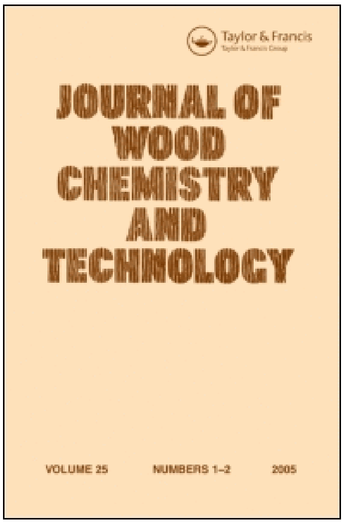

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article West, H. and Banks, W. B.(1986) 'Topochemistry of the Wood-Isccyanate Reaction an Analysis of Reaction Profiles', Journal of Wood Chemistry and Technology, 6: 3, 411 — 425

To link to this Article: DOI: 10.1080/02773818608085235

URL: http://dx.doi.org/10.1080/02773818608085235

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 6(3), 411-425 (1986)

TOPOCHEMISTRY OF THE WOOD-ISOCYANATE REACTION
AN ANALYSIS OF REACTION PROFILES

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ABSTRACT

The rate of reaction of Scots pine (Pinus sylvestris) with n-butyl isocyanate was followed by measuring weight percent gain (WPG) as a function of time (t). A model was developed to predict the form that an equation representing the WPG versus t 'reaction profile' might take. A curve of that form was fitted to the data using standard commercial software. The resulting 'whole wood' integrated rate equation was split into its component equations to yield information about the rate and extent of reaction in the lignin and holocellulose fractions of the wood. Assignment of equations, based on defined assumptions, indicate that in the initial stages of the reaction lignin reacts faster and to a higher degree of substitution than the holocellulose.

INTRODUCTION

Wood may be modified chemically in order to change its physical, chemical and biological properties. For example, bulky

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molecules bonded within the cell wall impart significant dimensional stability. Attachment of certain groups to polysaccharide functional sites gives enhanced resistance to biodegradation [Rowell (1)]. Of interest in any such chemical modification of wood is the topochemistry or site of the reaction. Attention to the location of a reacting species may be directed at the macroscopic levels of, for example, heartwood versus sapwood, earlywood versus latewood or lumen versus cell wall. At the molecular level, as noted by Rowell (1) 'the most important determination in the distribution of bonded chemicals in modified wood is the distribution of reacted chemicals in the holocellulose and lignin fractions of the cell wall', such determinations being aimed at establishing degree of substitution (DS) and/or the reactive sites substituted.

In the field of topochemistry of the wood-isocyanate reaction Rowell (1) has conducted a study using southern pine reacted to various weight percent gains (WPG) with methyl isocyanate. By means of holocellulose and lignin isolation from reacted wood, by the sodium chlorite and sulphuric acid procedures respectively followed by Kjeldahl nitrogen analysis, Rowell (1) was able to establish the DS by bonded urethane in the lignin and holocellulose fractions.

The research reported in this paper forms a small part of a detailed study of kinetics and mechanism in wood-isocyanate reactions and is intended to illustrate how useful topochemical information can be abstracted from a WPG versus time (t) 'reaction profile' (Figure 1) obtained from whole wood.

Provided such a profile is obtained under conditions of excess isocyanate then the interpretation of the gross shape of the curve is that the rate of reaction decreases as hydroxyl is depleted. Furthermore, in theory, such a curve results from the summation of a family of curves each representing the reaction of an individual component of the wood e.g.lignin and holocellulose.

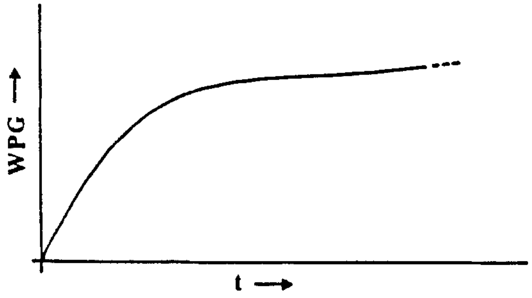


FIGURE 1 TYPICAL 'REACTION PROFILE' FOR WHOLE WOOD
(Formally a plot of the integrated rate equation)

If the profile for whole wood can be split into its component curves then information about the rate and extent of reaction within each fraction can be gained. The research reported in this paper illustrates such an analysis based on the reaction of Scots pine (Pinus sylvestris) with n-butyl isocyanate.

MATERIALS & METHODS

Scots pine (Pinus sylvestris) sapwood blocks 12 x 12 x 5 mm (radial x tangential x longitudinal), prepared from a single board, were solvent extracted by refluxing in toluene/acetone/ethanol (4 : 1 : 1 vol./vol.) for 4 hours. All blocks were oven dried (OD) to constant weight.

Experimental procedures were designed to exclude water and minimize errors in measuring reaction time associated with 'warm up' or cooling periods. Pre-heated blocks (OD condition at ~ 105° C) were transfered quickly (cooling by about 5° C) to a reaction flask containing an amount of pre-heated n-butyl isocyanate : anhydrous pyridine mixture (1 : 2 vol./vol.) sufficient to provide a three-fold excess of isocyanate over total hydroxyl groups (calculation based on data of Table 1).

TABLE 1

Assumed Chemical Composition of Extracted Scots Pine

Component	% of OD weight of whole wood	Molecular Weight of monomer unit	Mean no. of -OH per monomer unit
lignin	28(2)	194(1)	1.16(1)
holocellulose	72(2)	-	-
cellulose	40(2)	162	3
hemicellulose	32(2)	-	-
hemicellulose hexosans	17(1)	162	~ 3
hemicellulose pentosans	15(1)	132	~ 2

The reaction flask, fitted with thermometer, reflux condenser and drying tube ($CaCl_2$ and silica gel), was heated to 100° C ± 0.5° C in a thermostated oil bath. Blocks were removed (4 replicates per removal) at measured times and plunged into acetone at ambient temperature to stop the reaction. Blocks were cleaned by refluxing in acetone for 3 hrs. and oven dried at 105°C to constant weight. Infrared spectra recorded of flour produced from blocks after this procedure showed the total absence of the strong absorption characteristic of -N=C=O at $\sim 2250\ cm^{-1}$. Controls were reacted as above in anhydrous pyridine only. The experiment was duplicated (I and II of Table 2).

RESULTS

Results are given in Table 2 and illustrated in Figure 2.

ANALYSIS AND DISCUSSION

The analysis of the reaction profile (Figure 2) was approached in the following manner:-

TABLE 2

Time Dependence of the n-Butyl Isocyanate-wood Reaction

Reaction Time (Hrs.)	WPG mean of 4 blocks (1 SD)		Mean WPG of I & II (SD) (see Fig.2)
	Duplicate I	Duplicate II	
0	0	0	0
0.5	12.3 (0.2)	12.8 (0.2)	12.6 (0.3)
1	18.9 (0.1)	19.3 (0.5)	19.1 (0.4)
2	25.7 (0.1)	26.1 (0.4)	25.9 (0.4)
3	30.2 (0.3)	30.9 (0.5)	30.5 (0.5)
4	33.2 (0.5)	34.1 (0.4)	33.6 (0.6)
5	35.9 (0.7)	36.2 (0.2)	36.1 (0.5)
6	38.5 (0.2)	38.8 (0.7)	38.7 (0.5)
7	40.2 (0.3)	40.2 (0.3)	40.2 (0.3)
8	41.6 (0.3)	41.6 (0.4)	41.6 (0.3)
10	43.9 (0.5)	43.9 (0.4)	43.9 (0.4)
12	46.0 (0.5)	46.0 (0.1)	46.0 (0.3)

Step 1 - A model, based on defined assumptions, was set up to predict the form that a 'best-fit' equation might take

Step 2 - The experimental data were fitted to an equation of that form using a standard commercial software package (3) on a mainframe computer, the 'degree of fit' being used to accept or reject the model.

Step 3 - The fitted equation obtained in step 2 was split into its components to yield the integrated rate equations of the individual hydroxyl populations.

Of various attempted analyses, the best, i.e. that yielding the lowest order (that containing the least no. of terms in t.) equation which fits the data satisfactorily, is described below:

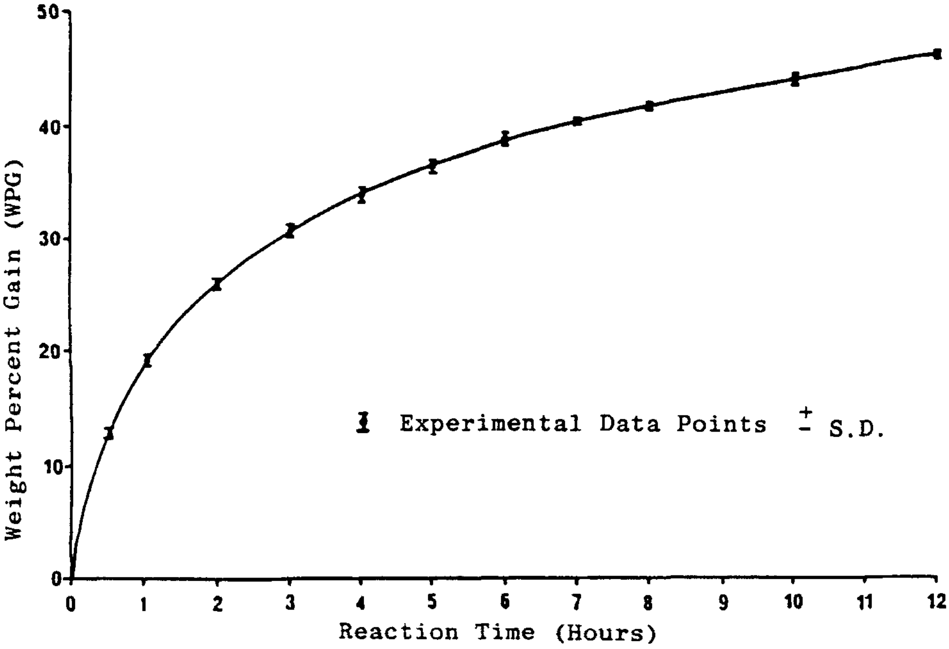
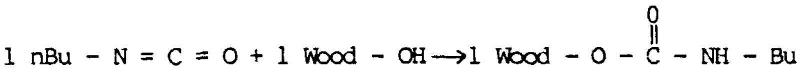


FIGURE 2 REACTION PROFILE OF n-BUTYL ISOCYANATE MODIFIED SCOTS PINE (Mean of replicates I & II)

Step 1 - The Model

The following assumptions are defined:-

(a) Under the conditions of the experiment (excess isocyanate) the reaction profile for whole wood is controlled solely by depletion of hydroxyl resulting from carbamate (urethane) formation in accordance with the stoichiometric equation....



$$1\ \mathrm{nBu-N=C=O} + 1\ \mathrm{Wood-OH} \longrightarrow 1\ \mathrm{Wood-O-}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{-NH-Bu}$$

(b) In terms of reactivity <u>two</u> principal populations of hydroxyl are assumed, these being...

(i) lignin
(ii) holocellulose

...hydroxyl reactivity being controlled by accessibility and/or hydrogen lability.

(c) The reaction is 1st order with respect to hydroxyl in each component.

(d) Both components start to react at t=0 i.e. neither displays an induction period.

From these four assumptions it is easy to show that the integrated rate equation representing the variation of weight percent gain of the whole wood (WPG_w) with time (t) will be of 'double exponential' form...

$$WPG_w = A - Be^{-Kt} - Ce^{-Lt}$$

...where A, B, C, K and L are positive constants and, as a consequence of assumption (d), the curve must pass through the origin such that A = B + C.

Step 2 - Curve Fitting

Fitting an equation of the double exponential form to the experimental data (column 4, Table 2), in the manner described above, yields equation [1A]. All constants are given to the nearest 2 decimal places although the plots of Figure 3 and the R^2 value were obtained using the full 5 decimal place output of the curve fitting program.

$$WPG_w = 49.48 - 16.53\, e^{-1.75t} - 32.94\, e^{-0.18t} \qquad [1A]$$

The degree of fit is illustrated graphically (Figure 3) and may be quantified simply by calculation of the coefficient of determination R^2 (in a manner analogous to the simpler linear

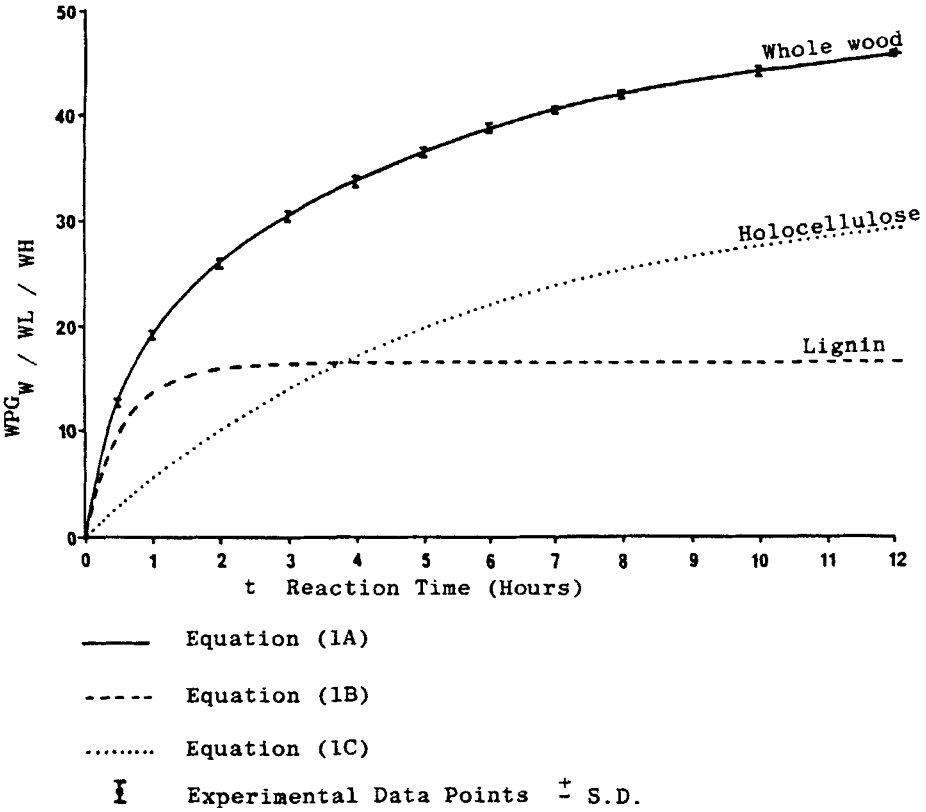


FIGURE 3 PLOT OF REGRESSION EQUATIONS

case). Assuming there is no error in measuring the independent variable t, R^2 may be calculated using equation [2]...

$$R^2 = 1 - \frac{\sum (Yi - \hat{Y}i)^2}{\sum (Yi - \bar{Y})^2} \qquad [2]$$

Yi = measured values of WPG_W
$\hat{Y}i$ = estimated WPG_W values from [1A]
$\bar{Y}$ = mean of measured WPG_W values

...yielding a value of $R^2 > 0.999$. It is apparent therefore, both visually and statistically, that the degree of fit is sufficient to accept the model.

Step 3 - Splitting Into Components

It can be shown that a double exponential equation of the form

$$Y = A - Be^{-Kx} - Ce^{-Lx}$$

(where A, B, C, K and L are positive constants and $A = B + C$), representing a curve of positive slope passing through the origin, can be represented uniquely as the sum of two single exponential curves, each of positive slope passing through the origin, of the form $y = a - ae^{-kx}$

i.e. if $Y = Y_1 + Y_2$

then by inspection $Y_1 = B - Be^{-Kx}$, $Y_2 = C - Ce^{-Lx}$.

By analogy with the model (step 1) the parameter WPG_W may split into components WPG_{WL} and WPG_{WH} (the contribution to WPG_W resulting from reaction within the lignin, L, and holocellulose, H, respectively) such that...

$$WPG_W = WPG_{WL} + WPG_{WH}$$

The remaining task is to assign the exponential terms of equation [1A] to lignin and holocellulose. In an equation of the form $y = a - ae^{-kx}$, 'a' represents the maximum y value as x tends to infinity, in this case the maximum theoretical WPG contribution which can be attained. Calculation, based on the data of Table 1 shows that substitution (under the conditions of assumption [a] step 1) of all lignin hydroxyls would result in a WPG contribution of 16.6%. Since 16.6% represents the maximum possible value of WPG_{WL} the 16.53 asymptote term of equation [1A] may be assigned to lignin and by elimination the 32.94 asymptote term of equation [1A] may be assigned to reaction within the holocellulose. The single exponential equations representing the contribution of reaction within the lignin and holocellulose to the observed weight gain of whole wood may thus be written as:-

$$WPG_{WL} = 16.53 - 16.53\,e^{-1.75t} \qquad [1B]$$

$$WPG_{WH} = 32.94 - 32.94\,e^{-0.18t} \qquad [1C]$$

Plots of equations [1B] and [1C] are shown in Figure 3. Calculation, as for lignin, shows that the maximum possible value of WPG_{WH} = 127.2% which is considerably greater than the observed WPG_{WH} asymptote value of 32.9%. This result implies, in contrast to the lignin, that the reactivity of the holocellulose hydroxyls is restricted in some way. This may result from either:

(i) limited hydroxyl accessibility (especially in crystalline cellulose).....

(ii) differences in reactivity of primary and secondary hydroxyl groups caused by differences in hydrogen lability.....

or a combination of both factors. Assuming that only accessibility is a limiting factor then applying Rowell's (1) assumption, that 35% of cellulose hydroxyls and 100% of hemicellulose hydroxyls are available for reaction, yields a maximum WPG_{WH} value of 79.4% still considerably greater than the observed value of 32.9%. Hearon, Hiatt & Fordyce (4) have observed that the pyridine catalysed reaction of methyl and ethyl isocyanate with cellulose and cellulose acetate is slow and incomplete, suggesting that even in homogeneous conditions (in the case of the acetate) full substitution of all available hydroxyls does not occur. These workers recorded a maximum urethane D.S. of 1.02 and 0.16 with cellulose acetate (acetate D.S. 1.66) reacted with methyl and ethyl isocyanate respectively, and observed 'little or no reaction' with cotton linters and regenerated cellulose reacted under similar conditions. More recently it has been shown by Banks (5) that it is relatively easy to react the primary (C_6) hydroxyl of methyl glucoside with n-butyl isocyanate to form the corresponding urethane. Reaction with the secondary (C_2, C_3 and C_4) hydroxyls has proved more difficult to achieve however. Assuming therefore, in addition to limited accessibility, preferential reactivity at only 1 hydroxyl per sugar unit, in both accessible cellulose and hemicellulose, yields a maximum WPGwh value of 30.2% in closer agreement with the observed value of 32.9%.

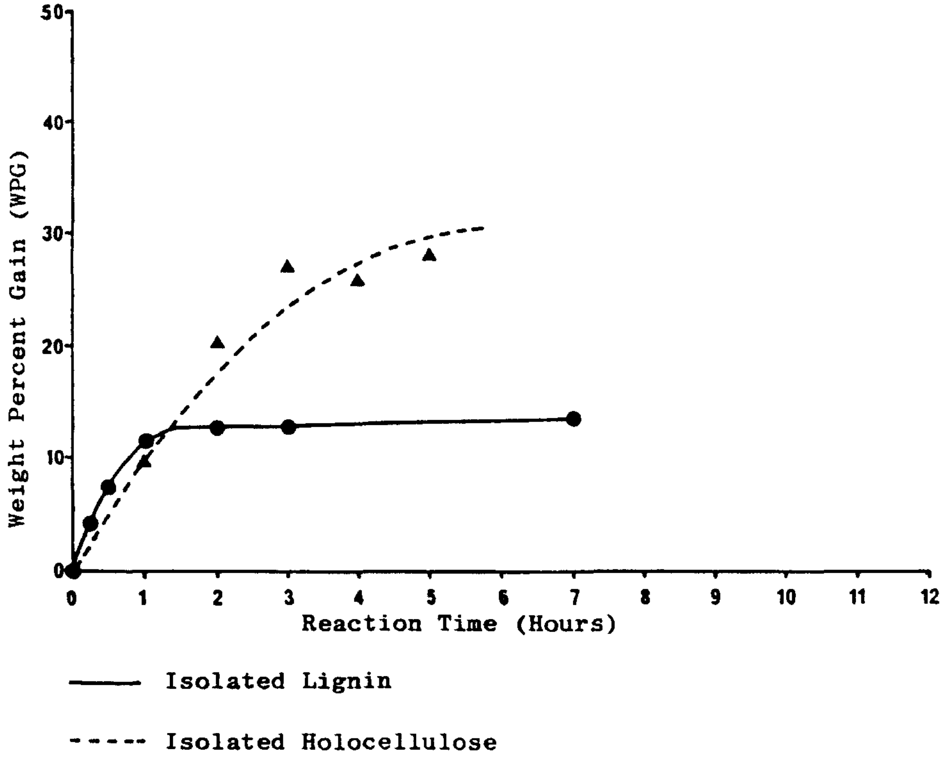


FIGURE 4 REACTION PROFILE OF ISOLATED BROWN ROT LIGNIN & SODIUM CHLORITE HOLOCELLULOSE MODIFIED WITH n-BUTYL ISOCYANATE

WPG values expressed as that value which would be observed in whole wood assuming 28% lignin and 72% holocellulose (W/W)

Comparison of the rate constants implicit from the single exponential assignments (equations [1B] and [1C]) shows that the lignin reacts (i.e. contributes to the observed WPGw) about 10 (1.75/0.18) times faster than the holocellulose.

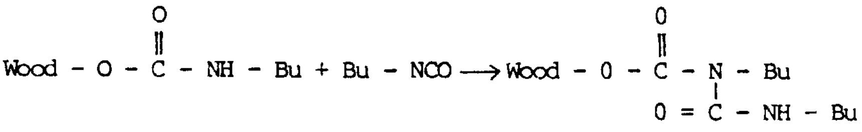
The maximum WPG_{WL} and WPG_{WH} results (16.5 and 32.9% respectively) are broadly consistent with preliminary observations made by us on reaction of isolated lignin (brown rot lignin) and holocellulose (prepared by the sodium chlorite method, Wise, Murphy and D'Addieco (6)) under the same conditions as those described above (Figure 4). Perhaps not surprisingly the initial rates of reaction of isolated lignin and holocellulose do not exhibit the order of magnitude difference suggested by the whole wood analysis since accessibility factors are altered by isolation. Furthermore, it should be recognised that the isolated lignin may have hydroxyl functionality different to that in the native state and the products of reaction may become partially soluble in the reaction medium resulting in low apparent WPG values.

The results of Rowell (1), obtained by analysis of the modified lignin and holocellulose isolated from whole wood reacted with methyl isocyanate, although expressed only as a function of WPG and not as a function of time, support the conclusion that native lignin reacts faster and to a higher D.S. than does the holocellulose.

Further Points

The values and conclusions obtained by this analysis should be treated as 'order of magnitude' results since their precision depends on the numerous assumptions made, the particular conditions of the experiment and the arbitrary 'end point' of the reaction profile. A different set of assumptions, conditions and choice of 'end point' will yield slightly different values. In addition, whilst there is no reason to suppose that this 2 component analysis is not essentially correct, it is probable that the reaction profile contains information of a higher order. For example it is feasible that the various hydroxyl types in lignin (primary, secondary, enolic, phenolic) might react at different rates and thus be represented by separate exponential equations. In the same way the hydroxyls of cellulose might be distinguishable from those of the hemicelluloses. Unfortunately the limited number of data points, obtained by the method given above, do not lend themselves to analysis in terms of an equation of higher order e.g. 'triple' or 'quadruple' exponential.

It should be stressed that the asymptote values generated by this analysis are NOT 'real', i.e. the reaction of whole wood under these conditions does NOT stop when a WPG of 49.5% is reached. It has been observed by us that the WPG continues to rise slowly well beyond 49.5%, e.g. a WPG of 65.1% being observed after reaction for 122 hrs. under these conditions. Presumably this results from slow penetration into crystalline zones aided by reaction induced swelling, and via slow reaction of less labile hydrogen sites. WPG's up to and <u>beyond</u> the theoretical maximum of 143.8% (calculation based on data of Table 1) for complete hydroxyl substitution by urethane have also been observed, at which point the wood has disintegrated into discrete fibres. This suggests that secondary reaction to form allophanate is possible.



$$\text{Wood}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{NH}-\text{Bu}+\text{Bu}-\text{NCO}\longrightarrow\text{Wood}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\underset{\underset{\text{O}=\text{C}-\text{NH}-\text{Bu}}{|}}{\text{N}}-\text{Bu}$$

allophanate

Under different catalytic conditions, where reaction occurs much faster, the time scale of a reaction profile is compressed causing the asymptote at a WPG of about 50% to appear as an inflection in an otherwise smooth curve. In addition, above 50% WPG, secondary physical factors complicate the reaction profile and limit its reproducibility e.g. blocks split at random causing rapid, non-reproducible, exposure of new hydroxyl populations and concomitant increases in reaction rate making the interpretation of profiles in this WPG region difficult.

SUMMARY AND CONCLUSION

The rate of reaction of Scots pine (Pinus sylvestris) with n-butyl isocyanate was followed by measuring weight percent gain (WPG) as a function of time (t). Mathematical analysis of the resulting reaction profile yielded the following equations:

[1A] $WPG_W = 49.5 - 16.5e^{-1.75t} - 32.9e^{-0.18t}$ WHOLE WOOD

[1B] $WPGH_{WL} = 16.5 - 16.5e^{-1.75t}$ LIGNIN

[1C] $WPG_{WH} = 32.9 - 32.9e^{-0.18t}$ HOLOCELLULOSE

Calculation showed that the lignin asymptote could be explained in terms of reaction of all available hydroxyls to form bonded urethane. Explanation of the holocellulose asymptote however, required some assumptions limiting the accessibility of cellulose to 35% and reactive hydroxyl density to 1 per sugar unit on both cellulose and hemicellulose. Comparison of the rate constants implicit from equations [1B] and [1C] indicated that the lignin reacts approximately 10 times faster than the holocellulose.

The techniques described here should be applicable to other reagent-wood reactive systems and may be used to complement the normal 'react - isolate - analyse' or 'isolate - react - analyse' procedures for establishing the topochemistry of chemical modifications.

ACKNOWLEDGEMENTS

The authors are grateful for the support given by Professor L. Roche in encouraging this work to proceed and to the S.E.R.C. for funding the research.

REFERENCES

1. R.M. Rowell. Wood Science 13(2), 102 (1980).
2. E. Sjostrom, Wood Chemistry. Fundamentals and Applications. Academic Press Inc.,New York. (1981)
3. Maximum Likelihood Program (MLP). Lawes Agricultural Trust, Rothamsted Experimental Station (1980)
4. W.M. Hearon, G.D. Hiatt & C.R. Fordyce. J.Am.Chem.Soc. 65, 829 (1943)
5. W.B. Banks, Bangor Department of Forestry & Wood Science - personal communication.
6. L.E. Wise, M. Murphy and A.A. D'Addieco, Paper Trade Journal, 122, No.2, 35 (1946)