# H-Factor concept and its relationship with delignification rate

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#### SUMMARY

The study on effects of Time and Temperature in Kraft pulping of Eucalyptus tereticornis has revealed that the rate of delignification is a pseudo first order rate reaction with an energy of activation of 33 Kcals/mole. Correlationship between H-factor and other parameters measured in terms of Pulp Yield, lignin content. Kappa No., ratio of lignin and carbohydrate have been established. Further it has been recommended to carry out exhaustive study on effects of E. A. and Sulphidity besides H-factor in Soda/Kraft/N.S.S.C. pulping of indigenous cellulosic raw materials so that correlationship between Total pulp yield, E. A. and sulphidity etc. may be

In view of increasing conciousness about quality of paper and its products the attention of paper technologists in the country has been diverted to evolve a technology for the production of uniform pulps i.e. which have uniform physical and chemical properties. Generally uniformity of pulp is assessed from simillar permaganate or Kappa No. and pulp yield. Each paper making raw material is a complex heterogenous multicomponent system consisting of three main components-cellulose, hemicelluloses and lignin, react with cooking chemicals at different rates and by different mechanisms. Thus it has never been possible to develop rigorous mathematical descriptions of pulping process, although process of kraft delignification has been treated as first order reaction<sup>1</sup>. In this direction an initiative has already been taken by K.E. Vroom<sup>2</sup> in 1957, who introduced H-Factor as one single variable in place of two cooking variables namely time and temperature. The principle is based on the assumption that an Arrhenius type rate increase in tignin removal from cooked chips occurs with increasing cooking temperature. Vroom's H-Factor has proved useful in mill operations and laboratory research studies for predicting required changes in cooking time to compensate for changes in cooking temperature, or vice versa. However H-factor is limited to changes in time and temperature i.e. it describes only, the physical energy input of the kraft process.

The technology has now advanced to such an extent that pulp yield, Kappa/Permanganate number, Effective alkali and H-Factor may be expressed by linear models of the form  $Y = A-B [(log_{10}H) \times (EA)^n]^{4.6}$ where Y=Yield, H=H-Factor, EA.=Effectivealkali and A, B & n are constants. The validity of these linear models has been established by the successful development of control strategies based on these models. The H-factor does not take in to account the chemical factors affecting the rate of pulping such as alkali concentration and sulphidity. In order to account for these chemical factors Edwards and Norberg<sup>7</sup> have developed a T-factor which is defined as

$$\Gamma = \left[\frac{S}{2-S}\right] \times \left[\frac{EA}{L:W}\right]^2 \times H$$

where S is sulphidity (expressed as fraction) and L: W is bath Ratio. Similarly the variables involved in carbohydrate dissolution reaction have also been expressed by a single expression known as Q-Factor. The Q-Factor is a differential equation that incorporates concentration, liquor strength, a carbohydrate reaction velocity constant and temperature.

Based on these lines the validity of H-factor in delignification of bamboo by kraft process<sup>8</sup> and Eucalyptus Grandis by N.S.S.C. process<sup>9</sup> has already been studied at the laboratories of Cellulose and Paper Branch, Forest Research Institute and Colleges, Dehradun and at I.I.T. Bombay respectively. The characteristics of lignin, present in

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bamboo and various hardwoods is quite different and therefore, it has been felt necessary to carry out an exhaustive study of kinetics of delignification in kraft pulping of Eucalyptus tereticornis wood which has become a major raw material in India for bleached grade pulps.

The work reported in this paper has been carried out with the following objectives :

- 1. An exhaustive study of kinetics of delignification in kraft pulping of Eucalyptus Hybrid.
- 2. Validity of H-Factor as a guide for control of pulp quality.
- 3. Relationship between H-factor and rate of delignification.

#### **RESULTS AND DISCUSSION RATE OF DELIGNIFICATION**

The results obtained from the experimental cooks were analysed for kinetic data.

The rate of reactions at various times at 170°C were obtained by plotting cooking time at temperature vs residual lignin (expressed on O.D. raw material) and finding out the slope of the tangents drawn at different times. The reaction rates at four different

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times at maximum temperature (170°C) are calculated from the graph<sup>1</sup>.

Log dx/dt was also plotted against log residual lignin. This gave a straight line with a slope of 1.1 (Graph 2). Thus the kraft delignification of Eucalyptus hybrid follows a pseudo first order of reaction the rate becoming slower at later stage of reaction. This is also confirmed by the linear relationship, between Log of residual lignin with time of reaction as shown in Graph (3).

#### **REACTION CONSTANTS**

The values of the first order rate constants for the kraft delignification reaction at different temperatures were calculated from the experimental data using the first order rate expression :

$$K = \frac{2.303}{T} \text{ Log } \frac{\text{Lo}}{\text{Lr}}$$

where T = Reaction temperature in °K Lo = Lignin concentration at the start. Lr = Lignin concentration at the end.

The rate constants are :

at  $443^{\circ}K (170^{\circ}C) = 1.2 \text{ hr}^{-1}$  $433^{\circ}K (160^{\circ}C) = 0.4971 \text{ hr}^{-1}$  $438^{\circ}K (165^{\circ}C) = 0.7416 \text{ hr}^{-1}$ 



Lignin to hydrate carbo-0.542 0.493 0.453 0.415 0.352 0.263 0.065 ratio, 0.321 0.231 0.121 0.041 0.041 0.042 Pento-10.6 san 11.4 9.9 6.0 8.9 9.2 8.5 8.4 8.7 8.7 8.6 8.4 8.2 % Alpha celul-51.27 57.37 63.11 70.98 54.1 85.37 82.46 60.5 80.93 lcse % 65.2 68.7 81.0 82.1 TABLE I-PULP CHARACTERISTICS AT DIFFERENT H-FACTORS Cellu-64.86 66.59 68.63 87.35 94.65 94.33 Holo 96.78 92.73 73.9 70.8 75.8 79.3 81.4 lose % Lignin 10.64 content 33.83 31.14 29.54 26.07 24.31 6.23 3.89 4.02 35.17 20.9 18.8 3.8 % Kappa 93.52 92.47 94.8 68.64 85.2 41.6 27.9 25.9 24.6 No. ł I 1 A.A. Gpl. as Na<sub>2</sub>O Residual 17.36 11.16 13.64 4.96 19.84 6.82 5.58 4.72 15.5 10.5 9.3 4.34 4.16 Unblea-48:83 <sup>e</sup> pulp yield %age 76.02 73.18 66.15 63.94 81.64 69.02 58.56 45.12 40.16 54.23 50.2 60.7 ched Factor 1096 l664 2192 4080 548 39 101 H. max. Cook- max. Cooking temp. HRS. Time at Cooking Total Cooking (ii) 1.0 1.5 2.0 1.5 0.5 period + ing temp. Time to 0.75 1.12 0.62 0.86 1.25 1.37 1.5 HRS. <u>.</u> Ξ 1.5 1.5 1.5 1.5 1.5 Temp. C 100 110 120 130 140 150 160 170 2 170 170 170 180 SI. No. 5 Ġ 10. 11. ~i ŵ 5 12. Б.

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pova % s	Dissolved	e l					18.36	24.00	26.82	31.90	33.85	36.06	39.30	41.44	45.77	49.80	51.17	54.88	59.24
l Constituent:	from wood I original	onstitutents Carbohvdra	Fraction	%		1	21.50	25.03	25.00	27.50	27.50	28.10	27.80	29.40	29.70	22.60	30.00	38.4	43.2
Chemica	removed based or	wood co Lienin	0	%	•	1	00.00	09.50	2.0.00	28.20	39.10	45.10	55.20	61.20	81.40	89.20	92.90	93.8	94.5
	n Moisture of pulp	Carbohy- hvdrate	Fraction	%		1	64.86	66.59	68.63	70.80	73.90	75.80	79.30	81.40	87.35	94.65	96.78	94.33	92.73
sis of Pulp	Based of free wt	Lignin		%		ļ	35.17	33.83	31.14	29.54	26.07	24.31	20.90	18.80	10.54	06.23	04.02	03.89	03.8
Analy	Moisture of wood	Carbohy- drate	Fraction	%		67.5	52.9	50.6	50.7	48.9	48.9	48.5	48.7	47.6	47.4	47.5	47.20	41.57	38.32
-	Based on free wt. c	Lignin		%		20.4	27.0	25.7	22.7	20.4	17.3	15.6	12.7	11.00	05.72	3.04	1.96	1.76	1.537
Unbleached	pulp yield % age	- • - •			•	,n	81.64	76.02	73.18	69.02	66.15	63.94	60.70	58.56	54.23	50.20	48.83	45.12	40.76
H-Factor		- - •4			•	MATERIAL	0	0	1	ŝ	9	17	39	101	548	1096	1644	2192	4080
Time				HRS		RAW ]	0.62	0.75	0.86	1.0	1.12	1.25	1.37	1.5	2.0	2.5	3.0	3.5	3.0
Blow	Temp.			ູ ບ			100	110	120	130	140	150	160	170	170	170	170	170	180
SI.	No.		•			1	5	i ri	4.	, v	<u>و</u>	7.	ø	. 6	10.	11.	12.	13.	14

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TABLE – II



### **CALCULATION OF ENERGY OF ACTIVATION**

The energy of activation is given by the expression :  $Log \quad \frac{K_2}{K_2} = -\frac{Ea}{T_2 - T_1}$ 

$$pg \quad \frac{r_2}{K_1} = \frac{r_2}{2.303 \text{ R}} \quad \frac{r_2 - r_1}{T_1 \times T_2}$$

where  $K_1 = Rate constant at T_1^{\circ}K$ 

$$K_2 = Rate constant at T_{2} K$$

 $\mathbf{R} = \mathbf{G}$ as constant.

Ea = Energy of activation

The average energy of activation was calculated to be 33 Kcal/mole. The value of energy of activation calculated graphically<sup>4</sup>=32.94 Kcal/mole.

#### ARRHENIUS FIRST ORDER RATE EXPRESSION CONSTANT

The Arrehenius first order rate expression in the following form was used for calculating the relative reaction rates :

 $Ln K = B - A/T \text{ where } \frac{Energy \text{ of activation}}{Gas \text{ constant}}$ 

A = 33000/1.987 = 16610

Assuming that the rate of reaction is unit at 100°C

$$\begin{array}{c} 0 = B - A/373 \\ B = A/373 = 44.5 \end{array}$$

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Thus the rate of reaction at any other temperature can be obtained from the relation,

Ln K = 44.5 - 16610/T

The relative reaction rates at various temperatures are given in Table 3. The relative reaction rate is found to increase from 2 to 2.5 times per every 10°C temperature rise.

## VALIDITY OF HSFACTOR

A standard cook with conditions, maintained in the previous cooks, at a max. temp. of 170°C for 90 mts at temperature was done. The cooking schedule and H-Factor of the cook came around 111750. Keeping the H-Factor constant, the cooking times temperature levels 160°, 165°, 175°C were calculated.

Chips of Eucalyptus Hybrid were digested at these different temperature levels for the predicted times. The pulps were washed and screened and evaluated for lignin content, holocellulose, Alpha cellulose, pentosan content and Kappa No., as per TAPPI standard test methods. The results are tabulated in table VI.

TABLE-III RELATIVE REACTION RATES (Calculated from derived arrhenius expression Ln K 44.5-16610/T)

S	l.No.	Tem	perature C	R	elative	Rate
1.	•		100		1.	0
2	•		110		3.	0
3.			120		9.	5
4.		-	130		<b>2</b> 6.	0
<b>.</b>			140		72.	0
6.			150		187	0
7.			160	14	465.	00
8.			170		1096.	0
. 9.			180		2588.	0
10.			190	<u> </u>	5534.0	0
T/	ABLE-	-IV H-F COC	ACTOR DK AT 17	FOR ST	AND	ARD
	Time 7	empera-	Relative	Average	Time	Н-
SI.	from	ture	reaction	reaction	inter	Factor
No.	start	°С	rate	rate	val	
	HRS					
1.	0	50	0	0	0	0
2.	0 33	100	1.0	0.5	0.33	Ō
3.	0.50	110	3.0	2.0	0.17	0
4.	0.66	120	9.0	6.0	0.16	1
5.	0.83	130	26.0	18	0.17	- 3
6.	1.0	140	72.0	49.0	0.17	9
7.	1.16	150	187.0	130	0.16	21
8.	1.33	160	465.0	326.0	0.17	55
9.	1.55	170	1096.0	<b>7</b> 80. <b>0</b>	0.17	133
0.	3.0	170	1096.0	1096.0	1.5	1644
				Тс	otal	1866

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TABLE – V CALCULATION	OF	COOKING
TIME AT 180°C REQUIRED	TO	ACHIEVE
IDENTICAL H-FACTO	R O	F 1865

S1. No.	Time from Start Minutes	Tempera- ture s)	Relative reaction rate	Average reaction rate	Time inter val H	H– Factor	
1.	0	50	0	0	<u> </u>	0	
2.	0.50	100	1	05	0.5	0	
3.	0.62	110	3	2	0 12	0	
4.	0.75	120	9	6	0.13	1	
5.	0.87	130	26	18	0.12	2	
6.	1.0	140	72	49	0.13	6	
7.	1.12	150	187	130	0.12	16	
8.	1.25	160	465	326	0.13	42	
9.	1.37	170	1096	780	0.12	94	
10.	1.5	180	2588	1842	0.13	240	
			· · ·	То	tal –	401	
H Bal	Factor lance H	required -Factor	= 1865 = 1464				
	,	Minus	= 401				
]	Therefor	re cooking	time				
		at 180°C	2588	0.55 hrs.	= 34 n	ITS.	

Similarly cooking times at different cooking temperature viz 160, I65, 170°C have been calculated).

A perusal of the data on yie'd, lignin content, carbohydrate contents and K: ppa No. of pulps recorded in Table VI shows that these are nearly the same as obtained with the pulp prepared at 170°C with standard cooking cycle employed. This indicates that H-Factor can be suitably used, as a guide for predicting compensating adjustments of pulping schedule. In other words regardless of cooking temperature equal H-Factor produce pulps of equivalent characteristics such as lignin content, yield, Kappa No. and carbohydrate content etc.

#### **PULP YIELD Vs. H-FACTOR**

A plot of percentage pulp yield Vs Ln H-Factor Graph (6) showed a linear relationship between pulp yield and H-Factor and the relationship can thus be expressed in the form :

	$\mathbf{Y} = \mathbf{A} + \mathbf{B} (\mathbf{X})$					
where	Y = Percentage pulp yield					
	A&B = Constants					
	X = is a function of H-Factor.					

The following equations hold good for this Raw Material. (Derived by linear regression analysis method<sup>11</sup>).

Y = 246.08 - 24.73 (Ln H)

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(for the pulp yield range 60 to 70 and E A 30 gpl as Na<sub>2</sub>O)

Similar Relationships were observed in case of (Graph 7) percentage lignin in pulp vs. Log H-Factor and (Graph 8), Lignin to carbohydrate ratio vs. Log H-Factor. These relationships establish the prediction capability of H-Factor in predicting parameters of pulp. Similarly, the Chemical charged in terms of effective alkali, concentration can be included into the expression of the form :

$$Y = A + B [(Ln H (EA)^n]$$
  
i.e. 
$$Y = A + B (X)$$
 Where

X would be a function of H-Factor and the effective alkali concentration. Expressions of these type have been developed, for certain soft wood species and their applicability, has been established by the development of Control Models based on them<sup>4-6</sup>.

#### **EXPERIMENTAL**

#### **RAW MATERIAL**

Eucalyptus hybrid chips procured from M/s Star Paper Mills Ltd., Saharanpur having the following



TABLE VI-COMPARISION OF YIELD, LIGNIN AND CARBOHYDRATE CONTENTS OF UNBLEACHED PULPS OBTAINED AT PREDICTED COOKING TIMES WITH THAT OBTAINED AT STANDARD COOK. I

ı	Lignin carbo- hydrat <b>e</b> ratio	0.041	0.042	0.042	0.042	0.042	
	Alpha cellu- lose %	 84.37	84.82	84.49	84.35	84.13	
	Holo- cellu- lose %	96.78	96.72	96.68	96.60	96.43	
	Pento- san %	8.6	8.2	8.5	8.4	8.4	
	Kappa No.	 27.9	28.2	2.86	28.4	28.1	-
	Lignin %	4.02	4.12	4.14	4.1	4.05	
	A.A. consu- med %	88.2	88.0	87.6	87.7	87.2	
	Residual A.A. Gpl. as Na <sub>2</sub> O	4.72	4.8	4.96	4.89	5.1	
	Rejects %	0.5	0.4	0.8	0.4	0.7	i a sa
	Pulp Yield %age	48.83	47.84	48.9	48.32	48.03	•
	H- Factor	1865	1865	1865	1865	1865	· ·
	redi- ted time t cooking emp. Mts.	 <b>06</b>	232	146	55	34	• ,
	Cooking P temp. c °C a	170 standard	160	165	175	150	
	SI. No.	• •	2.	с Э	4	5.	· ,

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proximate chemical analysis was used in this study :

1.	Ash	0.62%
2.	Silica	0.03%
3.	Alcohol-Benzene Solubility	1.20%
4.	Pentosans	15.50%
5.	Lignin (ash free)	28.40%
6.	Holo-Cellulose	67.50%
7.	Alpha Cellulose	42.30%

(The proximate analysis of the raw material was carried out as per standard TAPPI methods).

#### COOKING LIQUOR

White liquor was obtained from M/s Star Paper Mills Ltd, and analysed for active alkali and sulphidity. The liquor was fortified to an active alkali level of 100 gpl as Na<sub>2</sub>O and sulphidity 20%, by adding calculated amounts of commercial grade. N<sub>3</sub>OH & Na<sub>2</sub>S. The fortified liquor was decanted and stored for use in the experiments.

#### SULPHATE COOKING

Wood chips of uniform moisture content and size (500 gm O.D.) were taken in an electrically heated auto clave. The required amount of cooking liquor was added in autoclave. Tap water was used for dilution to maintain a bath ratio of 1:4. The following cooking conditions were maintained in all the cooks:

1. Active Alkali %	=16 (as $Na_2O$ on O.D. Chips)
2. Sulphidity %	=20
3. Bath ratio	=1:4
4. Initial active alkali concentration, gpl	=40 (as Na <sub>2</sub> O)
5. Initial temperature °C	= 50
6. Rate of rise of	· ·

• Rate of rise of temperature  $=10^{\circ}$ C per 7.5 minutes

In the first series of experiements under constant conditions as specified above, the chips were digested at temperatures ranging from 100°C to 170°C. The time required to reach the desired maximum temperature was carefully controlled to give a uniform rate of rise of temperature. The digester was blown at maximum temperature immediately without allowing any retention time. The semi-cooked chips were discharged and quenched with cold tap water to lower the temperature.

The semi cooked chips were refined in a laboratory disc refiner (Defibrator make, Type D) having a clearance of 0.05 mm. The refined pulps were washed thoroughly free from the cooking chemicals and air dried. The dried pulps were stored in polythene bags and sealed.

In the second series of experiments, under constant conditions as maintained in the earlier series, chips were digested at 170°C with 90 minutes to cooking temperature and cooking times of 30, 60, 90, 120 minutes at maximum cooking temperature. The pulps obtained were washed, screened, air dried and stored in polythene bags.

The pulps were evaluated for lignin content, holocellulose, alpha cellulose, pentosan and kappa Nos. as per TAPPI test methods. The pulping conditions and results of pulp evaluation are recorded in table-1. The chemical analysis based on moisture free wood and the percentage of constituents removed from wood under various cooking conditions are given in Table 2.

#### **CONCLUSION** :

In the foregoing article, the utility of H-Factor as a single major control variable has been elucidated. In the recent years, much of the world pulp industry's attention has been drawn towards improving pulping techniques & development of various controls in pulping. Based on the work done in this project, it is recommended to further carry out exhaustive study on chemical kinetics of alkaline pulping process for different indigenous cellulosic raw materials, which vary in their chemical composition & behaviour. We feel that the application of H-Factor, as a guide for predicting compesatory adjustements in pulping schedules and pulp characteristics. will be of great use in chemical pulping by continuous or batch processes. Recently H-Factor meters for continuous integration of time & relative reaction rates have been successfully used in advanced countries for the continuous recording and control of delignification level. The benefits of such technology can also be availed in India so as to improve the performance & quality of the products of pulp mills.

Further, with the increasing trend towards automation of pulping processes, it is necessary to derive kinetic models for Indian raw materials on similar lines as developed at Western Forest Products Lab., Canada so as to employ feed forward control systems to monitor the cooks. Also, study of kinetics of carbohydrate dissolution is essential to develop suitable models & thereby eliminate unnecessary degradation of pulp, by monitoring the pulping variables.

#### REFERENCES

- 1. Rydholm, S. A. "Pulping Processes" P. 618.
- 2. Vroom K. E. Pulp Paper Mag Canada Vol. 58 (6) 228 (1957).
- 3. Carron, C. W. Tappi 43 (6) 574 (1960).
- 4. Hatton J. V.m and Hejjas. J. Pulp Paper Mag Canada 73 (9) T 218 (1972).
- 5. Hatton J. V., Kaays T. L. and Hejjas J. Pulp Paper Mag Canada, 73 (4), T (103) (1972).
- 6. J. V. Hatton, Tappi/July 1973, Vol. 56, No. 7

- Edwards and Norberg S. E. Tappi 56 (11) 108 (1973).
- 8. S. V. Singh Etal-IPPTA 1970 (2).
- 9. S. V. Singh Etal-IPPTA Vol. 14 (2) 1977.
- 10. Kansal S. C., Basu S. IPPTA Souvenir. International Seminar 1977.
- 11. Advanced Engineering Mathematics By Kryesyig (Wiley Eastem).
- 12. Kerr A. J. APPITA 24 (3) 180 (1970).
- 13. Nallan C. S. Chan *Tappi/July* 1973 Vol. 56. No. 7.



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