Kinetics of Delignification in NSSC Pulping of Eucalyptus Spp. and Validity of H-Factor

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A kinetic study on NSSC pulping of Eucalyptus hybrid (mainly tereticornis) showed that rate of delignification followed a pseudo first order rate law with respect to both lignin and sulphite. The data on NSSC pulping of Eucalyptus obliqua as reported by Higgins et al[1], when analysed on a kinetic basis gave similar results. The concept of H-factor meter for representing time and temperature as one variable was found satisfactorily applicable to NSSC pulping of both the above species. The fact that NSSC pulping of aspen wood[2] and beech wood[3] also exhibited excellent correlation between H-factor and yield, makes it adequately apparent that NSSC pulping of hardwoods like kraft process can be controlled by using H-factor meter as a device to represent time temperature as one variable.

INTRODUCTION

The realities about resource short-world and growing conciousness about quality apecifications of the products in demand have diverted the attention of research laboratories to evolve the technology for obtaining high yield pulps and to develop process control parameters, so as to produce specified end product without any appreciable impairment in its properties throughout.

Neutral sulphite semi-chemical pulping is one of the processes in reference to high yield pulping. During last decade a considerable amount of interest has grown to study the operational parameters and their optimation during NSSC pulping process. The question of delignification is central to the whole process, since essential properties of fibre vary greatly as lignin is removed. The importance of developing quantitative relationships among pulping variables during chemical treatment has been long recognised. A knowledge of the kinetics of delignification reaction is essential for such purposes. Although considerable accounts have been given on NSSC pulping of eucalyptus species in Australia, the delignification process has not been visualised on a kinetic basis, and whether time and temperature can be combined to be represented by one numerical value (H-factor) has also not been evaluated.

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It was therefore of interest to study the kinetics of NSSC pulping of Eucalyptus species, plantations of which have been raised in our country, and examine the validity of H-factor concept for representing time and temperature as one variable for NSSC process, so as to provide process control measures such as H-factor meter. With these aims kinetics of NSSC pulping of *Eucalyptus hybrid* was followed with respect to lignin and sulphite and the data on NSSC pulping of *Eucalyptus obliqua* reported by Higgins et al[1] was examined on a kinetic basis.

EXPERIMENTAL

Raw Material

Eucalyptus hybrid (mainly tereticornis) of 10 years age having the following composition was used in this study.

Lignin	28.0%
Holocellulose	71.0%
Pentosans	15.2%
Alpha Callulose	41.7%(the persentages are expressed on oven dry wood means).

The wood was chipped in pilot plant Waterous 4 knife chipper. After screening the chips were air dried and packed in paper bags each containing 200g oven dry weight. In this work it was considered sufficient to use chips for which the average chip size and moisture content were constant.

Cooking Liquor

Cooking liquor was prepared by dissolving weighed amounts of sodium sulphite (LR, BDH) and sodium carbonate (AR, BDH) in the proportion 4 to 1 in distilled water. The concentration of the liquor was estimated as total sulphurdioxide.

Cooking Cycle

Wood chip (200 g.o.d.) were taken in a 5 L rotary autoclave. Required amount of cooking liquor was added into the autoclave. The water was used for dilution to maintain a ratio of 1 to 6 between chips and liquor in all the experiments. The following cooking cycle was employed:

Time from room temperature to 110°C	60 Min.
Time at 110°C	60 Min.
Time from 110°C to maximum cooking temperature level	30 Min.

Cooking to different levels of delignification was accomplished by varying the cooking time at maximum temperature level (150° to 170°C) used.

Refining

The semi-cooked chips were refined in 12" Sprout Waldron refiner to produce pulp of different freenesses. The refined pulp was washed free of alkali on a terylene cloth and stored in polythene bags for further analysis and strength determination.

Pulp Evaluation

Pulp yield was determined by weighing the wet pulp lot and taking two representative samples of 50 g. from the lot which were dried in an oven at 105 ± 5°C for 6 hours. The dried samples were weighed and percentage yield determined by simple calculation of percentage moisture in 50 g. of representative sample and conversion to the total weight of the wet lot of pulp. Lignin content was determined according to *Tappi* Standard Method. The strength properties of pulps were tested after conditioning the hand sheets (about 60 gsm.) at $65 \pm 2\%$ RH and 27 ± 1°C. The sheets were made from the refined pulps (without any further beating) on British Sheet making machine.

RESULTS

The pulping conditions, results of pulp analysis and strength properties of pulps are recorded in Table 1. Also the data of Higgins *et al*[1] on NSSC pulping of *Eucalyptus obliqua* used for comparative kinetic analysis and H-factor treatment are given in Table 2.

Discussion

Rate of Delignification

A plot of logarithm of residual lignin in pulp (on wood basis) with time of reaction gave a straight line correlation (Fig. 1):

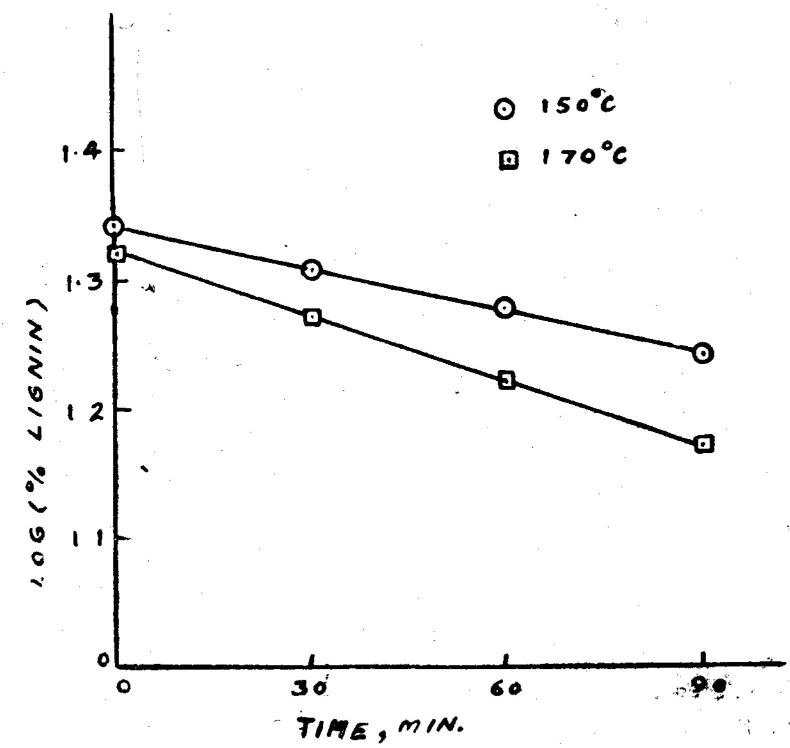

Fig. 1. First Order Rate of Delignification (E Hybrid)

TABLE—1

Cooking Conditions and Pulp Properties of NSSC Pulps from Eucalyptus Hybrid

Temp. °C	Time at temp. min.	Pulp yield %	Freeness CSF	Residual SO_2 % on wood	Klason Lignin in pulp, % on wood	Strength Properties Breaking length km.	Burst factor	Tear factor
150	0	90.0	180	3.3	22.04	2.6	6 6	33.0
150	30	83.0	255	2.0	20.33	2.4	7.2	31.1
150	60	81.0	140	1 5	19 36	4.7	17 2	41.3
150	90	77.0	212	1 0	18.0	5 0	20.2	42.5
170	0	88.0	280	3.0	21.20	2 9	8.3	30.6
170	30	83.0	200	1 6	19.00	4.2	18 0	47.0
170	60	80.00	200	1.1	16.88	6.0	25 0	42.0
170	90	68 0	240	0.5	15 00	5 5	21.0	45.0

Chemicals as SO_2 6% (on o.d. woods; pH of cooking liquor 8.0; Time from room temp. to 110°–60 min ; Time at 110°C; O° min ; Time from 110°C to maximum temp. 30 min

TABLE—2

Pulp yields and Halse Lignin, in NSSC pulps prepared under different cooking conditions from a regrowth tree of Eucalyptus Obliqua (Higgins et al)

Time at temp. (min)	Cooking temp 150°C Time to temp. 106 min Yield	Lignin	H-factor	160 113 Yield	Lignin	H-factor	170 120 Yield	Lignin	H-factor	180 140 Yield	Lignin	H-factor
0	86.2	18.9	—	84 8	17.1	—	80.0	14.7	—	75.9	13.1	—
15	—	—	2534	—	—	5259	80 6	13.1	6668	75.8	13 3	13546
30	85.9	16.2	4364	81.5	15.3	8919	74.1	11.6	10343	72.2	11 0	20311
60	81.1	16.7	8024	81.8	14.2	16239	74.3	10.9	17693	67 8	9 2	33841
120	81.7	14.0	15344	77.4	11.8	30879	70.4	18.9	32393	66.5	7.9	60800
240	76 3	12.3	22664	72.4	19.7	45519	62.8	6.9	61793	60.1	7.8	11092
360	80.6	13.1	—	72.0	10.4	—	—	—	—	—	—	—

*All results expressed as a percentage of the original oven dry wood.

showing thereby that rate of delignification in NSSC cooking of *Eucalyptus* hybrid followed a pseduo first order kinetics with respect to lignin.

A kinetic treatment of the data on NSSC pulping of *Eucalyptus obliqua* reported by Higgins *et al*[1] gave similar results (Fig. 2) with an additional information that after 2 hrs. of reaction time the rate of delignification slowed down. This observation of slowing down of rate of delignification at later stage of cooking (in the data of Higgins *et al*) is not uncommon in literature. It has been also reported by Wilder and Han[2] for NSSC pulping data of Walter and May on aspen wood. Recently Basu et al[3] have also reported that delignification in NSSC pulping of beechwood followed a first order kinetics in terms of lignin concentration, the rate becoming slower at later stage of reaetion. In the present investigation of *Eucalyptus* hybrid NSSC pulping, the slower rate portion was not observed because the reaction was studied only upto 90 min. and the slowing down of reaction occurs only after 90 min.

The values of first order rate constant for the delignification reaction in case of *Eucalyptus* hybrid and *obliqua* were calculated from the slope of the straight lines in Figs. 1 and 2 respectively, and are recorded in table 3. The energy of activation was found to be 24.6 and 25.0 k cals/g mole for

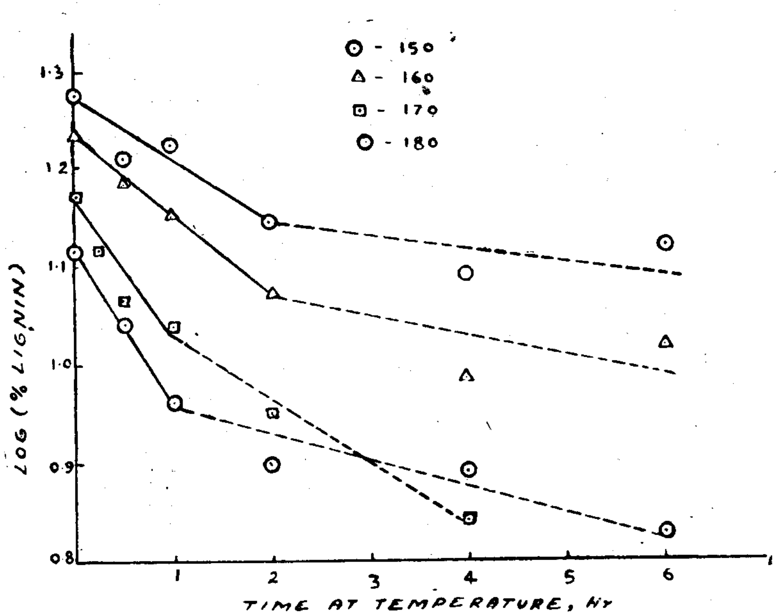

Fig. 2. First Order Rate of Delignification (E. Obliqua)

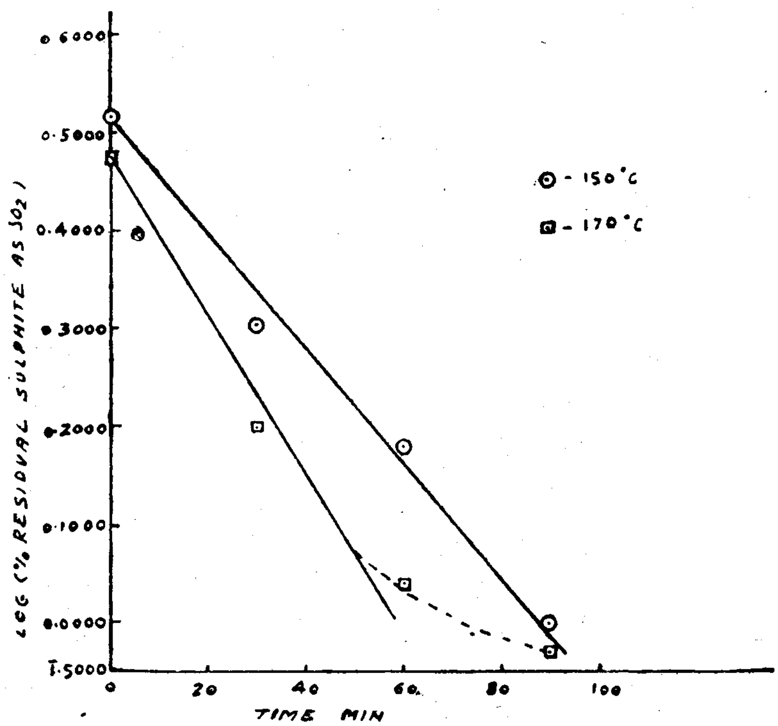

Fig. 3. First Order rate Sulphate Consuption (E. Hybrid)

TABLE—3

First order Constants of Delignification Reaction

Species	Temp °C	Rate constants $k_1 \times 10^3$, hr
Eucalyptus hybrid	150	68 0
Eucalyptus obliqua	150	28.6
	160	34.3
	170	56.4
	180	69.4

Eucalyptus hybrid and–*obliqua* respectively. Basu et al[3] have reported a value of 25.6 k cals/g mole for beechwood NSSC pulping reaction.

Rate of Sulphite Consumption

The rate of sulphite consumption is represented in Fig. 3 and 4 for *Eucalyptus hybrid* and *Eucalytus obliqua* respectively. It is seen that the consumption of sulphite also followed a first order kinetics with respect to sulphite concentration. Here also in case of *Eucalyptus obliqua* the rate of sulphite consumption slowed down after 1½ hr. reaction.

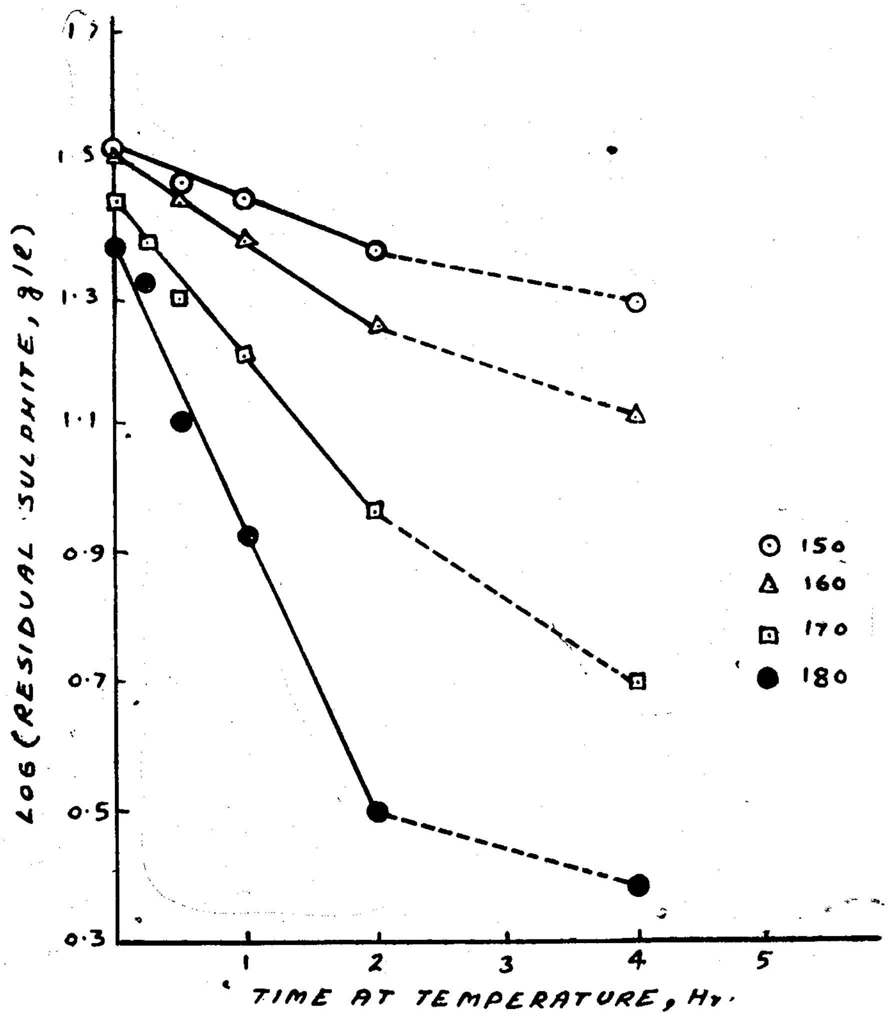

Fig. 4. First Order Rate of Sulphite Cousumption (E. Obliqua)

Overall Rate Law

The above discussions revealed that NSSC pulping process of both *Eucalyptus hybrid* and *Eucalyptus obliqua* followed a pseudo first order kinetics with respect to lignin and sulphite. This can be written as follow :

Rate of delignification $-\frac{d[L]}{dt} = k_1 [L]$

Rate of disappearance of $-\frac{d[S]}{dt} = k'_1 [S]$

Combining these two equations the overall rate law can be written as

$$-\frac{d[L][S]}{dt} = k_1 k'_1 [L][S]$$

Where,

$k'_1 > k_1$

Validity of H–Factor Concept

Rate Constants and H–Factor Calculation

It has been observed above that the rate of delignification in NSSC pulping followed a first order kinetics. Employing this finding the value of the rate constants at various temperature levels have been calculated by Basu et al[3] (the data are reproduced in Table 4).

TABkE—4

Rate Constants for NSSC Pulping at Various Temperatures

(Basu et al[3])

Temperature °C	Rate constants for NSSC Pulping
T	R
100	1.00
110	1.10
120	6.10
130	13.50
140	27.20
150	61.00
170	245.00
180	451.00

Therefore, in this kinetic treatment of data on NSSC pulping *Eucalyptus hybrid* (as recorded by the authors and *Eucalyptus obliqua* (as reported by Higgins et al[1]), the values of rate constants given by Basu, et al were used for calculating the H-factor.

The H-factor is equal to the factor obtained by multiplication of the average rate constant and time interval. The values of H-factor for *Eucalptus hybrid* schedule are recorded in Table 5 and those for *Eucalptus obliqua* in Table 5.

TABLE—5

H-FACTOR FOR NSSC PULPING OF EUCALYPTUS HYBRID

Tem. °C	Temp. at temp.	Rate constant B	H-factor Rav. xtime interval
150	0	61	1830
150	30	61	
150	60	61	3760
150	80	61	5590
170	0	245	7350
170	30	245	15700
170	60	245	2350
170	90	245	

Correlation of H-factor with degree of delignification and sulphite consumption

Percentage of lignin and residual sulphite concentration, when plotted against H-factor gave curves as in Fig. 5 to 8. It will be seen from these figures that the points for sulphite concentration and lignin percentages lie on or fairly close to one single smooth curve irrespective of time-temperature schedule. This shows that the concept of H-factor to represent time and temperature as one variable is applicable to NSSC pulping of *Eucalyptus* hybrid and *Eucalyptus obliqua* also, and therefore can be used for controlling the degree of delignification during the cooking by adjusting time according to temperature or vice versa.

Conclusion

The fact that NSSC pulping of aspen wood[2] and beach wood[3] also exhibited excellent correlation between H-factor and yield makes it adequately apparant that NSSC pulping of hardwoods like kraft process can be controlled by using H-factor meter as a device to represent time and temperature as one variable.

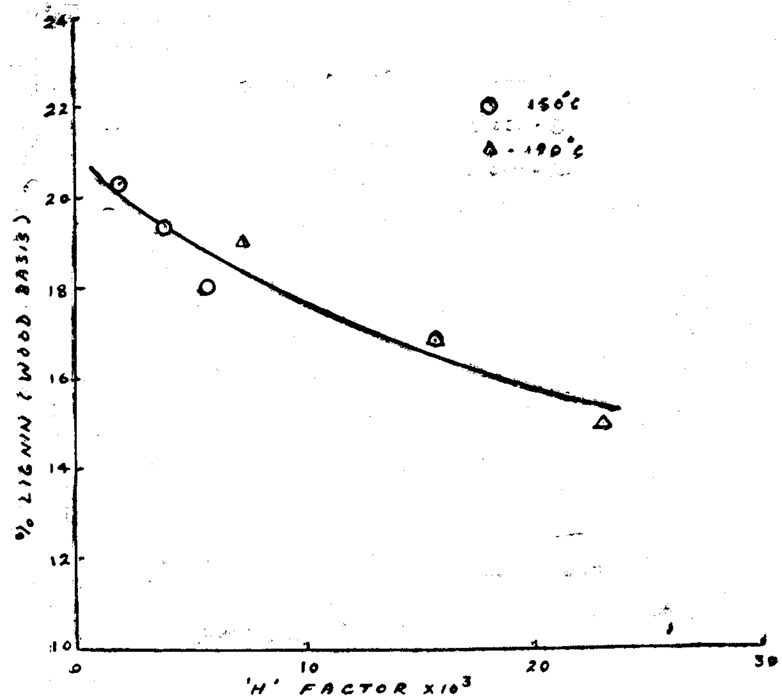

Fig. 5. 'H' Factor Versus Percentage Lignin (E. Hybrid)

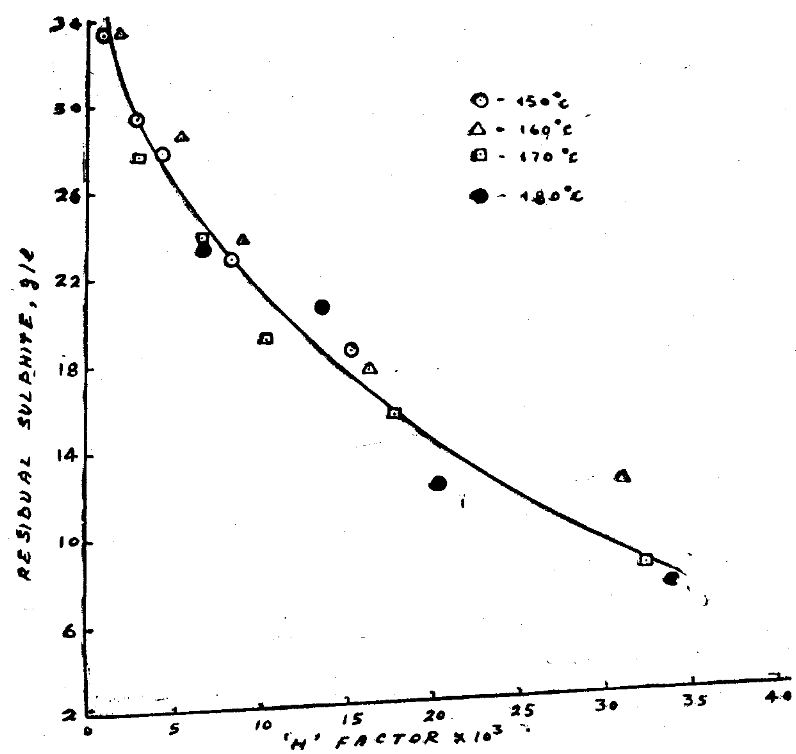

Fig. 6. 'H' Factor Versus Percentage Lignin. (E. Obliqua)

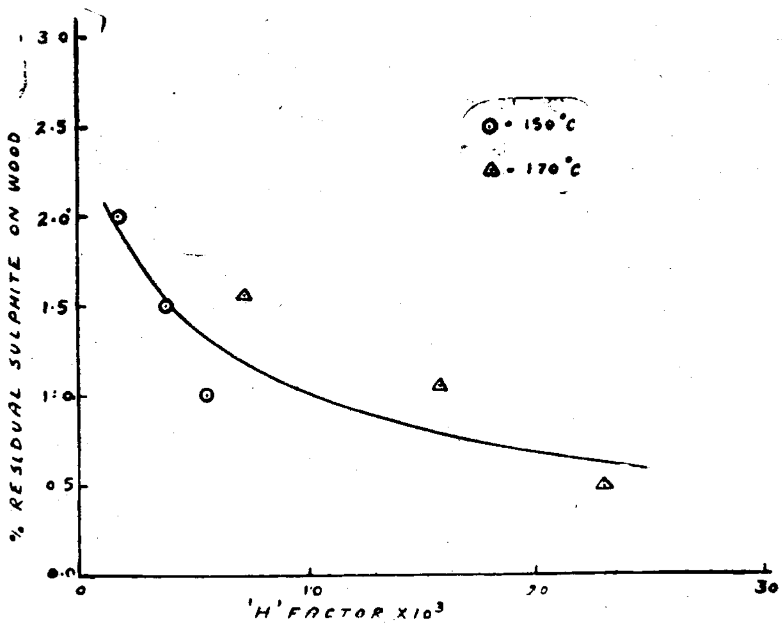

Fig. 7. 'H' Factor Versus Residual Sulphite (E. Hybrid)

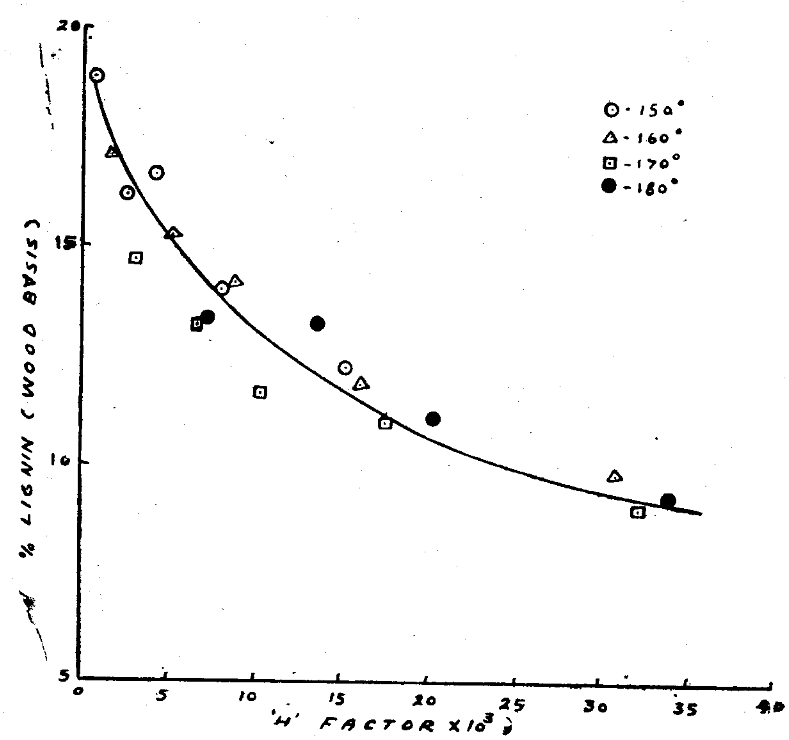

Fig. 8. 'H' Factor Versus Residual Sulphite Concentration (E. Obliqua)

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