Kinetic Studies on Delignification of N. S. S. C. Pulping of Adhatoda Vasica

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ABSTRACT

The Kinetic Studies on neutral sulphite semichemical (NSSC) pulping of Ahdatoda Vasica a non-wood fibre of Indian Origin and a promising raw material for small sca'e pulp & paper industry. were carried out. Basic Kinetic data i e. rate constant, reaction order, energy of activation and frequency factor were calculated The above studies on the Kinetics of NSSC pulping of Adhatoda Vasica reveals that the rate of delignification followed a pseudo first order rate law with reaspect to lignin and sulphite both. Moreover, the concept of H-factor for representing time and temperature both as one variable is also applicable to NSSC pulping of Adhatoda Vasica

INTRODUCTION :

The ultimate goal of any pulping study is to be able to predict with a certain degree of confidence the overall pulping rate (i. e. the time required under certain specified conditions of temperature, liquor concentration, liquor to wood ratio etc. to reach a particular yield level) and the quality of the resulting pulp. The realities about resource shortage and growing consciousness about quality specifications of the products in demand have diverted the attention of pulp & paper techologists for obtaining high yield pulps and to develop process control parameters, so as to produce specified end products without any appreciable impairment in its properties throughout.

Neutral sulphite semichemical (NSSC) pulping is one of the major high yield pulping process of commercial importance. By its use, a high yield pulp with good strength can be produced and the operation is economically competitive with the other pulping processes. During last decades a considerable amount of interest has been focussed to study the operational parameters and their optimisation during NSSC pulping process. Both the terms i.e. delignification and essential fibre characteristics responsible for strength development are inter-related to each other and the importance of developing quantitative relationships among pulping variables during chemical pulping treatment has been long recognised. A knowledge of delignification reactions is essential for such purpose. Although a considerable work has been done on the NSSC pulping of soft-woods[1,2] as well as hardwood[3,4] but no work has been reported so far on the NSSC pulping of Adhatoda Vasica[5] a non-wood fibre of Indian origin and a quite promising raw material for small scale pulp and paper industries.

It was, therefore, of interest to study the kinetics of delignification of Adhatoda Vasica in NSSC pulping and to examine the validity of H-factor concept for representing time & temperature as single variable for NSSC process, so as to provide process control measures. With these aims the kinetic studies on delignification of NSSC pulping of Adhatoda Vasica was followed with respect to lignin and sulphite ion concentration as two of the parameters of preseut study.

EXPERIMENTAL

Raw Material :

The mature plants of Adhatoda Vasica (Justicia adhatoda) were harvested for the present study. The principal constituents of the Adhatoda Vasica are listed in Table–1. For the kinetic studies the Adhatoda Vasica was chopped by hand to cut chips of approximately 3/4 inches in length and further screened and those passing through 1/2 inch screen but retained on

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a 1/4inch screen were collected. The accepted chips were air dried under atmospheric conditions. The moisture content of the fresh (green) chips was 53% and that of air dry chips was 8%. The raw material used for proximate chemical analysis was dried under the same conditions as the chips.

Proximate Chemical Analysis :

The selected air dried material was disintegrated in the laboratory WEVERK (Swedish Make) disintegrator. The portion passing through 40 mesh sieve but retained on 60 mesh sieve was utilized for proximate chemical analysis i.e. for their different constituents and other desirable properties to check the suitability of plant material in question for pulp & paper making. All the analyis were carried out as per standard TAPPI procedures and the results of proximate chemical analysis are reported in Table—I-A. The results of elemental analysis of Adhatoda Vasica are also reported in Table—1-B.

TABLE–I (A) : PROXIMATE CHEMICAL ANALYSIS OF ADHATODA VASICA

Sl.No.	Constituents	Percentage
1.	Holocellulose	67 02
2.	Hemicellulose	20.12
3.	Alpha Cellulose	46 9
4.	Acetyl Content	1 3
5.	Lignin	20 85
6.	Extraneous Materials	11.24
7.	Pentosans	16 21
8.	Ash	5 33

TABLE–I (B) : ELEMENTAL ANALYSIS OF ADHATODA VASICA :

Sl.No.	Constituents	Percentage
1.	Carbon	48.2
2.	Hydrogen	6 3
3.	Nitrogen	0 25
4.	Oxygen	45.25

Pulping Studies :

All cooks were made in a HAATO-TUOTECOY stainless steel vertical digester with a 0 02 M^3 capacity. The chips were held in a stainless steel basket that fitted inside the digester to facilitate the removal of softened chips. The liquor was circulated by a pump and heated by an external heat exchanger. The cooking temperature was controlled by automatic device. Required amount of cooking liquor was added to the digester. The water was used as diluent to maintain a bath ratio of 1 to 4 between chips and liquor in all the experiments. The following cooking cycle was employed :

(a) Time from room temperature to 110°C 60 minutes

(b) Time at 110°C 60 minutes

(c) Time from 110°C to maximum cooking temperature level 30 minutes

(d) Cooking to different levels of delignification was accomplished by varying the cooking time and maximum temperature level (140 to 170°C) used. 0 to 90 minutes

When a temperature of 105°C was reached, the digester was relieved to zero pressure. At the end of the cook, the pressure was relieved over a period of 15 minutes. The spent liquor was decanted and the semi cooked chips while still hot were centrifuged and defibered through a Bauer refiner. The refined pulp was washed thoroughly free of alkali with tap water dewatered, air dried and stored in polythene bags for further processing.

The pulp yield was determined by weighing the wet pulp lot and taking two representative samples of 50 gms from the lot which were dried in an oven at 105 ± 3°C for 6 hours The dried samples were weighed and percentage yield determined accordingly. The lignin content was determined according to TAPPI Standard method. The pH of the spent liquor is determined and it is further analysed for residual sulphite contents and the results are reported in Table—II.

Method of Calculation :

Reaction rate of delignification was determined by the graphical differentiation of the kinetic curves. Since for a first order reaction :

$$K = \frac{2.303}{t} \log \frac{Li}{Lr}$$

where Li = lignin at initial stage and

Lr = residual lignin

or $2.303 \log \frac{Lr}{Li} = -Kt$

TABLE–II : COOKING CONDITIONS AND PULP YIELD (DISSOLUTION OF LIGNIN AND CARBOHYDRATES) IN NSSC PULPING OF ADHATODA VASICA

Total Chemical as Na_2O (Based on % of oven-dry raw material) = 8.92% as Na_2O
Total Chemical as SO_2 available = 7.11%
Weight ratio of sodium sulphite to sodium carbonate. = 80:20
Wood to liquor ratio = 1:4
pH of the cooking liquor = 11.3

Temperature (°C)	Time at temp. (Min.)	Pulp Yield (%)	Klason lignin (Acid insoluble) in Pulp (%)	Carbohydrates (%)	H—Factor	Residual SO_2 (% on wood)	pH of spent liquor
1	2	3	4	5	6	7	8
140	0	85	20.0	65.0	8.725	3.2	7.0
	30	80	17.87	62.13	22.325	2.8	7.2
	60	78	16.30	61.70	35.955	2.5	7.2
	90	76	14.80	61.20	49.525	2.3	7.3
150	0	82	19.55	62.45	17.175	3.1	7.2
	30	77	17.35	59.65	47.675	2.6	7.3
	60	74	15.40	58.60	78.175	2.2	7.3
	90	72	13.60	58.40	108.675	1.9	7.4
160	0	80	18.60	61.40	40.175	2.8	7.3
	30	75	15.58	59.42	116.675	2.2	7.4
	60	70	13.13	56.87	193.175	1.7	7.5
	90	68	11.10	56.90	269.675	1.4	7.5
170	0	76	17.74	58.26	63.175	2.5	7.5
	30	71	14.20	56.80	185.675	1.9	7.6
	60	66	11.38	54.62	308.175	1.5	7.7
	90	62	9.12	52.88	430.675	1.1	7.9

$$\text{or } \log Lr = \frac{-K}{2.303}\, t + \log Li$$

$$\text{then slope or gradient } = \frac{-K}{2.303}$$

i. e. If a curve is plotted between log percentage residual lignin (Lr) and time (t), and a straight line is obtained, then the reaction will be of first order.

For the determination of temperature dependence of (K) in terms of energy of action (E) and frequency factor (A), with the help of Arrhenius equation.

$$K = Ae^{\frac{-E}{RT}}$$

$$\ln K = \ln A - \frac{E}{RT}$$

On differentiating the above equation with respect to temperature

$$\frac{d}{dT} \ln K = \frac{E}{RT^2}$$

On integrating the above equation

$$\int_{K_1}^{K_2} d\ln k = \int_{T_1}^{T_2} \frac{E}{RT^2}\, dT$$

or

$$\ln \frac{K_2}{K_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log_{10} \frac{K_2}{K_1} = \frac{E}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where K_1 & K_2 are the rate constants at two temperature T_1 & T_2 respectively.

Thus by measuring the rate constants K_1 & K_2 at temperature T_1 & T_2, it is possible to calculate E,

the energy of activation and frequency factor (A) by using the above equations.

Results and Discussion :

The plots of residual lignin associated with pulp (on wood basis) with time of reaction gave a straight line correlation (Fig. 1), showing thereby that the rate of delignification in NSSC pulping of Adhatoda Vasica followed a pseudo first order kinetics with respect to lignin.

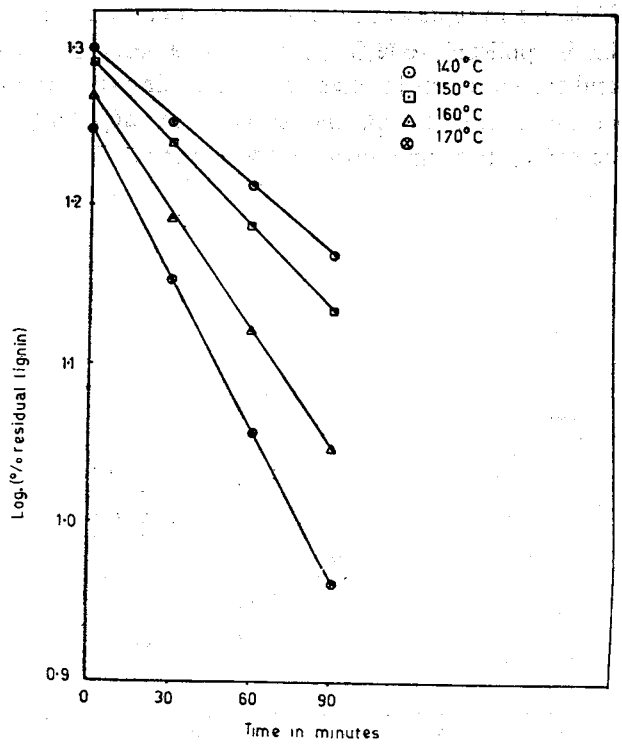

Fig.1—Plots Of Log. (% residual lignin) vs Time During NSSC Pulping Of Adhatoda Vasica

The values of first order rate constant for the delignification reaction during NSSC pulping of Adhatoda Vasica were calculated from the slope of curves represented in Fig. I and are reported in Table-III. The values of energy of activation (E) and frequency factor (A) calculated on the basis of these reaction rate constants are also reported in Table—III.

The plots of residual sulphite versus time (Fig. 2) during NSSC pulping of Adhatoda Vasica clearly indicates that the consumption of sulphite also followed a first order kinetics with respect to sulphite concentration.

The above discussion revealed that the NSSC pulping of Adhatoda Vasica followed a pseudo first order

TABLE-III KINETIC DATA OF N.S.S.C. PULPING OF ADHATODA VASICA

Sl. No.	Property	Values
1.	Cooking Temperatures (°C)	140–170
2.	Reaction order	First Order
3.	Rate constant h^{-1} at 140 °C	1994
	at 150 °C	2425
	at 160 °C	3439
	at 170 °C	4460
4.	Energy of activation (E) KJ/Mole	38.99
5.	Frequency factor (A), Per minute	1.5753×10^4

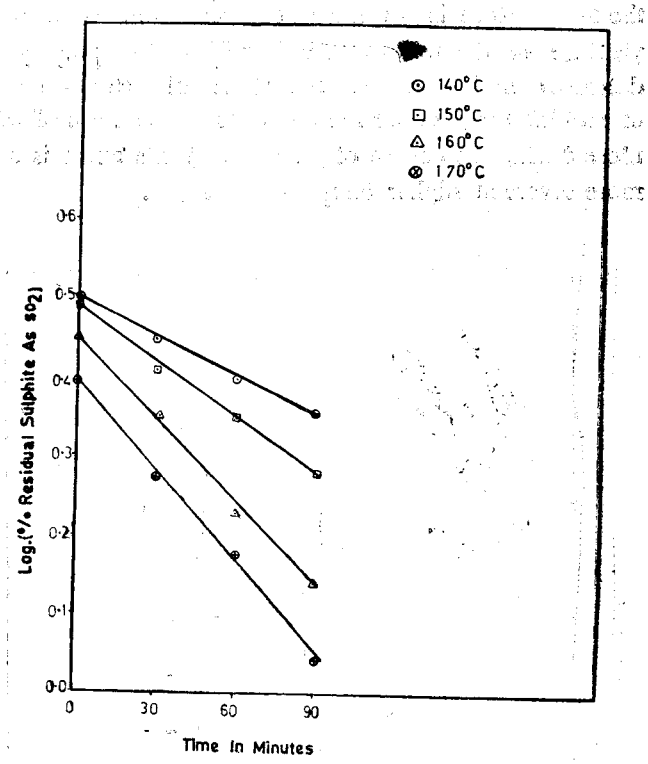

Fig. 2. PLOTS Log. (% RESIDUAL SULPHITE AS SO_2) VS TIME DURING NSSC PULPING OF ADHATODA VASICA.

kinetics with respect to lignin and sulphite both. This can be written as follow :

Rate of delignification $\frac{d[L]}{dt} = K_1'[L]$ where $K'_1 = K_1[S]$ and

Rate of sulphite consumption $= -\frac{d[S]}{dt} = K_2' S$ where

$K'_2 = K_2[L]$ where K_1' is the rate constant for pseudo unimolecular reaction

considering [S] does not change through the entire progress of reaction and

K_2' is analogously rate constant for pseudounimolecular reaction when [L] remains constant and K_1 & K_2 are the respective rate constants when both the components are in the reaction rate expression.

Hence from the above two expressions, the overall rate of delignification for NSSC pulping (r) can be written as

$$r = \frac{-d[L]}{dt} \text{ over all } K_1'[L] + K_2'[S]$$

The plots percentage pulp yield versus time during NSSC pulping of Adhatoda Vasica (Fig. 3) indicates that the temperature is in indirect proportion with pulp yield i.e. as the temperature increases, the pulp yield decreases and moreover the effect of retention time at cooking temperature increases the degradation of cellulose during the course of pulping and this effect is still more severe at higher temperature ranges.

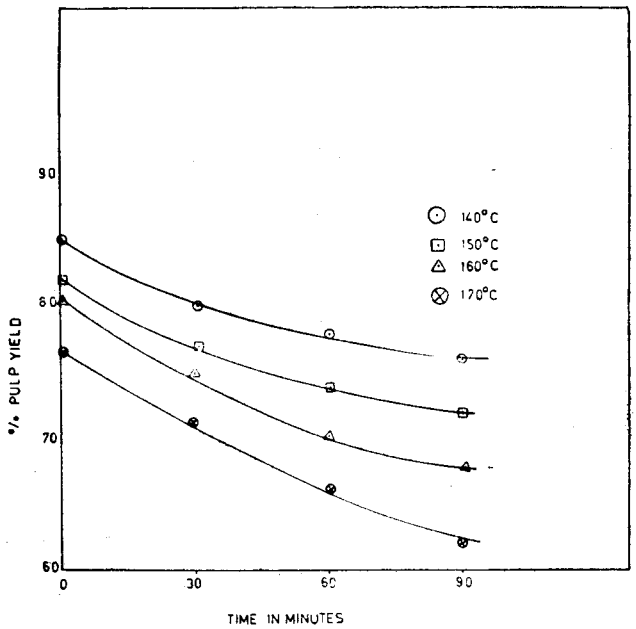

Fig. 3.-PLOTS OF % PULP YIELD VS TIME DURING NSSC PULPING OF ADHATODA VASICA

Validity of H—Factor Concept :

It has been observed above that the rate of delignification during NSSC pulping followed a first order kinetics. Employing this finding the values of rate constants at various temperature levels have been calculated by Basu etal[6], were used for calculating H-Factor. The values of H-factor are recorded in Table-III.

The plots of log percentage residual lignin and log percentage residual sulphite versus H-factor gave curve as shown in Figure-4 and Figure-5 respectively. It will be seen from these figures that the points for lignin concentration and sulphite concentration lie on fairly close to one single smooth curve irrespective of time-temperature schedule. This shows that the concept of H-factor to represent time & temperature as one variable is applicable to N.S.S.C. pulping of Adhatoda Vasica, and therefore can be used for cotrolling the degree of delignification during the cooking by adjusting time according to temperature and vice-versa.

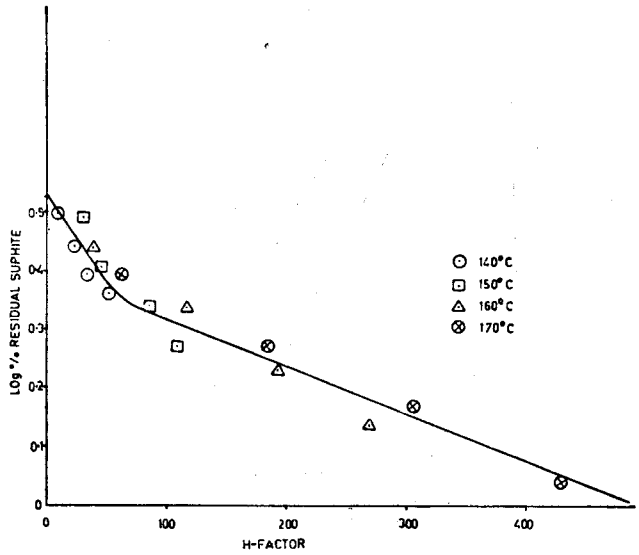

Fig. 4. PLOTS OF Log. % RESIDUAL SULPHITE VS H-FACTOR DURING NSSC PULPING OF ADHATODA VASICA

Conclusions :

The results of kinetic studies of N.S.S.C. pulping of Adhatoda Vasica reveals that it follows a pseudo first order kinetics with respect to lignin and sulphite both. The values of rate constants were found to be 0.1994, 0·2425, 0·3439, and 0·4460 at corresponding temperatures of 140°C, 150°C, 160°C, & 170°C respectively. The values of energy of activation and frequency factor were also calculated and found to be 38.99 KJ/mole and 1.5753×10^4 per minute respectively.

It has been shown that the values of the kinetic data are in many ways comparable to that for temperate hardwoods.

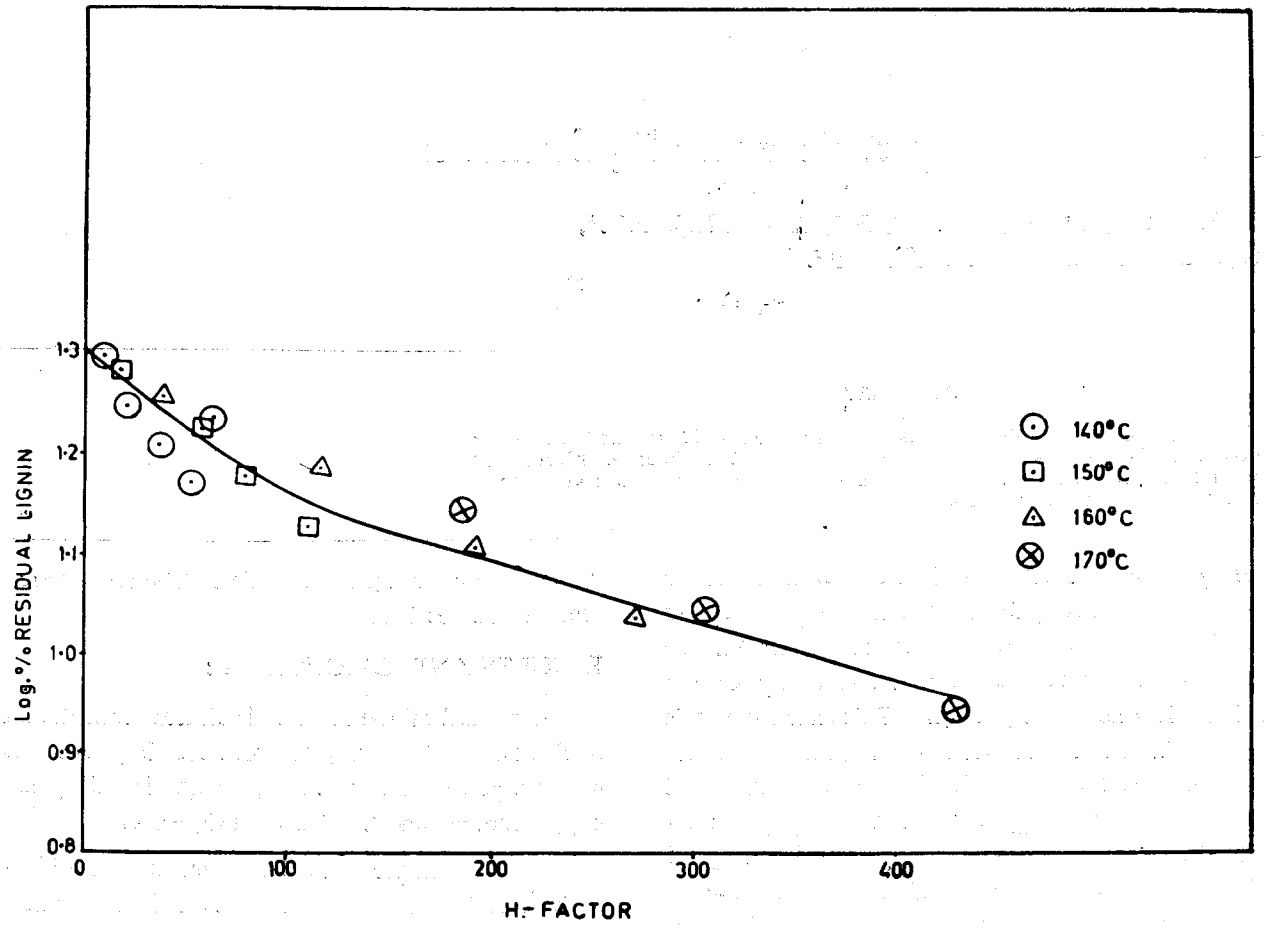

Fig. 5. PLOTS OF Log. % RESIDUAL LIGNIN VS H-FACTOR DURING NSSC PULPING OF ADHATODA VASICA

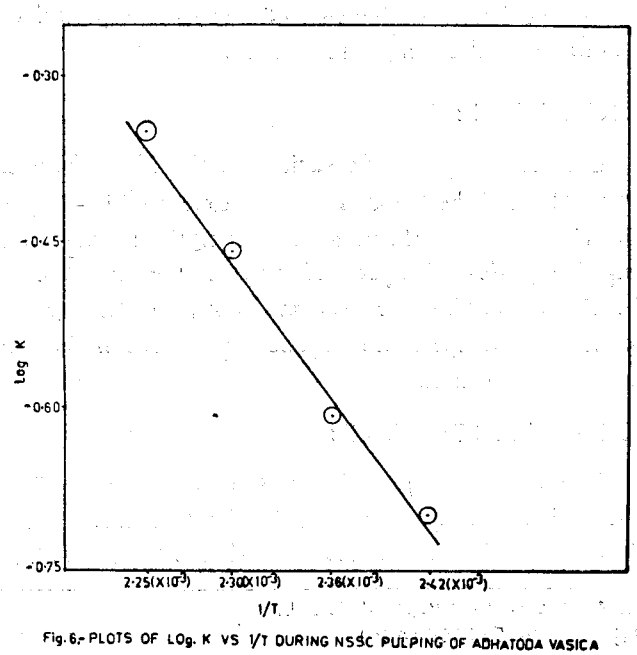

Fig. 6. PLOTS OF LOg. K VS 1/T DURING NSSC PULPING OF ADHATODA VASICA

REFERENCES

1. Findley, M.E. & Nolan W.J.—*Tappi* 39 (11) : 758 (1956).
2. Chari, N.C.S. Ind. Eng. Chem. Process Des Develop. 7:372 (1968).
3. Higgins, H.G., Watson, A J., Nelson, P. J. & Harrington K.J., Division of chemical Technology, Technical Paper No. 1, CSIRO, Australia, 1974.
4. Guha, S. R. D., Pant, R. and Singh, S. V.–*Ippta* 14 (2) : 103 (1977).
5. Wealth of India *"Raw Materials" "Adhatoda Vasica"* Vol. I, page–31, Council of Scientific & Industrial Research, New Delhi 1948.
6. Basu, S., Krause, Th. and Schurz, J.–Holzforschung, 28 : 121 (1974).