Validation of and deviation in Lin et al's kappa prediction equation as verified for E. tereticornis, E. grandis and D. strictus

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SUMMARY

The uniqueness of Lin *et al*'s (1) suggested Kappa prediction equation is its universal application to all types of hardwood species. The equation relates the Kappa number to H-factor, alkali to wood ratio, liquor to wood ratio and a co-efficient called Species Coefficient. By evaluating the Species Coefficient for any individual species the Kappa number of the pulp could be predicted, as the knowledge of other parameters is known. This work attempts to validate Lin *et al*'s equation by verifying it with three common Indian raw materials viz., *E. tereticornis, E. grandis* and *D. strictus*, out of which *D. strictus* is nonwood. While the equation holds good for *E. tereticornis* and *D. strictus*, for all Kappa number values with high Correlation Coefficient Values, (above 0.98), in case of *E. grandis*, is limited only to Kappa number ranges of 15-25. The evaluated species Coefficient Values for *E. tereticornis*, *E. grandis* and *D. strictus* is respectively at 2150, 1267 and 2102. The residual distribution and deviation from the Calculated Species Coefficient has been plotted for the species tested.

Time and again attempts have been made to relate pulping process outputs such as pulp yield and Kappa number to input variables like time, temperature, alkali to wood and H-factor etc.[2-5]. These mathematical models help to monitor and control the pulping operation specially to get a constant Kappa batch cooks. Kerr[6] derived a Kappa prediction equation, in which the residual lignin content is equated to the Kappa number of the pulp. The other variables included to the equation are the initially applied Effective alkali and the total H-factor. As Rydholm[7] pointed out, the permanganate number (to an extent Kappa number too) cannot be linearly correlated to the residual lignin content of the pulp, the usefulness of Kerr's equation is handicapped to solve practical problems. Service[8] developed a Kappa prediction equation using six different parameters inculding chip size. Many other attempts were also made to relate either the Kappa number or yield or both to the input variables[9-13].

Lin et al[1] proposed a Kappa prediction equation claiming its universal application to all species of Hardwoods. While doing so they have introduced a proportionality constant in their derived equation, calling it the "Species Coefficient". Since the "Species Coefficient" for individual raw material has to be calculated to make use of their equation in predicting the Kappa number of pulp obtained from the raw material under specified conditions, the Species Coefficient in a way gives the relative pulping merits of the tested raw material over the other species (whose Coefficiant is already known). Unlike the other proposed equations, Lin et al's equation is linear in character and could be used relatively easily because the only unknown variable in the prediction equation is the Species Coefficient. The better side of this equation is its applicability to mixed Hardwood

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pulping also, and hence of particular interest to Indian context as mixed Hardwood pulping has already been an accepted vogue.

The reported work of ours, is confined to find out the Species Coefficient of hitherto mainly used three Indian raw materials viz. *E. tereticornis*, *E. grandis* and *D. Strictus* (Bamboo), to verify the versatility of Lin *e —al's* equation and also to evaluate the deviation in the equation, if any. In the tested raw materials *D. strictus* is a non-wood species.

RESULTS AND DISCUSSION

Lin *et—al's* equation in its numerical form is written as :

$$Ka = (KD_0^{0.135}) / Q_0^{1.171} H^{0.175}) \quad \ldots\ldots\ldots \quad (1)$$

Where Ka—Kappa number, K—Species Coefficient, D_0 - liquor to wood ratio, Q_0—alkali to wood ratio, H—H-factor.

Vroom's H-factor[13], is a function of time and temperature and has a relative delignification rate of 1 at 100°C, calculated from the assumed activation energy for delignification during kraft cook as 32,000 Kcal/kg. mole; and the rate increase is an exponential function of temperature.

Rearranging equation (1)

$$K = Ka. Q_0^{1.171} H^{0.175} / D_0^{0.136} \quad \ldots\ldots\ldots \quad (2)$$

D_0 carries a power of 0.136, approaching a value of zero and D_0 if raised gives a value equal to 1. In other words the influence af D_0 i.e. the bath ratio in the Species Coefficient calculation and hence in the Kappa prediction during pulping is for all practical purposes can be said to be minimal and could be kept at a constant ratio. It has been fixed at 4:1 in our studies.

This alters the equation (2) as given below:

$$K = Ka\ Q_0^{1.71} H^{0.175} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3) \text{ or}$$

$$K = Ka.\ (Q_0, H) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

From the equation (4) it is evident that Kappa number and Species Coefficient are two dependent variables, dependent on the alkali to wood ratio and H-factor, wherein the Species Coefficient is constant for any value of Kappa number obtained by manipulating Q_0, H. In other words equation (4) can be rearranged to :

$$Ka = K/Q_0^{1.171} H^{0.175} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5) \text{ or}$$

$$K = 1/Q_0^{1.171} H^{0.175} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where K is a proportionality (equation) constant depends purely on the species used. For dfferent species, the K has different values. Since Q_0 and H are inversely proportional, if a constant species Coefficient value is assumed then an increase in any one of them will decrease Kappa number. So, the raw material which has a lower Species Coefficient will result iu a pulp of lower Kappe number for a particular input of Q_0 and H, Secondly, from the power analysis of the equation (3), out of the variables, the alkali to wood ratio has a significant effect on Kappa number. It could be said that though D_0 and H carries more or less the same power, because H is in Denominator, H can effect the Kappa number more pronouncedly than the D_0 value. But among Q_0 and H, the Q_0 has a greater effect than H.

Besides. since Vroom's H-factor is a temperature-time dependent function, the H-factor can be manipulated in a distinct way mainly temperature can be raised while lowering the time to temperature (TTT) especially during the cooking of *E. tereticornis* and *D. strictus* has insignificant contribution to the Kappa number of these pulps as professed by Veeramani and Chowdhary[14]. Moreover the contribution of TTT to the total H-factor for a whole cooking cycle if not negligible, certainly not significant.

Another importat aspect of Lin *et al's* Species Coeffcient equation is that, unlike other equations as proposed by Hatton, Hatton *et al's* (1-4) it is linear in character and so a straight line fit could be obtained between the predicted and actual Kappa numbers. Furthermore the interrelation of Species Coefficient and Kappa number gives a high confident prediction of the residual lignin in the pulp. In other words, the implication of such Species Coefficient value for a particular raw material especially for Hardwoods could be explained as a supplement to the already existing physical gradation of the Hardwoods, so that such gradation can be substantiated in a more logical way.

SPECIES COEFFICIENT VALUE FOR E. TERETICORNIS :

The Species Coefficient (S.C.) value calculated from Lin *et al's* equation for *E. tereticornis* is 2150 (Table 1 & 4). The residual distribution frequency character has been plotted. (Figure 4). From the figure it is obvious that the variation from the mean (among 2150 as the mean and having a residual distribution of zero, Coefficients about 2150 has positive residual distribution and below 2150 negative residual distribution) has shown

TABLE—1 CALCULATION OF SPECIES COEFFICIENT FOR E. TERETICORNIS

Sl. No.	Cooking temperature t°C	H-factor H	Active alkali % as Na_2O Qo	Kappa Number Ka	Species Coefficient K
1*	170	750	14	41.9	2430*
2	170	750	16	31.7	2149
3	170	750	18	27.5	2140
4	170	750	20	24.5	2157
5	170	1000	14	36.7	2238
6-	170	1000	16	30.2	2154
7	170	1000	18	26.3	2153
8	170	1000	20	21.2	1963*
9	170	1250	14	33.2	2105
10	170	1250	16	28.5	2113
11	170	1250	18	23.8	2025
12	170	1250	20	23.3	2147
					= 2150

*taken into the average calculations but omitted for residual frequency distribution calculations.

–Species coefficient equation : $Ka = K\ Do^{0.36}/Qo^{1.171}\ {}^{0.175}$

–Constant conditions : Sulphidity = 20%

Liquor—to— wood ratio = 4:1.

TABLE—2 CALCULATION OF SPECIES COEFFICIENT FOR D. STRICTUS

Sl. No.	Cooking temperature t°C	H-factor H	Active alkali % as Na_2O Qo	Kappa Number Ka	Species Coefficient K
1	170	750	14	39.1	2268
2	170	750	16	31.2	2116
3	170	750	18	24.6	1914
4	170	750	20	22.7	1999
5	170	1000	14	37.4	2281
6	170	1000	16	28.7	2047
7	170	1000	18	25.0	2046
8	170	1000	20	20.7	1917
9	165	750	13	44.0	2344
10	165	750	15	34.8	2188
11	165	750	17	29.5	2143
12	165	750	19	24.5	2034
13	165	1250	14	37.2	2359
14	165	1250	16	26.8	1987
15	105	1250	17	28.5	2179
16	165	1250	19	25.6	2229
					= 2102

— Species coefficient equation: $Ka = K\ Do^{0.136}/Qo^{1.17}\ H^{0.175}$

— Constant conditions : Sulphidity = 20%

liquor—to—wood ratio = 4:1.

TABLE—3 CALCULATION OF SPECIES COEFFICIENT FOR E. GRANDIS

Sl. No.	Cooking temperature t°C	H-factor	Active alkali % cs Na_2O Qo	Kappa Number Ka	Species Coefficient K
1	160	750	10	32.1	1255
2	160	750	11	27.1	1186
3	160	750	12	22.6	1096
4	160	750	13	20.4	1083
5	160	480	13	32.0	1572
6	160	480	15	20.9	1213
7	160	480	17	19.7	1325
8	160	480	19	17.7	1358
9	165	1250	14	17.7	1119
10	165	1250	16	17.3	1280
11	165	1250	18	15.8	1343
12	165	1250	20	14.1	1360
13	170	1000	14	18.1	1141
14	170	1000	16	17.0	1252
15	170	1000	18	16 1	1319
16	170	1000	20	15.0	1367
					= 1267

— Species coefficient equation : $Ka = K\ Do^{0.136} / Qo^{1.171}\ H^{1.75}$

— Constant conditions : sulphidity = 20 %
liquor—to—wood ratio = 4:1.

TABLE - 4 SPECIES COEFFICIFNT VALUES FOR E. TERETICORNIS, E. GRANDIS AND D. STRICTUS.

SPECIES	SPECIES COEFFICIENT
E. Tereticornis	2150
E. Grandis	1267
D. Strictus	2102

that the maximum distribution frequency lies around 2100. This amounts to 45%. Two more distribution frequencies are also has a major percentage frequency values (27% and 17% respectively). One important observation is that no residual value has a positive distribution. This has been amply proved by plotting S. C. values versus percentage distribution (figure 7a). In this it has been observed that 60% of the total observed value lies between 2100 and 2150. Fitting the actual versus predicted Kappa number (Table 5) values for the S.C. of 2100, 2125 and 2150 for a straight line fit, has shown that though S.C. values 2100 has a correlation coefficient of 0.97, 0.98 respectively with the slope of 1.04, and 1.02, for 2150 the correlation coefficient has improved to 0.98689 with a slope of 1.005 (0=45°8′) giving an intercept value —0.647455 (Figure 1). This has shown that at a predicted

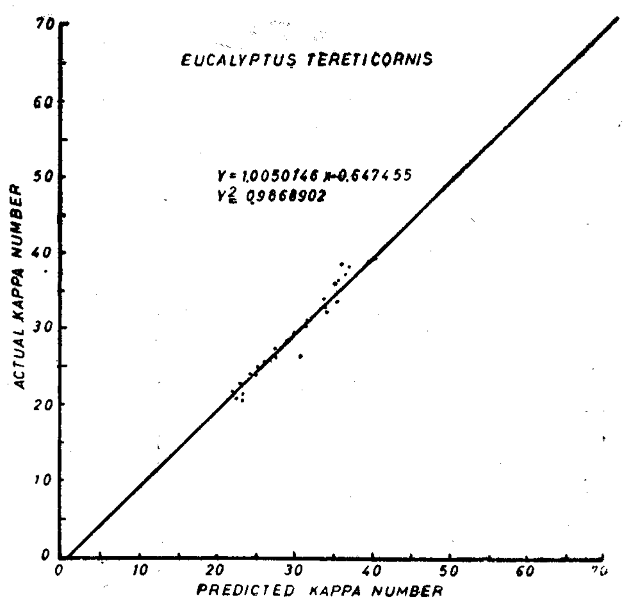

Fig. 1

zero Kappa number value, the actual value is around —0.65 or can be fairly approximated to be zero. The implication of this S.C. 2150 at a

TABLE -5 PREDICTED VS ACTUAL KAPPA NUMBER EUCALYPTUS TERETICORNIS SPECIES COEFFICIENT = 2150

Sl. No.	H-factor	Active alkali % as Na_2O	Actual 160°C	Kappa 165°C	Number 170°C	Predicted Kappa Number
1	750	14	41.1	36.5	41.9	37.1
2	750	16	31.4	31.1	31.7	31.7
3	750	18	26.2	27·6	27 5	27.6
4	750	20	—	21.5	24.5	24.4
5	1000	14	33.8	32.7	36.7	35.3
6	1000	16	—	26.9	30.2	30.2
7	1000	18	26 4	23.8	26.3	26.3
8	1000	20	22.0	22.8	21.2	23 2
9	1250	14	32.8	32.3	33.2	33.9
10	1250	16	28.9	29.0	28.5	29.0
11	1250	18	23.8	25.0	23.8	25.3
12	1250	20	21.9	22.4	22 3	22.3

— Constant conditions : Sulphidity = 20%
liquor—to—wood ratio = 4:1.

confident limit of 0.9934 indicates a 3 σ distribution. In other words out of the 100 predicted Kappa numbers using this S.C. 99 will tally with the Kappa number of the pulp obtained by experimentation which is statistically highly significant In other words Lin *et al*'s equation unreservedly hold good for *E. tereticornis*. This prediction and S.C. holds good for a Kappa range of 5 to 100 (with a percentage error less than 2%) (Table 5a).

TABLE—5a

Sl. No.	Predicted Kappa Number	Actual Kappa Number
1	5	4.3779181
2	10	9.4032912
3	15	14.428664
4	20	19.454034
5	25	24.47941
6	30	29.504784
7	35	34.530154
8	40	39.55553
9	45	44.580903
10	50	49.606272
11	75	74.733141
12	100	99.860007

Correlation Coefficient (R^2) = 0.9168902
Slope = 1.0050746
Inter-cept = -0.6474550
St. Line fit Equation
$Y = 1.0050746 \times -0.6474550$

SPECIES COEFFICIENT VALUES FOR D. STRICTUS :

The *D. strictus* also follow the similar pattern as that of *E. tereticornis*. The S.C. evaluated for *D. strictus* is 2102 (Table 2 and 4). The near S.C. values of *E. tereticornis* (2150) and *D. strictus* (2102) show their similarity to behave during alkaline sulphate pulping under similar pulping conditions. Since it is a well known fact that the chemical constituents of Bamboo species resemble Hardwoods in most respect, except for the additional syringyl and cumaryl aldehydes in the lignin structure, the delignification kinetics of bamboo in most respect should resemble *E. tereticornis* and also appears to be so from the S.C. value. A generalization could be arrived at from this. Lin *et al*'s S.C. equation can be successfully applied not only to Hardwood species but also to non wood species like bamboo. From the calculated S.C., the drawn relation between predicted and obtained Kappa number has an excellent straight line fit with correlation coefficient 0 9826416 (Table 6 and 6a) which corresponds to a confidence of 0.9912828 with the slope 1.027934 (0=45° 47') and intercept value —1.1736193 (Fig. 2). The intercept value indicates that at a predicted zero Kappa number the obtained Kappa number will be 1.1736193. In other words it can be presumed that the straight line more or less passes through the origin. The residual distribution and frequency functions are represented by figures (5 & 7b) which also follows a similar trend as that of *E. tereticornis*.

TABLE—6 PREDICTED VS ACTUAL KAPPANUMBER DANDROCALAMUS STRICTUS
SPECIES COEFFICIENT = 2102

Sl. No.	H-factor	Active alkali % as Na_2O	Actual Kappa Number 160°C	Actual Kappa Number 165°C	Predicted Kappa Number
1	1000	14	35 6	35.2	34.5
2	1000	16	29.4	29.7	29.5
3	1000	18	26.5	26.4	25.7
4	1000	20	18.6	20.0	22.7
5	1250	14	32.8	34.2	33.2
6	1250	16	26.0	26.3	28.4
7	1250	18	24.2	23.9	24.7
8	1250	20	21.5	20.8	21.8
9	1104	13.5	34.9	—	35.4
10	1104	14.78	32.1	—	31.8
11	1104	17.48	25.9	—	26.1
12	1104	19.50	23.0	—	23.0
13	662	13	—	39.5	40.3
14	662	15	—	32.9	34.2
15	652	17	—	28.7	29.6
16	662	19	—	24.1	25.9

— Constant conditions : Sulphidity = 20%
liquor—to—wood ratio = 4:1.

TABLE—6a

Sl. No.	Predicted Kappa Number	Actual Kappa Number
1	5	3.9628477
2	10	9.0993146
3	15	14.235782
4	20	19.372248
5	25	24.508715
6	30	29.645182
7	35	34.781649
8	40	39.918116
9	45	45.054583
10	50	50.19105
11	75	75.873385
12	100	101.55572

Correlation Coefficient (R^2) = 0.9826416
Slope = 1.0272934
Intercept = - 1.1736193
St. Line fit Equation

$$Y = 1.0272934\ X - 1.1736193$$

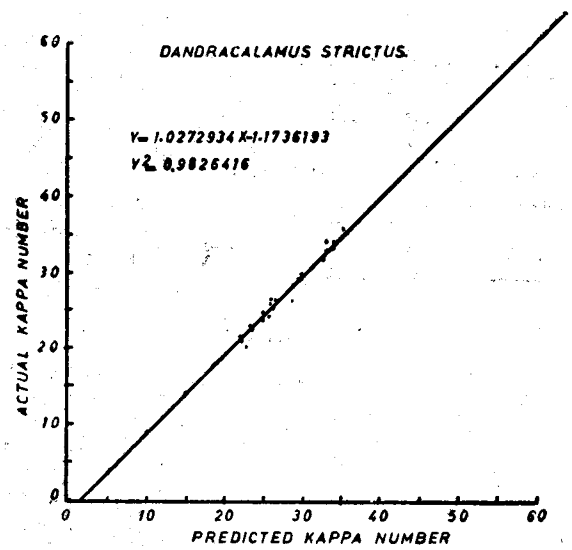

Fig. 2

SPECIES COEFFICIENT OF E. GRANDIS :

Even at a lower H-factor (480) than that is applied to other species, the *E. grandis* has yielded a very low Kappa number. The maximum Kappa number

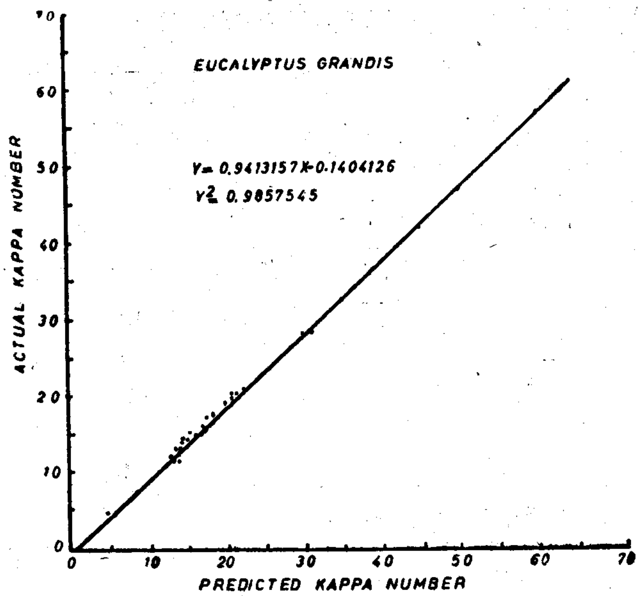

Fig. 3

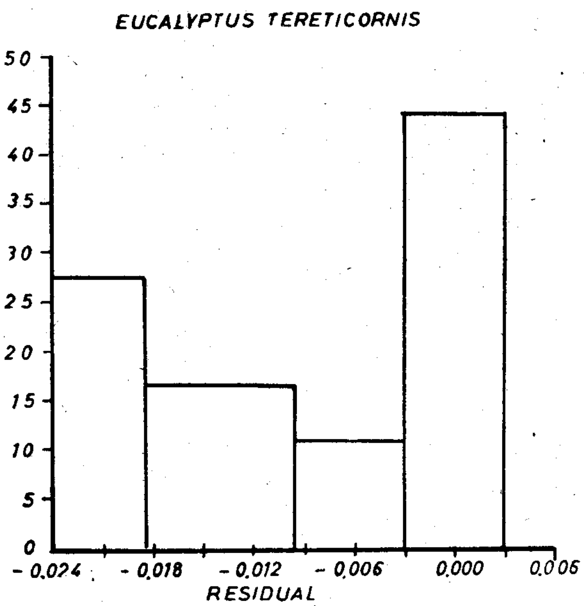

Fig. 4

obtained for *E. grandis* at equivalence H-factor level (750) is 20 compared to 45, for *E. tereticornis* and *D. strictus*, the S.C. value for this species is considerably low, 1267, (Table 3) half to that of the *E. tereticornis* and *D. strictus* showing the relative ease at which this species could be delignified. The predicted to actual Kappa number calculations (Table 7), using the calculated Specific Coefficient was valid only between the Kappa number ranges 15-25, beyond which a high scattering is observed. The confidence of the straight line fit obtained for the plot between the Kappa number predicted and actual Kappa number (Table 7) is 0.9928517 with a highly significant correlation coefficient of 0.9857545 with slope 0.9413157 ($\theta = 43°16'$) and intercept -0.1404125, (Fig. 3), showing that the straight line if approximated passes through the origin. The figures between predicted to actual Kappa number, residual and frequency distribution are drawn and shown in Figure 3, 6, 7c. The S. C. calculation can be obtained from Table 3 and 4.

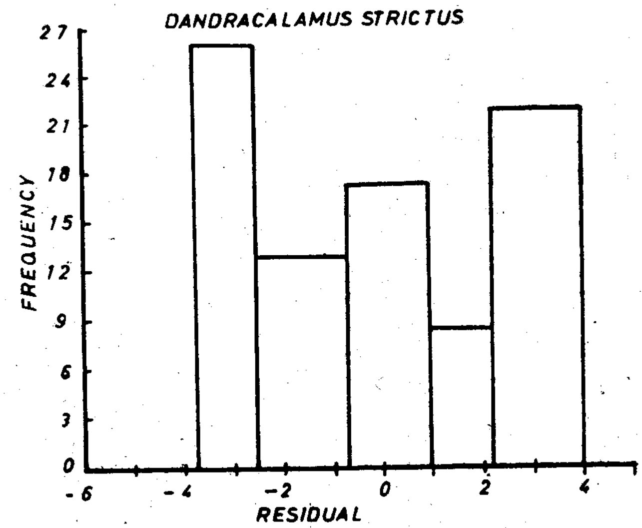

Fig 5

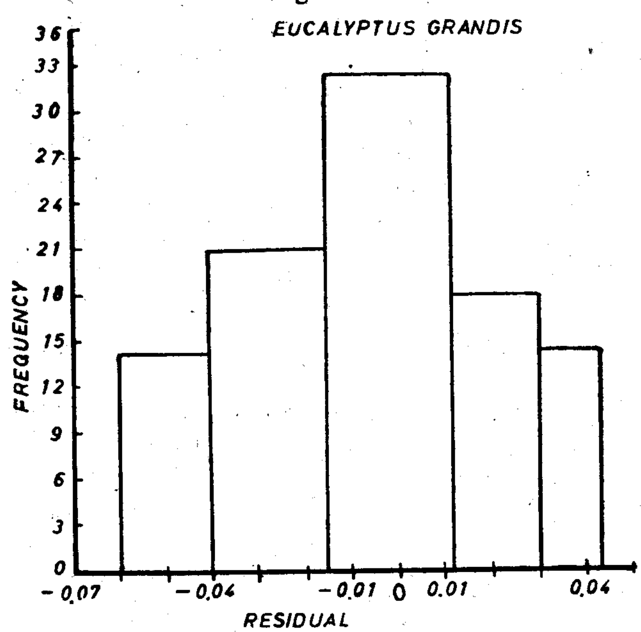

Fig. 6

TABLE—7 PREDICTED VS ACTUAL KAPPA NUMBER EUCALYPTUS GRANDIS SPECIEUS COEFFICIENT = 1267

Sl. No.	H-factor	Active alkali % as Na_2O	Actual Kappa Number 160°C	165°C	170°C	Predicted Kappa Number
1	750	14	19.9	20.6	20.9	21.8
2	750	16	16.4	17.1	17.4	18.7
3	750	18	15.8	15.2	14.9	16.3
4	750	20	14.1	13.2	13.7	14.4
5	1000	14	19.9	20.1	—	20.9
6	1000	16	17.1	16.8	—	17.9
7	1000	18	15.1	14.6	—	15.6
8	1000	20	12.9	12.5	—	13.4
9	1250	14	18.4	—	18.9	20.1
10	1250	16	15.9	—	15 3	17.2
11	1250	18	13.1	—	13.8	14.9
12	1250	20	12.5	—	11.8	13.2

— Constant Conditions : Sulphidity = 20%
liquor—to—wood ratio = 4:1.

TABLE—7a

Sl. No.	Predicted Kappa Number	Actual Kappa Number
1	5	4.5661662
2	10	9.2727448
3	15	13.979329
4	20	18.685902
5	25	23.392481
6	30	28.099059
7	35	32.805638
8	40	37.212217
9	45	42,218795
10	50	46.925374
11	55	51.631952
12	60	56.338531

Correlation Coefficient (R^2) = 0.9857545
Slope = 0,9414157
Intercept = — 0.1404125
St. Line fit Equation
$Y = 0.9413157 \times - 0.1404125$

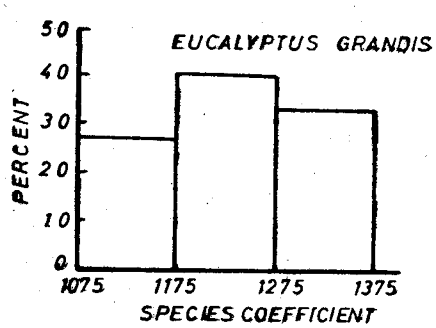

Fig. 7a

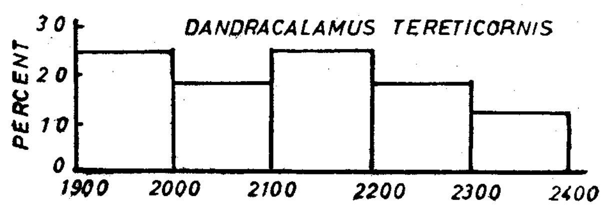

FIG.7b

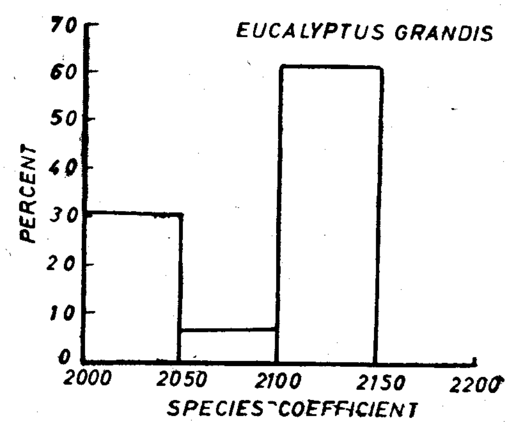

FIG.7c

CONCLUSION

1. The S.C. calculated for *E. tereticornis*, *E. grandis* and *D. strictus* are respectively 2150, 1267 and 2102.

2. The statistically significant straight line fit with tan 0 value of almost 1 between the predicted and the actual Kappa uumber validates the Lin *et al*'s equation's applicability to Hardwood species and more so because the equation also gave high correlation coefficient in predicting the Kappa number of non wood species like *D. strictus*.
3. Lin *et al*'s predicted equation applies to *E. tereticornis* and *D. strictus* to Kappa number ranges between 5 to 100, whereas in the case of *E. grandis* the equation's application is limited between the Kappa number values of 15-25.
4. Since the Lin *et al*'s predicted equation is for Hardwoods, its significant application to Bamboo shows that as long as the chemical constituents of the raw materials are going to remain constant, S.C. can be used to predict the Kappa number ranges of raw material under a wider conditions of applied alkali to wood ratio and H-factor.
5. For two species whose Species Coefficient values are identical, it may be fairly said that they may yield identical pulps.
6. To have a better gradation of hardwoods, Species Coefficient evaluation can be supplemented in addition to physical characteristics.

EXPERIMENTAL

ALKALINE PULPING : The digester assembly consists of 4 bombs (1.5 litre capacity each) mounted vertically in a rotating Weverk auto-clave. 200 gms of o.d. chips were used in each bomb. The temperature inside the digester was maintained with the thermocouple. White liquor of 80-90 gpl as Na_2O as active alkali and about 20% sulfidity was used. Cooked chips were thoroughly washed with fresh water and defibrated. The defibrated pulps were screened in Weverk flat vibratory screen with parallel slots. The screened pulp was centrifuged and then fluffed in a Pin-defibrator. The pulps then were stored in polyethylene bags Kappa Number of screened pulps was determined according to Tappi—Standard Procedures T-236m60.

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