large
+ 1844 g
considered fiber large
Operation 1
Operation 2



[a]All weights based on green weight

Appendix Figure 1. Flow diagram showing conversion of Douglas-fir bark into desired sample fractions.

during milling. The previously extracted large sized particles were used to generate the smaller sized extracted particles. It was felt that if large and small sized particles had been extracted separately, an unneeded variation in sample material might have been created because of the removal of greater amounts of extractives from the smaller particles.

Although all eight bark fractions needed for this study have now been described, one final step was necessary to complete the processing. Operation 4, the last step in processing the bark material for this study, consisted of randomly dividing each of the eight fractions into two groups, one group to be equalized in the L room (dry bulb temperature 70 $^{\circ}$F, wet bulb depression 10 $^{\circ}$F) and the second group to be equalized in the H room (dry bulb temperature 90 $^{\circ}$F, wet bulb depression 4 $^{\circ}$F).

APPENDIX B

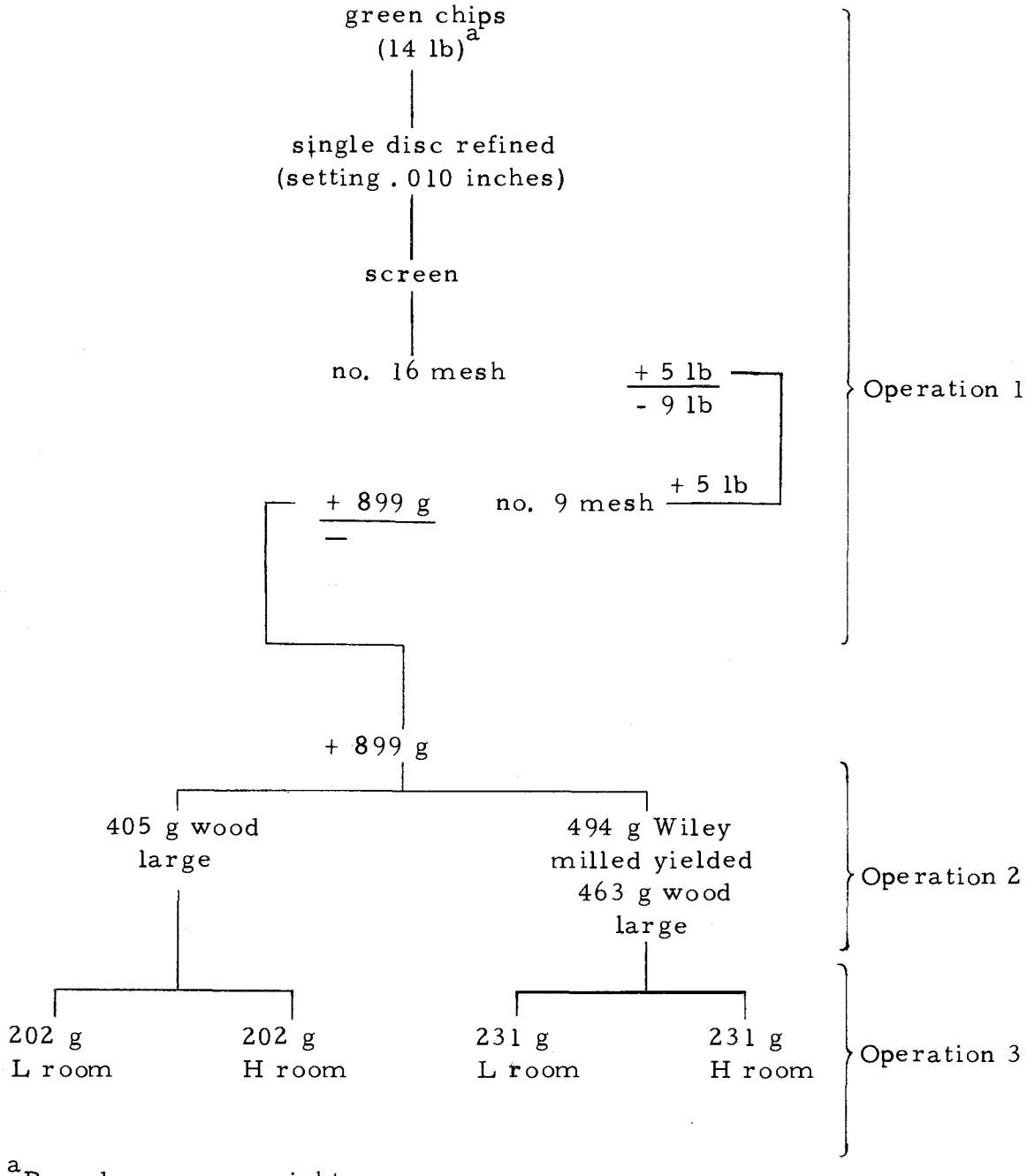
WOOD PROCESSING

The flow sheet in Appendix Figure 2 shows that the processing of the wood involved only three operations instead of the four used for bark. The missing operation in wood processing was extraction.

Since the wood was collected as chips, the only part of operation 1 needed was disc refining. Other processing and treatment of wood was the same as for the bark.

Operation 2 consisted of creating smaller sized particles. This was also accomplished by passing the larger sized material through a Wiley mill with a screen size of .047 inches.

Operation 3 was randomly dividing each of the two fractions into two lots for the conditioning rooms.



[a]Based on green weight

Appendix Figure 2. Flow diagram showing conversion of Douglas-fir wood into desired sample fractions.

APPENDIX C

RANDOMIZATION OF SAMPLE MATERIAL

Once the bark sample material was equilized in moisture content it was randomized into individual samples for Study II. An explanation of this procedure follows.

Estimates on precision of moisture content determination needed, cost of Fischer titration for various sized samples at the two equilibrium moisture content levels, and other factors dictated that a sample weight of approximately 2.0 grams oven-dry basis was needed for all samples except the Cenco samples which required a much larger sample (approximately 6 g) due to the operating principles of this instrument. All material of one fraction in a given conditioning room was collected from the equilizing tray and put into a large plastic bag.

A beam balance was set up in the conditioning room and from the large plastic bag random samples of the approximate weight needed (2.2 g, L room; 2.5 g, H room; Cenco, higher weights) were selected. These individual samples were then placed in a coded plastic bag. This process was repeated until all the samples needed from that particular fraction were collected. The remaining material was then placed back on the equilizing tray. The above process was then repeated for the other nine material fractions until all fractions had been completely sampled. Once this was accomplished, all the

individual sample bags were rearranged by their codes into groups for use in methods of moisture content determination and replications. Therefore, there were 21 groups (7 methods x 3 replicates) of ten (8 bark + 2 wood) bags for the conditioning room. These groups of bags were then randomly placed on dowel rods (two groups per dowel rod). These dowel rods were hung on racks with the sample bags open to the conditioning room atmosphere.

Once this sampling procedure was accomplished for a conditioning room, the same procedure was undertaken in the other conditioning room. Therefore, all samples were randomly selected and grouped by method of moisture content determination for easy access when needed during the study.

APPENDIX D

COMPOSITION ANALYSIS OF SAMPLE MATERIAL

A stage and an elevated overlying grid were made as shown in Appendix Figure 3 for this study. The composition for a sample was determined as follows:

1. A sample bag containing large sized particles was taken from the sample rack.
2. The bark sample was poured over the plastic overlay on the composition stage.
3. The large particle material was randomly distributed over the stage.
4. The dot grid overlay was positioned over the stage.
5. Particle type was determined and counted. Count was kept by handheld counters, one for cork and one for phloem (only those particles under the dots were counted).
6. Grid was removed and sample returned to sample bag.
7. Sample bag was returned to rack.

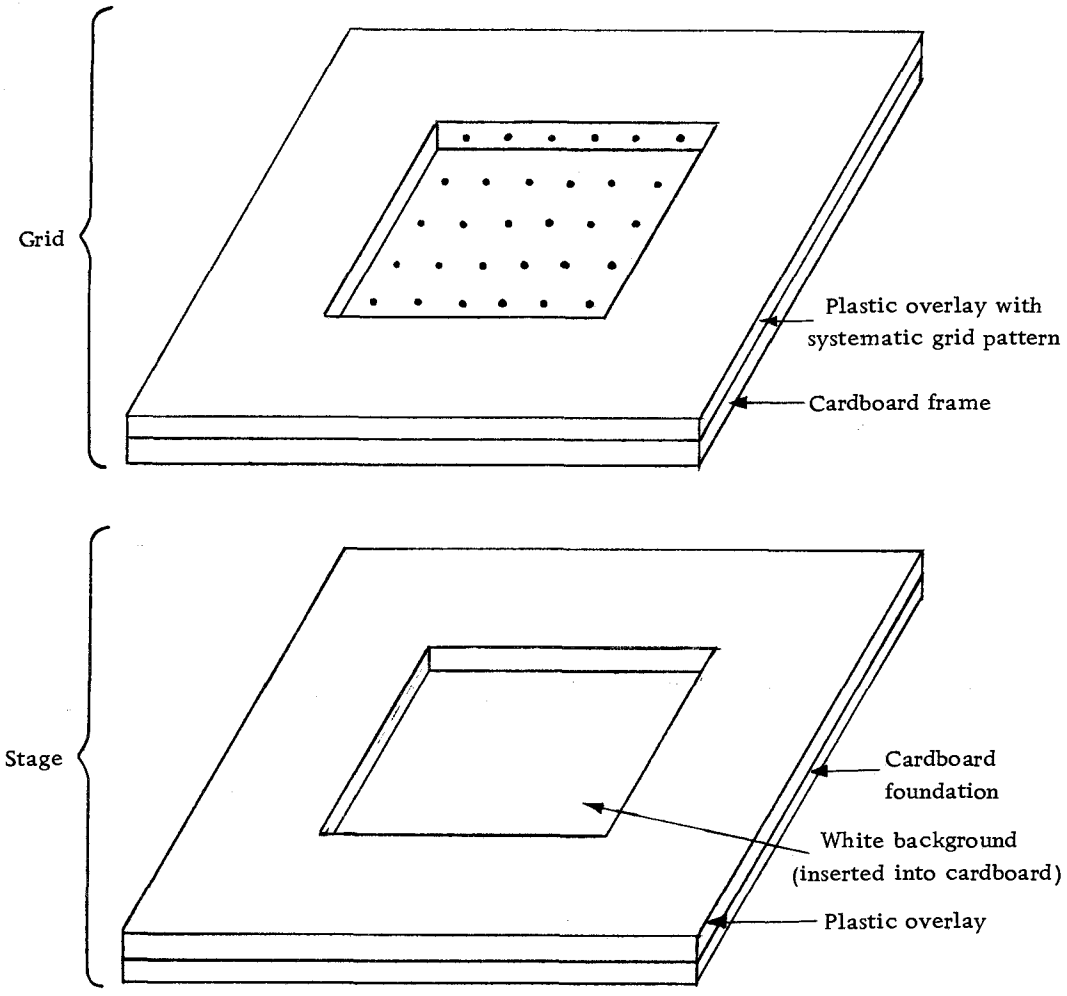
The equations used to determine cork composition are as follows:

$$\% \text{ composition of cork in cork-rich material} = \left(\frac{\text{total number of observations of cork from cork-rich material}}{\text{total number of observations (of cork and phloem material) for cork-rich material}} \right) \times 100$$

$$\%\ \text{of fiber in cork-rich material} = 100\% - \%\ \text{composition of cork in cork-rich designated material}$$

$$\%\ \text{composition of fiber in fiber-rich material} = \left(\frac{\text{total number of observations of phloem from fiber-rich material}}{\text{total number of observations (of both phloem and cork material) for fiber-rich material}} \right) \times 100$$

$$\%\ \text{composition of cork in fiber-rich material} = 100\% - \%\ \text{composition of fiber in fiber-rich designated material}$$



Appendix Figure 3. Diagram of composition sampler.

APPENDIX E

KARL FISCHER TITRATION

Description of Instrument

An "Aquatrator" (Precision Scientific, Inc.) was used in the Fischer titration treatment for determining an end point. This instrument has an electrical end point and does not depend upon a color reaction or color change. The Aquatrator measures conduction through the use of a platinum electrode whereby the presence of more water results in the sample solution having more resistance. In the method used, Karl Fischer reagent is added and reacts with the water in the sample to give a resistance change (less water, therefore less resistance, consequently more conduction). When the electrode is completely depolarized, no water is left and an appropriate endpoint is reached. Once the meter is zeroed and an end point determined, the same end point should be used for all samples. The definition of an end point used for this method of titration is as follows: an end point is chosen such that when an additional drop of titrant (Karl Fischer reagent) is added it is detected but the meter needle reading is not permanently deflected or changed. The meter needle remains oscillating around the end point for a period of time (9).

Preparation of Sample for Titration

A known weight of sample was placed in a reaction flask. The

flask was then clamped onto the Aquatrator and the flask purged with dry air. Fifty ml of dry methanol was then dispensed into the flask. The flask was removed from the instrument and sealed with Parafilm. The samples were immersed in methanol for 18 hours. An occasional mixing or sloshing of the samples helped break up any water miniscii that may have formed.

Titration of Sample

The titration of a sample by the Karl Fischer method was as follows. The Parafilm seal around a sample which had been immersed in methanol for 18 hours was removed and a stirring bar was dropped into the reaction flask. The reaction flask was clamped into place on the Aquatrator, the flask was purged with dry air and the sample was stirred. The meter was checked to see that it was zeroed and then switched to the titration mode. Karl Fischer reagent was added until an end point was reached (in this study the end point value was 9 micro-amps). The amount of reagent added was noted and the stirring stopped. The instrument was switched to the zeroing or standby mode and the reaction flask removed. The stirring bar was removed from the flask and the flask placed out of the way. The stirring bar was cleaned with acetone. Then the burett was refilled with Karl Fischer reagent and the sequence repeated. To calculate the amount of water in a sample the following equation was used.

$$\text{wt water} = (\text{ml reagent used} - \text{correction factor for extraneous water}) \times \text{titer}$$

Titer

The titer of the Karl Fischer reagent is the average amount of water, in grams, titrated by a milliliter (ml) of Karl Fischer reagent. The following equation was used to calculate titer.

$$\text{Titer} \quad \frac{\text{g water}}{\text{ml Karl Fischer reagent}} = \sum_{i=1}^{N} \left(\frac{\text{wt water, in g}}{\text{ml Karl Fischer reagent}}\right)_i / N$$

where N = the number of times known water samples were titrated (for this study N = 3).

The sequence of events to calculate titer was as follows. Fifty ml of methanol was dispensed into a reaction flask and titrated to the end point. A known amount of distilled water was introduced into the flask through a special port by an eyedropper. The port was resealed and the flask purged with dry air. This known amount of distilled water (determined by weighing the eyedropper before and after introduction of water) was titrated to an end point. Additional water was added and titrated two more times. Thus, three known amounts of water were titrated by three known amounts of Karl Fischer reagent. The titer was then calculated from the above equation.

Calibration of Extraneous Water

In addition to the calculation of titer, an estimate of water not

associated with the sample was needed to calculate the water in the sample. This extra water was the result of (1) water in the methanol, (2) water adsorbed on the reaction flasks, (3) water picked up during sealing and opening of reaction flask, and (4) water picked up by the methanol while the sample remained sealed for the required immersion time.

1. Water in methanol. Fifty ml of methanol were dispensed into a reaction flask and titrated to an end point. Fifty additional ml of methanol were then added to the flask. This additional methanol was titrated, thus giving the error due to water in the methanol.

2. Water adsorbed on flasks. Fifty ml of methanol was dispensed into a reaction flask and titrated to an end point which gave the total error due to water in methanol and water pickup due to dispensing the methanol into the flask and water vapor adsorbed from the air and collected on the reaction flask.

3. Water collected during sealing and opening of flask. Fifty ml of methanol was dispensed into a reaction flask and the flask was removed and sealed. It was immediately uncovered, replaced on the titration apparatus and titrated. This gave the total error due to water from points 1, 2, and 3 above.

4. Water collected during immersion period. The total error due to all four of the above points was determined by dispensing 50 ml

methanol into a flask, sealing it and then 18 hours later titrating this blank. Appendix Table 1 gives the respective error values found for five such replications. The amount of water due to all four errors was approximately .0215 g [3.5 ml of reagent x titer (.00613 g/ml)].

Time Required to Immerse Samples

The length of time required to immerse the samples so all the water in a sample was titratable was determined by a technique described in Mitchell and Smith (16). Selected bark fractions were placed in 50 ml of dry methanol and were immersed for various lengths of time (2 to 30 hours). The methanol was decanted, the samples re-immersed in 50 ml of methanol for 24 hours, and the original decanted methanol titrated. The second immersion lasted 24 hours, after which the sample and methanol were titrated together in the reaction flask. The samples which on the second immersion showed no further evidence of water were assumed to contain no more moisture. Therefore, the immersion time had made all moisture available for titration. Consequently, this length of time for immersion was acceptable in that only one immersion for a specific period of time was required for complete titration of all water. From this analysis and the convenience of an 18-hour immersion period, 18 hours was chosen as the time of immersion for all fractions.

Appendix Table 1. Determination of error caused by sources of extraneous water in the Karl Fischer titration method of determining moisture content.

Error		Calculated ml of reagent for error
1	Water in 50 ml methanol	= 1.2 - 1.3 ml Karl Fischer reagent[a]
2	Water in 50 ml methanol + water due to dispensing into flask	= 2.2 - 2.4 ml Karl Fischer reagent
	Water due to dispensing into flask	= no. 2 - no. 1 above = 2.4 - 1.2 = 1.2 ml Karl Fischer reagent
3	Water in 50 ml methanol + water due to dispensing into flask + capping and uncapping procedure	= 3.3 - 3.5 ml Karl Fischer reagent
	Water due to capping and uncapping procedure	= no. 3 - no. 2 above = 3.5 - 2.2 = 1.3 ml Karl Fischer reagent
4	Water in 50 ml methanol + water due to dispensing + water due to capping and uncapping + water due to 18-hr extraction period	= 3.2 - 3.5 ml Karl Fischer reagent
	Water due to 18-hr standing period	= no. 4 - no. 3 above = 3.5 - 3.3 ml Karl Fischer reagent = .2 ml Karl Fischer reagent

[a] Titer for Karl Fischer reagent = .00613 g water/ml Karl Fischer reagent.

APPENDIX F

OVEN-DRYING DETERMINATION

Calibration of Oven

In order to get accurate temperature measurements while oven-drying the sample, a calibration check on both the thermometer and the actual temperature of the oven when loaded with samples was conducted. A thermocouple and potentiometer were used for this calibration. The thermocouple was attached to the thermometer just opposite the mercury bulb of the thermometer. Both were then placed in boiling water (100 ^{o}C) and ice water (0 ^{o}C) and the respective readings noted. The thermocouple and the thermometer varied 1 ^{o}C, with the thermometer reading 1 ^{o}C higher at both temperatures tested.

The oven used in this study (a Telco, convection oven Model 28 with no drying tubes or desiccants) was allowed to equilibrate at a given temperature. The temperature reading for the thermometer was noted and the thermocouple was inserted into the oven next to the thermometer. The thermocouple was placed at various heights above the bottom of the oven until a height was reached where the temperature of the oven was consistent with the thermometer reading. The oven shelf was placed approximately the length of a weighing bottle lower than that point in the oven. A grid pattern (4 x 5) was marked on the oven shelf with adhesive tape and the oven was loaded with 20

sample weighing bottles. When the oven reached operating temperature, the temperature inside the weighing bottle, and directly above but outside the weighing bottle, was noted. This was done for various locations throughout the oven and at the different temperatures used in the study. At each temperature used in the study, the outside temperature control knob was marked so that it would be easy to re-equilibrate the oven at certain desirable temperatures. The variation in temperature in this calibration of the oven was less than $1^{\circ}C$.

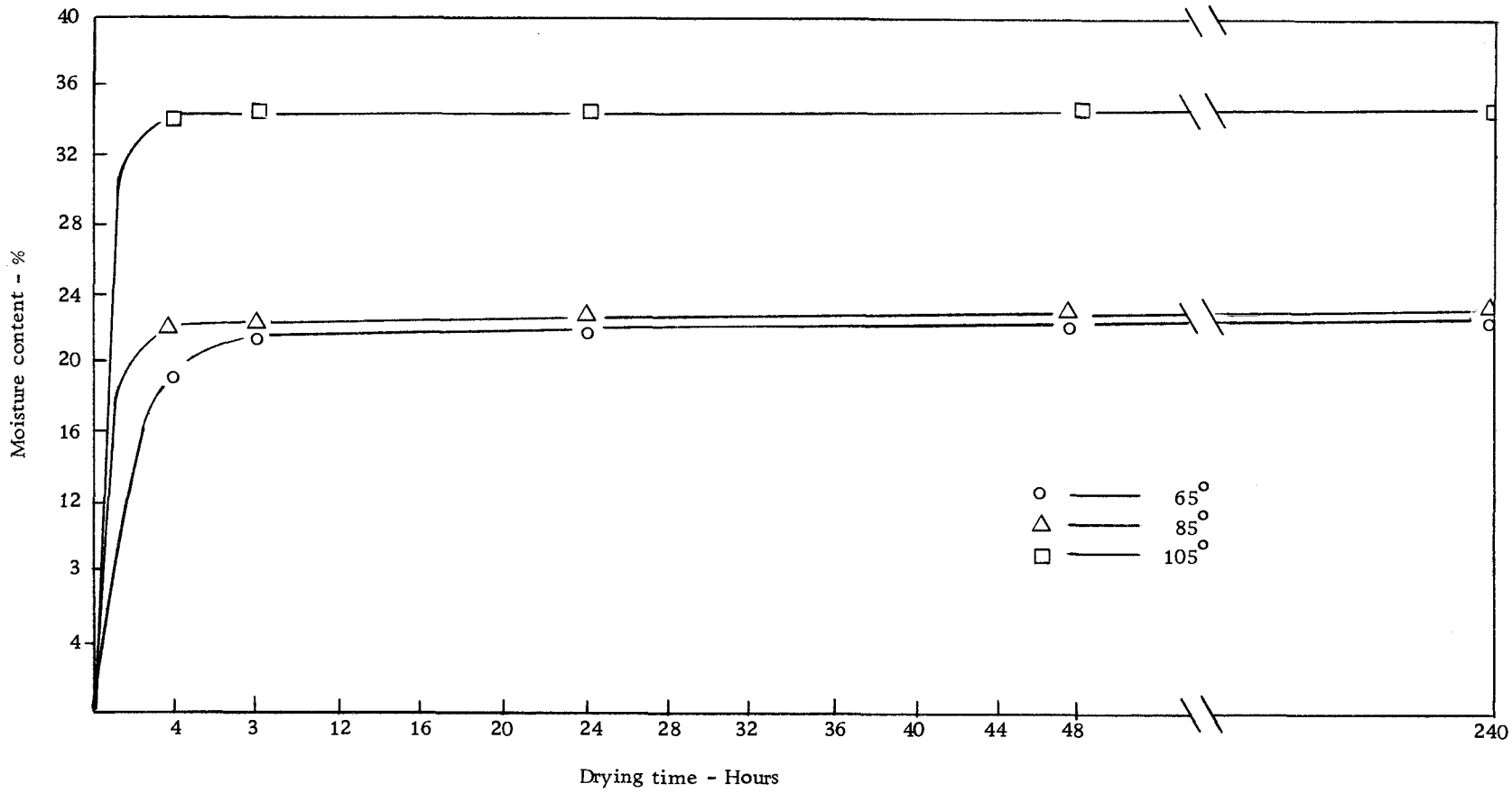
Oven-Drying Procedure

The sequence of events for an oven-drying treatment was as follows. The samples in the conditioning rooms were sealed and placed in a large sealed plastic bag. The bag of samples was brought to the laboratory where the weighing balance and drying oven were located. The samples were removed one at a time and the proper amount of material measured into an already tared weighing bottle (all weighing for Study I was done on a Mettler Model H20T). The sample weighing bottle was capped, the weight recorded, and placed in a desiccator. This procedure was repeated until all samples were weighed. The bottles were randomly placed by a grid pattern (4 rows x 5 columns) in an oven which had already been equilibrated at the proper temperature. The bottle caps were removed when each bottle was placed in the oven and placed directly in front of the bottle. After

drying for a given time period, all samples were capped before being removed for weighing. The first four bottles in the front row were removed and placed in a desiccator to cool. When they were cool, the next four samples were removed and placed in a desiccator to cool. While the second group was cooling the first group was weighed. This procedure continued until all bottles were weighed. A group of samples remained in the desiccator until all individual samples had been weighed. The bottles were returned to the oven for further drying by selecting a desiccator at random, removing the bottles and placing them in the oven on the grid pattern; however, the bottles were replaced to fill the columns of the grid rather than the rows. This was done to eliminate any systematic errors in weighing.

The samples were weighed after 1, 2-1/2, 7, 11, and 24 hours of drying time. The 24-hour drying time was selected as maximum because a preliminary study indicated that bark, although not completely equilibrated after 24 hours, did not lose significant weight thereafter (Appendix Figure 4). After drying, a sample was either discarded or titrated for residual moisture. After all samples were removed, the oven was reset for the next temperature test.

The samples to be titrated for residual moisture were returned to the oven capped. One sample at a time was removed from the oven and taken to a nearby hood which contained the Karl Fischer Aquatrator. The sample bottle was uncapped and quickly emptied into a



Appendix Figure 4. Variation in Moisture Content of Douglas-fir bark with time at Different Drying Temperatures from Preliminary Study

waiting reaction flask. The reaction flask was clamped in place, purged with dry air and 50 ml of dry methanol was added and mixed with the sample. The reaction flask was removed and sealed. Another sample was obtained and treated in the same way until all had been prepared for titration. After 18 hours of immersion the samples were titrated.

APPENDIX G

DRYING OVER PHOSPHORUS PENTOXIDE

Samples for P_2O_5 were treated similarly to the samples for oven-drying except that the uncapped weighing bottles were placed in desiccators containing P_2O_5 for 11 days. Two replications were also titrated by the Karl Fischer method for residual moisture. However, as stated previously, the third replication of the P_2O_5 technique was used to help estimate the relative accuracy of the Karl Fischer method in determining the residual moisture content of the wood and bark samples.

As the samples dried the top of the P_2O_5 became deactivated and had to be removed. The following describes the steps taken to remove the spent P_2O_5.

The P_2O_5 was contained in a petri dish at the bottom of the desiccator. The capped samples after weighing were placed in an auxiliary holding desiccator. The petri dish was then removed with forceps. The layer of spent P_2O_5 was removed with the forceps and a glass stirring rod and placed into a glass beaker. Once the spent P_2O_5 was removed the forceps were rinsed off and dried, the petri dish and samples were then replaced.

Once all the desiccators had been serviced the beaker containing the spent P_2O_5 was placed under a hood in a shallow pan containing

water. The water in the shallow pan allowed the beaker to remain cool while the P_2O_5 further reacted with the atmospheric moisture. After the study was completed the P_2O_5 in the beaker was discarded as any acid would be; namely, by diluting small quantities of the P_2O_5 into large quantities of water.

Other less costly and less dangerous desiccants such as $CaSO_4$ could be used; however, the residual moisture remaining in the samples would be greater.

APPENDIX H

CENCO MOISTURE METER

Because the Cenco Moisture Meter was close to the conditioning rooms, it was not necessary to seal all the samples. Instead, each sample as needed was removed from the racks, sealed, and taken to the Cenco Moisture Meter. The correct amount of sample (approximately 6 g green) was dispensed on the balance pan of the instrument. The sample chamber was closed and the instrument turned on.

During the Cenco moisture content determination, continuous adjustments were made on the instrument to insure that sample distance from the heat source was constant. Also, at one minute intervals, readings of moisture content were taken and recorded. The time required for a sample to come to equilibrium in the Cenco varied between 10 and 15 minutes. All samples in this study were run for 15 minutes. After 15 minutes, the instrument was turned off and the sample either discarded or placed in a reaction flask for a Karl Fischer titration. The sample pan was cleaned of any residue from the previous sample and returned to the instrument. The instrument was then zeroed and a new sample was obtained and tested.

APPENDIX I

DETERMINATION OF RELATIVE HUMIDITIES USED IN STUDY II

The relative humidity values were determined for the adsorption-desorption study in the following manner. The approximate values of relative humidities to be used were selected. Appropriate settings were obtained from the Aminco operating manual for dry bulb temperature and water bath temperature to achieve the desired relative humidities. A controlling cam was cut for the recorder to set the dry bulb and water bath temperatures. Since water bath temperature was being measured and not wet bulb depression or dew point temperature, the actual relative humidity obtained differed slightly from that expected. Once the samples were removed from the Aminco, an Assmann Psychrometer was placed in the Aminco and the conditions of the experiment repeated. This was necessary because of insufficient room in the Aminco during the experiment.

At each relative humidity position readings were obtained and the relative humidity was calculated. A thermocouple was also placed in the Aminco to check the dry bulb temperature. Once the study was complete and the moisture contents of the wood samples found and the dry bulb temperature known, the relative humidities at each condition could also be estimated from relative humidity and equilibrium moisture content tables for wood. The relative humidities used for

charting purposes were the values obtained from the Assmann Psychrometer. Appendix Tables 2 shows the relative humidity values obtained.

Appendix Table 2. Determining relative humidity values used to equilize samples in the Aminco Climate Laboratory.

Method	Relative humidity (%)										
Values from Aminco Manual	20	30	40	60	80	95	80	60	40	30	20
Values from Assmann Psychrometer	20	23	30	63	79	95	79	63	30	23	20

APPENDIX J

ANALYSIS OF VARIANCE TABLES (ANOVA) FROM FACTORIAL ANALYSES

Appendix Table 3 gives an explanation of the coding used in all the Analysis of Variance Tables (Appendix Tables 4, 5, 6, 7, 8, and 9).

Appendix Table 3. Coding used in the analysis of variance (ANOVA) tables.

Source of variation	Factors studied
M	Methods of determining moisture content
S	Particle size
E	Extractive content
C	Sample composition
R	Replications
Multiple designations such as MS are the interaction factors	
MS	Interaction of methods by particle size

Appendix Table 4. Five-factor analysis of variance table for Douglas-fir bark using data obtained from the various methods for samples conditioned in the L room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
M	2.6139788E 04	6	4.3566313E 03	71.311[a]
S	1.9977524E 02	1	1.9977524E 02	3.270
MS	1.9894143E 02	6	3.3156905E 01	.540
C	9.8073152E 03	1	9.8073152E 03	160.530[a]
MC	2.2512143E 02	6	3.7520238E 01	.614
SC	5.5315238E 01	1	5.5315238E 01	.905
MSC	4.7930976E 02	6	7.9884960E 01	1.308
E	1.2308595E 04	1	1.2308595E 04	201.47[a]
ME	3.2532976E 02	6	5.4221627E 01	.888
SE	2.2587524E 02	1	2.2587524E 02	3.697
MSE	1.3925810E 02	6	2.3209683E 01	.380
CE	1.2160952E 01	1	1.2160952E 01	.199
MCE	4.2445714E 01	6	7.0742857 00	.116
SCE	2.9866667E 00	1	2.9866667 00	.049
MSCE	8.3625000E 01	6	1.3937500E 01	.228
R	7.6278633E 03	2	3.8139317E 03	62.428[a]
Error[b]	6.7102498E 05	110	61.093	

[a]Significant at 1% level.

[b]Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.

Appendix Table 5. Five-factor analysis of variance table for Douglas-fir bark using data obtained from the various methods for samples conditioned in the H room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
M	2.0637157E 04	6	3.4395262E 03	35.633[a]
S	9.7489339E 02	1	9.7489339E 02	10.100[a]
MS	8.1071786E 02	6	1.3511964E 02	1.400
C	2.2566657E 04	1	2.2566657E 04	233.78[a]
MC	4.7710905E 02	6	7.9518175E 01	.824
SC	4.4135292E 02	1	4.4135292E 02	4.572
MSC	2.8363000E 02	6	4.7271667E 01	.490
E	8.7556793E 04	1	8.7556703E 04	907.06[a]
ME	2.4500167E 02	6	4.0833611E 01	.423
SE	1.4821488E 01	1	1.4821488E 01	.154
MSE	2.8890643E 02	6	4.8151071E 01	.499
CE	7.8823339E 02	1	7.8823339E 02	8.166[a]
MCE	3.9828952E 02	6	6.6381587E 01	.688
SCE	1.5951006E 02	1	1.5951996E 02	1.652
MSCE	6.5248619E 02	6	1.0874770E 02	1.127
R	4.0052351E 03	2	2.0026176E 03	20.747[a]
Error[b]	1.0018014E 06	110	96.527	

[a] Significant at 1% level.

[b] Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.

Appendix Table 6. Three-factor analysis of variance table for Douglas-fir wood using data obtained from the various methods for samples conditioned in the L room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
R	2104.615	2	1052.307	12.057[a]
S	160.877	1	160.877	1.843
M	3860.809	6	643.468	7.372[a]
SM	484.003	6	80.667	.924
Error[b]	2270.272	26	87.280	

[a]Significant at 1% level.

[b]Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.

Appendix Table 7. Three-factor analysis of variance table for Douglas-fir wood using data obtained from the various methods for samples conditioned in the H room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
R	364.289	2	182.144	2.641
S	451.459	1	451.459	6.546
M	3357.818	6	559.636	8.115[a]
SM	691.619	6	115.269	
Error[b]	1793.084	26	68.965	

[a]Significant at 1% level.

[b]Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.

Appendix Table 8. Five-factor analysis of variance table for Douglas-fir bark using corrected moisture content values[a] for samples conditioned in the L room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
M	1.3479412E 04	6	2.2465687E 03	35.390[b]
S	2.2448595E 02	1	2.2448595E 02	3.536
MS	1.3658655E 02	6	2.2764425E 01	.358
C	1.0796847E 04	1	1.0796847E 04	170.82[b]
MC	1.2707250E 02	6	2.1178750E 01	.334
SC	5.5545000E 01	1	5.5545000E 01	.875
MSC	5.0590417E 02	6	8.4317361E 01	1.328
E	1.3821229E 04	1	1.3821229E 04	217.724[b]
ME	3.9771369E 02	6	6.6285615E 01	1.044
SE	2.0504381E 02	1	2.0504381E 02	3.230
MSE	6.3012124E 01	6	1.0502004E 01	.165
CE	1.9611667E 01	1	1.9611667E 01	.309
MCE	5.4634167E 01	6	9.1056944	.143
SCE	3.2595238E 01	1	3.2595238E 01	.513
MSCE	5.6597262E 01	6	9.4328770	.149
R	8.1692573E 03	2	4.0846286E 03	64.345[b]
Error[c]	6.9828339E 05	110	63.480	

[a] Includes residual moisture.

[b] Significant at 1% level.

[c] Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.

Appendix Table 9. Five-factor analysis of variance table for Douglas-fir bark using corrected moisture content values[a] for samples conditioned in the H room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
M	1.3505537E 04	6	2.2509228E 03	24.346[b]
S	7.8953357E 02	1	7.8953357E 02	8.539[b]
MS	6.6998226E 02	6	1.1166371E 02	1.208
C	2.4072149E 04	1	2.4072149E 04	260.368[b]
MC	5.4385036E 02	6	9.0641726E 01	.980
SC	4.3008000E 02	1	4.3008000E 02	4.652
MSC	5.7182417E 02	6	9.5304028E 01	1.031
E	9.2468059E 04	1	9.2468059E 04	1000.148[b]
ME	5.2848321E 02	6	8.8080536E 01	.953
SE	7.1500952E 01	1	7.1500952E 01	.773
MSE	3.8636988E 02	6	6.4394980E 01	.697
CE	6.2640095E 02	1	6.2640095E 02	6.775
MCE	2.6184988E 02	6	4.3641647E 01	.472
SCE	2.0108595E 02	1	2.0108595E 02	2.175
MSCE	5.5307988E 02	6	9.2179980E 01	.997
R	3.3779044E 03	2	1.6880522E 03	18.268[b]
Error[c]	1.0169984E 06	110	92.454	

[a] Includes residual moisture.

[b] Significant at 1% level.

[c] Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.

Appendix Table 10. Three-factor analysis of variance table for Douglas-fir wood using corrected moisture content values[a] for samples conditioned in the L room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
R	2269.560	2	1134.780	12.336[b]
S	192.001	1	192.001	2.087
M	2371.162	6	395.194	4.296[b]
SM	510.162	6	85.027	
Error[c]	2391.672	26	91.987	

[a]Includes residual moisture.

[b]Significant at 1% level.

[c]Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.

Appendix Table 11. Three-factor analysis of variance table for Douglas-fir wood using corrected moisture content values[a] for samples conditioned in the H room.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F value
R	410.695	2	205.357	2.733
S	520.819	1	520.819	6.932
M	2958.049	6	493.008	6.562[b]
SM	533.866	6	88.977	1.184
Error[c]	1953.332	26	75.128	

[a]Includes residual moisture.

[b]Significant at 1% level.

[c]Error term consists of all replication interactions. Replication interactions were found to be non-significant before pooling interactions.