'H' Factor—Rice Straw Soda Pulping

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ABSTRACT

The relative reaction rates were evaluated during soda pulping of Rice Straw, applying the concept of representing the times and temperatures of the cooking cycle by a single numerical value referred to as Vroom's 'H'—factor. The experimental results showed that the relative reaction rate values can be used to determine the 'H'—Factor and which can be employed for predicting the compensating adjustments of cooking times and temperature to give the same yield of pulp kappa number and lignin content with varying cooking cycles. Therefore, it is conduded the Vroom's 'H'—Factor which is a single variable to replace the two cooking variables i.e time and temperature can suitably be applied as a guide for controlling soda pulping process of Rice Straw.

The supply of conventional fibrous raw material like bamboo, hardwoods etc. are dewindling which forced the paper industry to investigate the suitability and technical feasibility of other raw materials such as grasses, agricultural residues, hemp, Jute etc, Among these straw is one of the oldest raw material for paper-making. In most parts of the country rice cultivation is main vocation hence, availability is no problem. However, main hurdle in exploring this potential rawmaterial is collection, transportation and storage.

Compared to wood, rice straw is much easier to be pulped because of its open structure low lignin content i.e. 10-12%. The open structure with thin walls of straw gives large initial surface area for chemical attack and minimise the problem of diffusion encountered during the wood pulping. The pulping reactions are therefore rapid and chemicals required are lower compared to other rawmaterials. However, due to high ash content, which is mainly silica, processing of black liquor is quite difficult.

The relative reaction rates of its delignification are supposed to be different due to reasons mentioned above, compared to other woody raw materials. Relative reaction rates for Bamboo, hardwoods and soft woods have been already reported (1-4). The relative reaction rate for any of the agricultural residue have not been so far reported. Since, most of the small papermills are using rice straw as their main rawmaterial, it becomes quite imperative to carryout an exhaustive study of its kinetic delignification.

The process of pulping is devided into two parts[1] rise to cooking temperature[2] at cooking temperature. Normally a curve of time Vs. temperature is employed to define these variables for any cook. It was felt that it should be possible to develop a single numerical value which would combine the time and temperature represented by a pulping curve and relate to degree of pulping accomplished in the cycle.

Vroom[4] introduced 'H' factor as a single variable in place of two variables i.e. time and temperature. The principle is based on assumption that the Arrheneus equation of dependence of rate of reaction with temperature will satisfactorily describe the relationship between rate of delignification and temperature in pulping process and calculated the relative reaction values for a range of temperature levels to develop a single numerical factor called 'H' factor. Vroom difined the 'H' factor as the area under relative reaction rate versus time curve.

This project has bean undertaken to determine the relative reaction rate at different temperature for rice straw soda pulping.

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EXPERIMENTAL :

SAMPLE AND ANALYSIS :

Rice straw was collected from local fields and ch-pped manually of about 5 cm. The proximate chemical analysis was carried out according to TAPPI Standard methods. The results are recorded in Table—1.

TABLE—1
PROXIMATE CHEMICAL ANALYSIS

Sl. No.	Particulars, %	Results
1.	Cold water solubility	12.2
2.	Hot water solubility	15.5
3.	1% NaOH solubility	49 4
4.	Alcohol-Benzene solubility	7.4
..	Klason lignin*	10.6
6.	Holocellulose*	70.2
7.	Ash	14.8

*Corrected value for ash

PULPING :

Straw samples were cooked electrically heated rotory digester using bombs. The following constant conditions were maintained during pulping :

NaOH on O.D. Raw material	—	8 0 %
Bath ratio	—	1:4
Initial temperature	—	50°C
Time to raise temp. to cooking temp.	—	1.5hr.

The cooking temperature and time were varied. At particular temperature cooking time was also varied. After the pulping, pulps were washed and analysed for pulp yield, kappa no., lignin content. The pulping conditions and results are recorded in Table—2.

TABLE—2
COOKING RESULTS OF RICE STRAW SODA PULPING

Sl. No.	Cooking Schedule Max. Temp°C	Time, Min.	Unbleached Yield,%	Kappa No.	Ash Free Lignin,% (On Pulp Basis)	Ash Free Lignin, % (On Raw Material Basis)
1.	90	0	76.5	60 2	10.85	8.30
2.	90	15	75.1	58 4	10.75	8.07
3.	90	30	73.4	54 9	10.57	7.76
4.	90	45	72.8	52.8	10.29	7.49
5.	90	60	72.1	52.1	10.11	7.29
6.	90	75	70.8	50.5	9.89	7.00
7.	90	90	70.2	48.5	9.68	6.76
8.	100	0	73.2	54 3	10.45	7.65
9.	100	15	72.1	52.5	10.17	7.25
10.	100	30	69.8	49.0	9.84	6.87
11.	100	45	68.7	46.5	9.53	6 50
12.	100	60	66.1	43.2	9.20	6.08
13.	100	75	64.4	40.5	8.94	5.76
14.	100	90	63.8	38.3	8.40	5 36
15.	110	0	70.2	49.2	9.83	6.90
16.	110	15	68.7	47.0	9.53	6.50
17.	110	30	66.5	44.2	9.12	6.06
18.	110	45	64.7	40.5	8.70	6.63
19.	110	60	64.0	37.2	8.08	5.17
20.	110	75	63.6	34.4	7.44	4.73
21.	110	90	63.2	31.0	6.81	4.30
22.	120	0	69.5	48.9	9.84	6.84
23.	120	15	67.4	45 1	9.30	6.27
24.	120	30	64.5	41.0	8.73	5.63
25.	120	45	64.1	35.8	7.59	4.86
26.	120	60	63.3	32.0	6.90	4.37
27.	120	75	62.8	28.1	6 10	3.83
28.	120	90	62.6	27 8	6 01	3.73

RESULTS AND DISCUSSION :

It has been observed from Table—1, the ash content is high i.e. 14.8% in comparision to other woody raw materials. The percentage of klason lignin content is very low i.e. 10-11%. Due to low lignin content and open structure of straw, the rate of delignification is supposed to be rapid and easier, i.e., even if below 100°C the delignification starts which is not in the case of other woody raw materials.

The percentage of residual lignin in pulp (Table–2) after the maximum cooking temperature of 130°C & its onwards, has no remarkable different values, therefore it is concluded that there is no bulk delignification at and above this temperature under the specified cooking condition. Hence, in the soda pulping process of rice straw maximum lignin is removed in the temperature range af 90-120°C. The results obtained in this temperature range were analysed for kinetie data.

Before going to establish the values of the relative reaction rate at different temperature we have to determine first the order of reaction for delignification during pulping process. For this determination we adopted two methods (i) Graphical method, (ii) Statistical method.

(i) Graphical method :

In order to determine the order of reaction of soda pulping of rice straw a graph is plotted between log of residual lignin (on raw material basis) and various times at a particular maximum cocking temperature. A linear relationship is observed at a 100°C from the Fig.—1. Similarly, for other

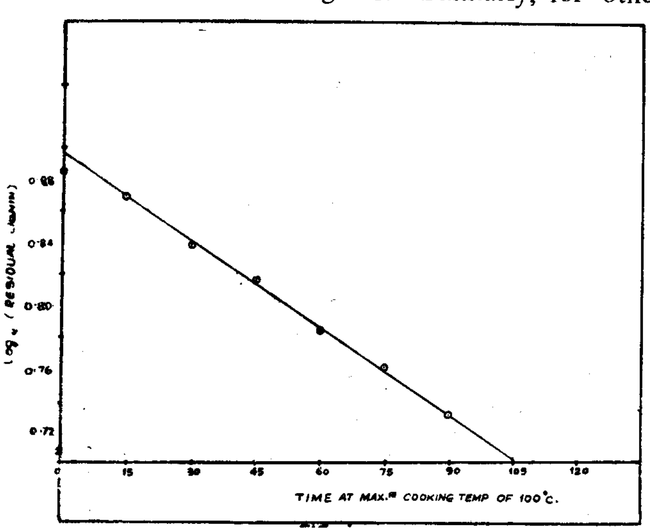

FIG. 1

maximum cooking temperature the same relationship is observed by plotting the graph. This shows that the order of delignification reaction during soda pulping process of rice straw is of first order.

(ii) Statistical method :

In this method, we first considered the general equation for 1st order reaction ;

$$\Sigma Y = na + b\Sigma X \ldots\ldots\ldots(1)$$

$$\Sigma XY = a\Sigma X + b\Sigma X^2 \ldots\ldots\ldots(2)$$

Where 'n' is the no. of cooks for a particular temperature 'a' & 'b' are constants.

X = time at maximum temperature

Y = concentration of residual lignin in pulp (observed value)

Putting the corresponding values of x & y and after solving those equations we got the values of y for different values of x. Those values of y are called as expected values.

Similarly, we again considered for 2nd order reaction ;

$$\Sigma Y = na + b\Sigma X + C\Sigma X^2 \ldots\ldots (3)$$

$$\Sigma XY = a\Sigma x + b\Sigma X^2 + C\Sigma X^3 \ldots\ldots(4)$$

$$\Sigma X^2Y = a\Sigma X^2 + b\Sigma X^3 + C\Sigma X^4 \ldots\ldots (5)$$

Where, 'C' is the another constant and after solving those equations we got the values of 'Y, (expected values) for different values of 'X'.

By putting the observed values of Y (O) and expected values of Y (E) for respective order of reacdon, we can get the value of Chi-square (x^2) for tiifferent order of reaction as per equation given :

$$X^2 = \Sigma \frac{(O-E)^2}{E}$$

For which order of equation the values of x^2 is very low. then that order is taken as the order of reaction during cooking i.e., rate af delignification.

By adopting this statistical method for determination of order of reaction of our experiment it is found that the value of X^2 is very low for the 1st order of equation which concludes the rate of delignification during soda pulping of rice straw is of first order.

In order to calculate the activation energy of the reaction in soda pulping of rice straw, we have to find out the values of rate constant at different maximum cooking temperature of particular time. Hence, the values of the first order rate constants for the soda delignification reaction at different temperature are calculated from the experimental data using the first order rate expression.

$$K = \frac{2.303}{T.} \log \frac{Lo}{Lr}$$

Where, T=time in hour at particular maximum cooking temperature

Lo=lignin concentration at the start which can be calculated by extrapolating the Fig. 2 drawn between the percentage of residual lignin against the time at maximum temperature.

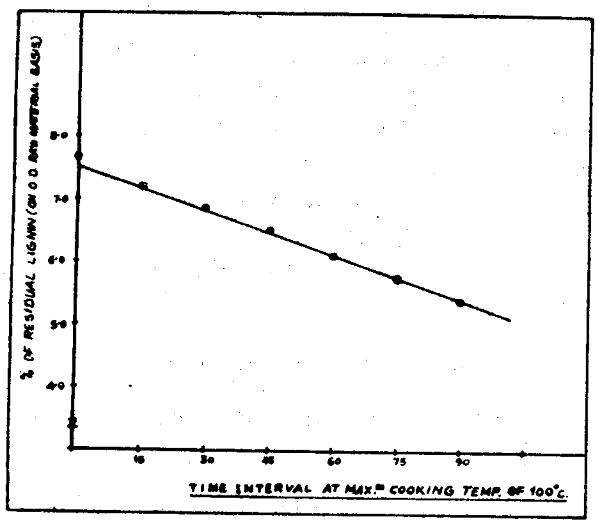

FIG. 2

Lr = Lignin concentration at the end i.e., at the time of maximum cooking temperatures.

According to this expression the rate constants at

363°K (90°C) = 0.1062028 hr^{-1}

373°K (100°C) = 0.1908355 hr^{-1}

383°K (110°C) = 0.2783899 hr^{-1}

393°K (120°C) = 0.4557477 hr^{-1}

The value of energy of activation calculated graphically is 14483.7 cal/mole by plotting the graph (Fig. 3) between $\log_{10}$ (Rate constants) and inverse of temperature in Kelvin.

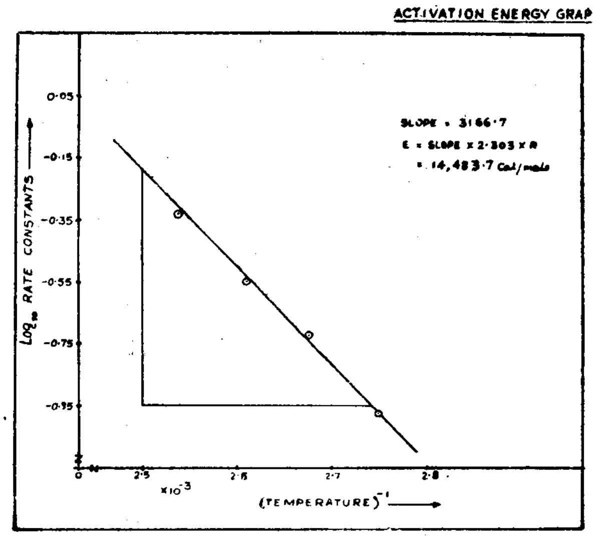

FIG. 3

Calculation for Relative Reaction Rate :

The relative reaction rate values can be calculated by taking Arrhenius first order rate expression in the following form.

ln K = B—A/T

Where, K = reaction rate

T = temperature in degree absolute

and B is constant

$$A = \frac{\text{Energy of activation}}{\text{Gas constant}}$$

Hence A = 14483.7/1.986 = 7292.9≃7293

Assuming that the rate of reaction is unit at 80°C

O = B—A/353

or B = A/353 = 20.7

Thus the relative rate at any other temperature is given by m^{-1} (20.7—7293/T)

The relative reaction rates at various temperature are given in Table 3.

The values of K (relative reaction rate), for the temperatuae range of 80—120°C when plotted against time required to reach that temperature from 50°C gave a curve as snown in Fig. 4. The area under the curve represented by oblique lines is then designated the H-factor and represented the value of 17. This numerical value represents H-factor for the particular standard cycles of soda pulping of Rice Straw employed in this experimental study. Likewise the H-factor for any cooking cycle can be determined.

TABLE—3

RELATIVE REACTION RATES

Sl. No.	Temperature, °C	Relative Reaction Rate
1.	80	1.0
2.	90	1.8
3.	100	3.1
4.	110	5.2
5.	120	8.5
6.	130	13.6
7.	140	20.9
8.	150	31.8
9.	160	47.9
10.	170	69.3
11.	180	99.4
12.	190	140.8
13.	200	196.6
14.	210	270.4
15.	220	367.6
16.	230	493.2
17.	240	654.3
18.	250	857.6

(Calculated from derived Arrhenius expression : Lnk=20.7—7293/T)

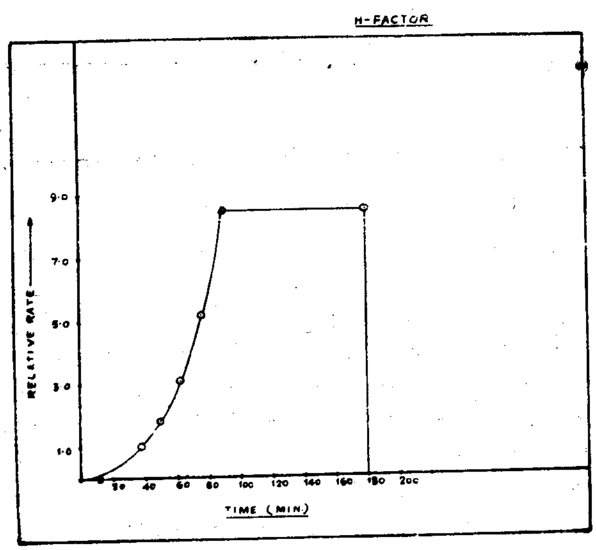

FIG. 4

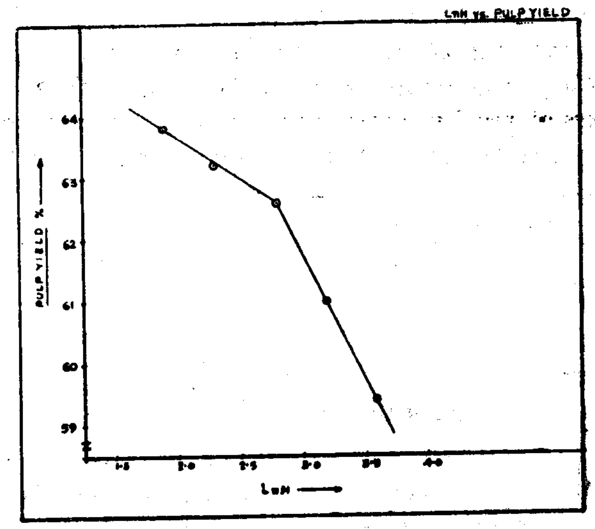

FIG. 5

VALIDITY OF H-FACTOR

In order to test the applicability of the H-factor for rice straw soda pulping, a standard cook with conditions maintained in the previous cooks; at a maximum temperature of 120°C for 90 min. was done. The required cooking times at other four temperature levels (110, 115, 125, 130) were predicted with the aid of the H-factor value of 17. As indicated in Table—4 : H = R.t.

Where, R = Relative reaction rate

and t = time interval at temperature level.

The values of R are known from Table—3 for various at temperature levels. The values of time at-temperature of 110, 115, 125 & 130°C were 173 min., 125 min., 66 min., 53 min., respectively. Pulping experimentation and pulp analysis were carried out as mentioned earlier.

The results of these cooks are recorded in the Table—5. It is observed that the percentage of pulp yield, kappa no. and the residual lignin content in pulp are more or less the same as that of the results obtained with the pulp prepared at 120°C taken as standard cook. Similarly, we have taken two other standard cooks for which H-Factors were calculated and four other 'at temperatre' cooks were done for same H-factor. The results were obtained in the similar manner.

TABLE—4

VALIDITY OF H—FACTOR

H—Factor Standard Cook of Rice Straw at 120°C—90 MIN.

Time From Start Hrs.	Temp.°C	Relative Reaction Rate	Avg. Reaction Rate	Time Interval	H—Factor
0	50	0	0	0	0
0.63	80	1	0.5	0.63	0
0.84	90	1.8	1.4	0.21	0
1.05	100	3.1	2.5	0.21	1
1.26	110	5.2	4.1	0.21	1
1.50	120	8.5	7.0	0.24	2
3.00	120	8.5	8.5	1.5	13
				Total	17
Calculation of cooking time at 125°C required to achieve identical H—Factor of 17.					
0	50	0	0	0	0
0.60	80	1	0.5	0.6	0
0.80	90	1.8	1.4	0.2	0
1.00	100	3.1	2.5	0.2	1
1.20	110	5.2	4.1	0.2	1
1.40	120	8.5	7.0	0.2	2
1.50	125	10.8	9.7	0.1	1
				Total	5

H—Factor required = 17

Balance H—Factor = 12

Minus = 5

Therefore, cooking time at 125°C... = $\frac{12\text{hr.}}{10.8}$ = 1.11 hrs. = 66min.

Similarly, the calculations are done for other cooks to achieve the H—factor of 17. The cooking conditions are : (where the time to attain the max^{m}. temp. is same i e. 1.5 hrs.)

At 130°C — 53 min.

At 115°C — 125 min.

At 110°C — 173 min.

TABLE 5

COMPARISION OF PULPS AT FIXED 'H' FACTOR

Cooking Temperature °C	Predicted Time At-Temperature Minutes	H—Factor	Yield %	Lignin %	Kappa No.
110	173	17	63 5	4 01	27.2
115	125	17	63.0	4.02	28.3
125	66	17	62 0	3.80	26.9
130	53	17	62 2	3.85	27.4
—	—	—	—	—	—
120	90	17	62.6	3.73	27.7

These results indicate that the use of H-factor as mean of expressing cooking time and temperature as a single variable in soda pulping of rice straw has been found quite satisfactory. It also concludes that, regardless of cooking temperature equal H-factor produces pulps of equivalent kappa no. & lignin content etc.

CONCLUSION :

The importance of 'H' factor concept to monitor pulping of woody rawmaterial is well established. Based on the present study it has been concluded that rice straw differs significantly in the relative reaction rates at particular temperature compared to other wood rawmaterial during pulping. This is due to its open structure and comparatively very low lignin content. However, validity of 'H' factor exists and established for soda pulping of rice straw under the different relative reaction rates at varying temperature. Finally it has been concluded that 'H' factor concept can very well be used to monitor the soda pulping of rice straw.

ACKNOWLEDGEMENT :

Authors are thankful to the management, PAPRI, for giving permission to publish this paper. Thanks are also due to Shri S.D. Sharma, M/s. Straw Products Ltd., for helping in statistical calculations.

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