Bleaching of Egyptian Bagasse and Rice Straw Pulps with Hydrogen Peroxide

Part II Thermal Characterization of Unbleached and Bleached Pulps

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ABSTRACT

Thermo Gràvimetric Analysis (TGA) and Differential Thermo Gravimetric Analysis (DTGA) of the unbleached and bleached bagasse and rice straw pulps with hydrogen peroxide were investigated. The changes in the shape of the thermograms, kinetics of degradation and other thermal parameters were studied. A slight deterioration in thermal properties due to the slight oxidation of the pulp was obtained but recommendation to use hydrogen peroxide for bleaching has been given.

INTRODUCTION

Thermo Gravimetric Analysis (TGA) and Differential Thermo Gravimetric Analysis (DTGA) provide us tools to investigate the thermal behaviour of different fibres and polymers. Natural fibres vary in their structure, chemical composition and origins. Consequently, their reactions to thermal treatment will differ. Thermo analytical studies on the thermal behaviour of cellulosic materials have been subjected to a large number of studies (1-5). Three main stages of degradation are generally accepted. a) dehydration stage, b) fragmentation through random cession of macromolecular structure, which is accompanied by evolution of gaseous components which represents the main degradation step and c) carbonization stage. The last two stages exhibit exothermic effect due to the successive splitting and reformation of new components ready for the next splitting on continuous thermal treatments. Thermal resistivity of the natural fibres depend mainly on the chemical constituents, the structure and many other experimental factors, such as the rate of heating, duration of treatments etc. It seems logical to extend the previous studies on the properties of the unbleached and bleached bagasse and rice straw pulps with hydrogen peroxide to explore their behaviour towards thermal treatments.

EXPERIMENTAL

Sample preparation

Bagasse (B) and rice straw (RS) pulps were obtained from an Egyptian local mil, possessing the following specifications:

B: 0.8% ash, 64.6% α-cellulose, 27.8% hemicellulose and 4.95% lignin.

RS: 13.5% ash, 56.1% α-cellulose, 24.4% hemicellulose and 6.06% lignin.

The pulps were beaten to 45 SR^0 and then subjected to treatments with hydrogen peroxide, as indicated before in previous work (6).

Thermal analysis of the prepared samples

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) of the untreated and treated samples were carried out using "Perkin-Elmer" thermobalance. A linear rate of 10% min. was applied and the measurements were taken from ambient temperature up to 973^0K.

RESULTS AND DISCUSSION

TGA of bagasse samples are illustrated in Fig. 1, untreared sample denoted as A, while B represents the bleached sample with H_2O_2. It is clear that the main degradation stage is restricted in stage b, thus our present study is mainly on this stage in which a more or less linear behaviour is obvious in case of unbleached sample (A), and a very slight deviation occurs in the treated sample (B). This may be related to consecutive splitting with the formation of new molecules with evolution of gases, also it may be related to the changes occuring in the chemical constituents of the samples. Stage c represents the carbonization stage with formation of more stable final product.

b) Rice straw pulp

The stages observed in bagasse samples also occur in

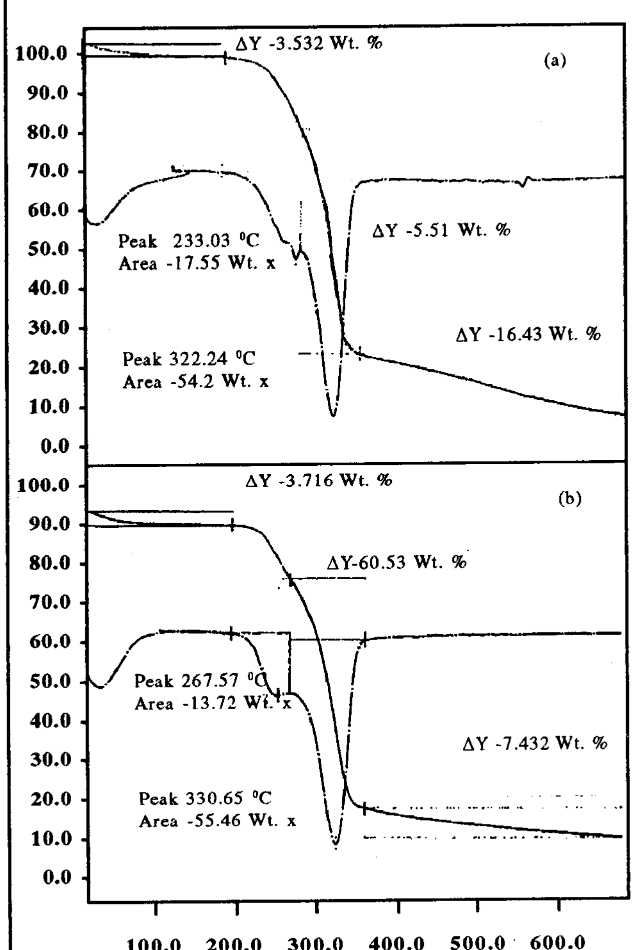

Fig. 1 DTA & TGA profiles of unbleached a, & bleached (b) bagasse pulp.

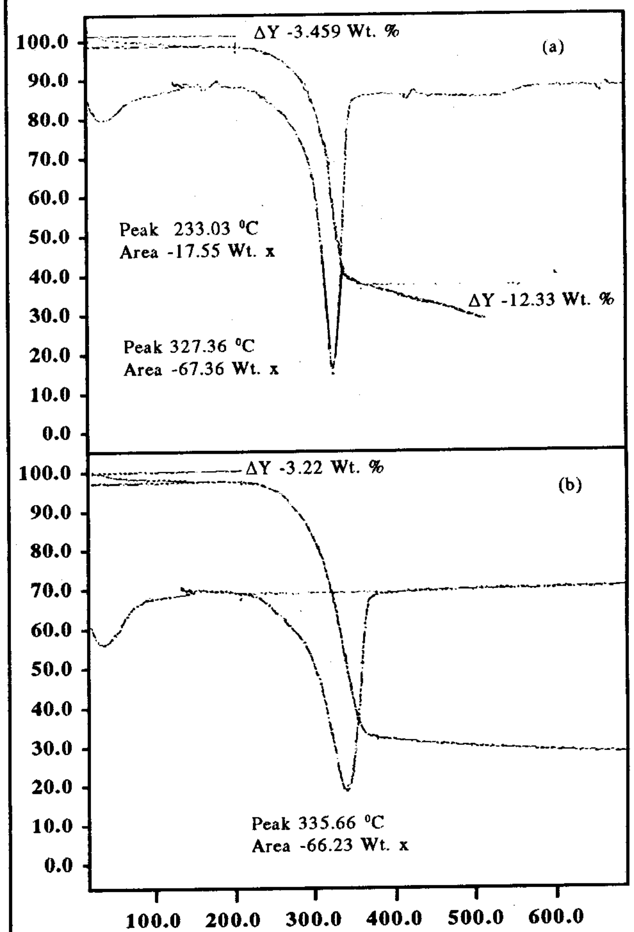

Fig. 2 DTA & TGA profiles of unbleached a, & bleached (b) rice straw pulp.

rice straw samples. Sample A represents the untreated pulp, while sample B represents the RS pulp treated with H_2O_2.

The same three stages are observed regarding the shape of TGA except the untreated sample A, in which stage b splits in 2 substages b' and b". A different degradation rate is shown between those two substages which is related to the effect of high amount of silica in the untreated pulp. This amount of silica possesses dual effect on the pulp: i) may act as a catalyst accelerating degradation rate in the finest part and at the end of this stage degradation rate decreases. ii) due to the amount of silica contained in the innermost part of the pulp, degradation rate decreases in stage b", as the amount of degraded materials is exposed directly to thermal energy, leaving the innermost part with silica to the end of this stage. Stage c represents the final and stable stage.

Changes in the thermal stability of the samples

In order to account for the effect of above treatments on the thermal resistivity of the samples towards thermal degradation, the loss percentage mass in the samples against the temperature is plotted in Fig. 3. From this figure, it is clear that bleached RS pulp resists to some extent the thermal energy compared to B pulp. This can be explained on the basis of the difference in the fibre structure and chemical constituents of the samples since RS pulp usually contains a higher ratio of silica than B pulp.

Kinetics of degradation

Generally, the rate of any chemical reaction "k" is expressed by:

$$K = - dc / dt = Kc^n \quad (1)$$

where c represents the concentration of reactants at time t, K is the specific rate constant and n is the order of reaction. In a thermogravimetric analysis, the concentration c is replaced by the mass of remaining non-evaporated materials at time t for each process i.e. W_t-W_∞, where W_t represents the mass of the samples at time t, and W_∞ is its value at the end of the process. Using the above presentation, equation (a) can be written as follows:

$$k = - dW / dt = K (W_t - W_\infty)^n \quad (2)$$

Applying Arrheniuseqn. (7) we obtain:

$$\text{In } K = \text{In } (dW / dt) / (W_t - W_\infty)^n = \text{In } A - \Delta E_a /RT \quad (3)$$

The rate of reaction (-dW / dt) can be calculated as:

$$-dW / dt = - (W_2 - W_1) / (t_2 - t_1) \quad (4)$$

where W_1 and W_2 are the masses of the samples

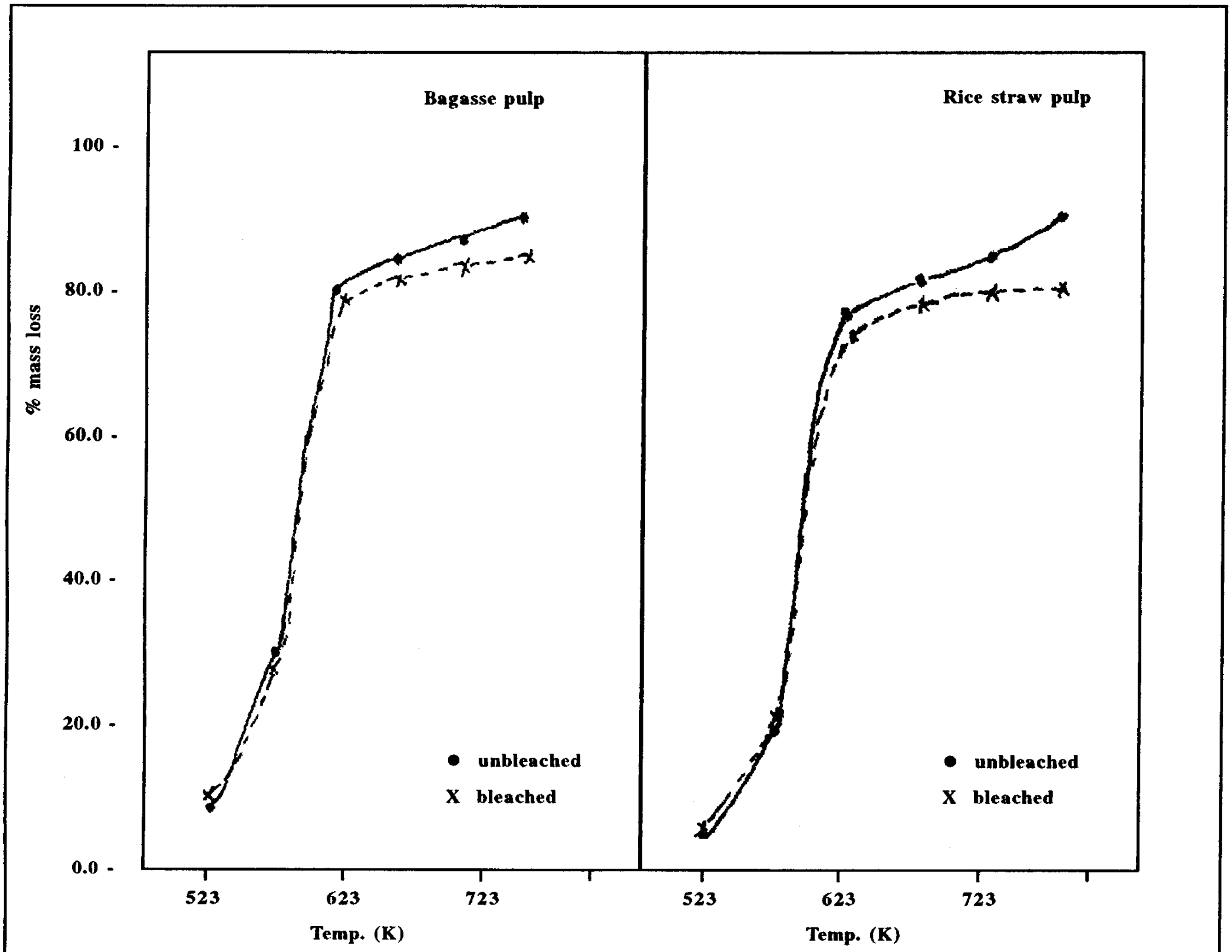

Fig. 3 Relation between % mass loss and temperature.

Table 1. Values of n, k, E_a and W_∞ for the samples.

	Bagasse pulp				Rice straw pulp			
	n	k $s^{-1}*10^{-5}$	E_a kJ/mol K	$\%W_\infty$	n	k $s^{-1}*10^{-5}$	E_a kJ/mol K	$\%W_\infty$
Untreated pulp	0.6	5.6	15.3	4.06	0.4	21.5	13.1	13.13
Treated with H_2O_2	0.6	240	23.5	13.44	0.6	107	20.3	22.19

remaining after times t_1 and t_2 respectively.

Thus plotting the left hand side values of eqn. 3 i.e. In K versus 1/T, using various values of n should give the best straight line with the most appropriate order of reaction n. If the method of least squares is applied using eqn. 3 and taking different values of n ranging from 0.0 to 3.0 with increments of 0.2, then calculating for each value of n the correlation coefficient "R_c" and the standard deviation "S", the appropriate n value is that which would give a maximum R_c and minimum S.

The activation energy E_a is then calculated making use of eqn. 3 and applying the appropriate value of n. The values of n,k,E_a and % W_∞ are tabulated in Table 1.

Changes in the order of reaction

In all samples investigated, the order of reaction is beyond unity indicating a nearly similar mechanism for the decomposition. It should be noted that rice straw samples possess a higher amount of silica than bagasse samples.

Changes occuring in the specific rate constant k

The specific rate constants of the thermal gradation process were calculated and included in Table 1. It is clear that treatments with hydrogen peroxide solution affect to some extent and some degradation may occur due to the oxidizing effect of OH. so, an acceleration in the rate of thermal degradation may be expected although the rate of acceleration differs according to the differences in the fibre structure and chemical constituents of the samples.

Changes in the activation energy values

Activation energy values of the studied samples are calculated and their values increase due to the treatments with hydrogen peroxide since these treatments oxidize first the short fibres (possessing a low DP) leaving the relatively longer fibres (higher DP) leading to the increase in the activation energy. In this junction, it should be noted that the values calculated depend on the amount of sample remaining at the end of the reaction (W_∞) which differs from one sample to another (Table 1).

CONCLUSION

From the above results, it can be concluded that: Bleaching of rice straw and bagasse pulps with hydrogen peroxide affects thermal stability of the samples. Rice straw shows a little lower stability than bagasse pulp. In spite of the slight deterioration shown in the thermal properties, bleaching of agricultural residues with hydrogen peroxide is recommended, since it can be considered as a way to minimize environmental pollution caused by the utilization of traditional chlorine - containing bleaching agents.

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