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THE THERMAL STABILITY OF SOME PULPING MATERIALS

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ABSTRACT

The thermal stabilities of three annual plants (reed, kenaf and *Glycyrrihiza glablra L.*) are studied. Various types of pulps were prepared from reed stalks by employing the soda, kraft and soda–anthraquinone processes. Their thermal stabilities are reported.

It is shown that the thermal stability measured thermogravimetrically depends, to some extent, on the amount of lignin remaining in the raw materials, i.e. the kappa number.

The activation energy of the decomposition process and the decomposition temperatures of the pulps are also reported.

INTRODUCTION

The thermal stability of polymers is one of the important characteristics from the processing and application points of view, because cellulosic materials are usually subjected to high temperatures during the pulping process. Therefore we decided to study the thermal stability of three cellulosic raw materials used in the pulping industry and we studied the effect of some pulping processes such as bleaching on the thermal stability of these natural polymers.

RAW MATERIALS

Numerous samples were prepared for the purpose of this study. These were either pulps or sawdust of the raw materials. The types of pulps included were soda, kraft and soda–anthraquinone pulps of reed (*Phregmites communis*), mixed softwood pulp and mixed hardwood pulp. Fine powdered particles of reed, kenaf bark (*Hibiscus sabdariffa*) and *Glycyrrihiza glablra* L. were the raw materials used in this experiment. These fine particles were prepared by using a Wiley mill. Fractions passing 40 mesh and retained on 60 mesh were accepted for analysis. All samples were air dried and kept at room temperature until they were used for analysis.

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PULP PREPARATION

Reed stalks (grown in marshes in Iraq) were used to prepare pulps by employing soda, kraft and soda–anthraquinone (soda–AQ) methods [1]. In both the soda and kraft processes, a constant active alkali (14% as Na_2O) was used. The total sulfidity of the kraft process was 15% as Na_2O. The soda–AQ pulps were prepared using a constant active alkali of 14% as Na_2O and varying the percentage of anthraquinone form 0.02 to 0.3% based on oven-dry wood.

All pulps were prepared by charging 1 kg (oven-dry basis) of chopped reed stalks into a 20 l rotating electric autoclave. Pulping conditions were held constant in all cases and were as follows: total cooking time 180 min, heating-up time 90 min, maximum temperature 140°C and liquor to wood ratio 4:1.

Pulp evaluations regarding total yield, rejects and kappa number were carried out for each pulp according to TAPPI standard methods [2] and the results are listed in Table 1.

BLEACHING

Soda–AQ pulps were bleached to minimize the lignin content in each pulp. A bleaching sequence [3] represented as hypochlorite (H), extraction (E), peroxide (P)

TABLE 1

Evaluation of soda, kraft and soda–AQ pulps obtained from reed stalks

AQ (%)	Unscreened yield (%)	Rejects (%)	Kappa number
Kraft	53	3	33
Soda	51	28	59
0.02	48	11	46
0.05	49	6.6	39
0.10	51	6.5	37
0.20	50	6.2	34
0.30	50	5.2	31

TABLE 2

Bleaching sequence of soda-AQ pulps

	H	E	P	H
Chemical [a]	NaOCl	NaOH	H_2O_2	NaOCl
Percent	5	2	2	5
Consistency (%)	5	5	5	5
pH	10	11	10	10
Temp (°C)	43	80	45	45
Time (min)	120	120	120	180

[a] Available chlorine was 5% in stage H.

and hypochlorite (H) was applied to all pulps and at conditions given in Table 2. The purpose of employing a constant bleaching condition was to remove as much lignin as possible without causing corresponding degradation of the cellulose. Thus, all soda–AQ pulps were treated almost equally prior to thermal analysis.

THERMAL ANALYSIS

Thermogravimetric analysis was carried out on a MOM derivatograph. The measurements were obtained by (a) increasing the temperature of the sample rapidly (20° min^{-1}) to the desired temperature (210°C) then keeping the sample at this temperature by using the lowest heating rate 0.6° min^{-1} as shown in Fig. 1, under which conditions the isothermal study was carried out; (b) by raising the temperature of the sample at a steady rate (10° min^{-1}) until the polymer is substantially decomposed (Figs. 3–6).

The measurements were carried out against standard α-Al_2O_3 in the presence of air.

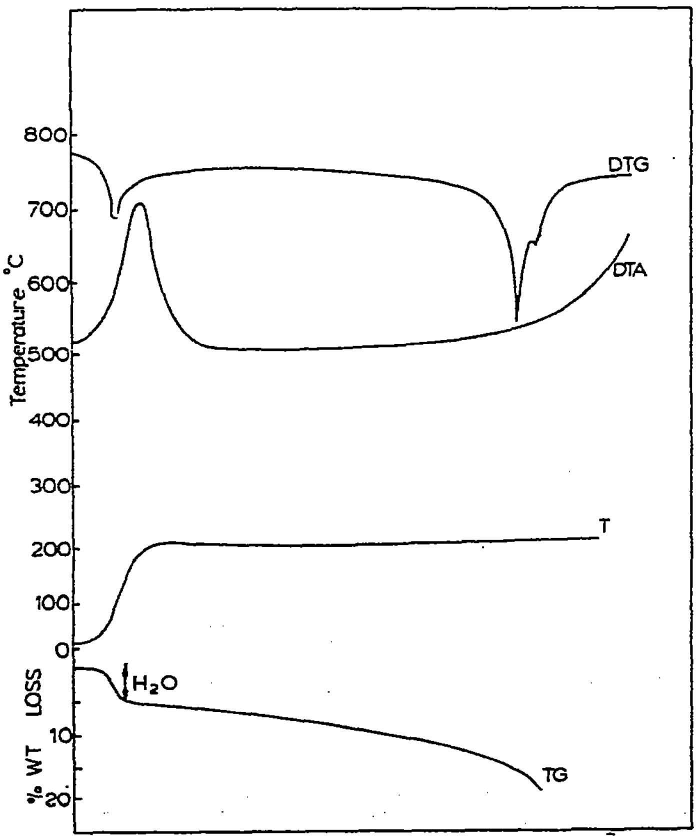

Fig. 1. Typical thermogram obtained in the isothermal decomposition study.

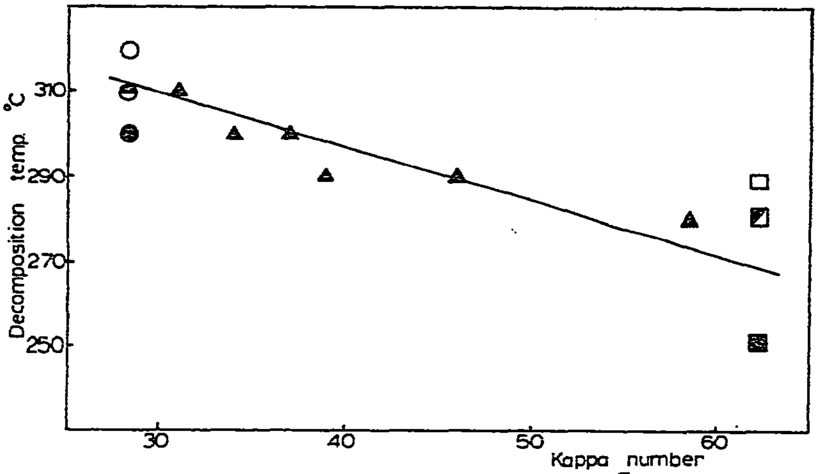

Fig. 2. The relation between the kappa number and the decomposition temperature of different types of pulps as estimate from DTG. ▲, Soda–AQ. pulps (0–0.3% AQ): ●, bleached kraft (mixed soft wood): ○, bleached soda (reed): □, *Glycyrrihrza glablra* L. (sawdust): ○, bleached sulfite (mixed softwood): □, kenaf bark (sawdust): ■, reed (sawdust).

RESULTS AND DISCUSSION

The thermogravimetric curves show that the thermal stability of the different pulping materials varies with the kappa number of the product. In other words, it depends on the amount of lignin in the pulping materials. The results obtained are shown in Fig. 2. Thus, bleached pulps having no lignin content show a higher thermal decomposition temperature (as measured from DTG) than the unbleached product (Table 3). Typical thermograms are shown in Fig. 3.

On the other hand, the pulping products obtained from soft wood are thermally more stable than those obtained from hard wood (Fig. 4). This is probably due to the difference in the molecular weight of these two types of pulp. The effect of molecular weight on the thermal stability of many synthetic polymers has been well established [4,5].

Regarding the untreated raw materials used in this study, the reed is shown to

TABLE 3

Type of pulp	Activation energy (kcal mole^{-1})	Decomposition temp (°C)
Unbleached soda (reed)	21±1	270
Unbleached kraft (reed)	38±2	280
Bleached soda (reed)	49±2	310
Soda–anthraquinone (reed)	34±3	300
Bleached kraft (mixed hardwood)	35±3	290
Bleached kraft (mixed softwood)	48±2	300

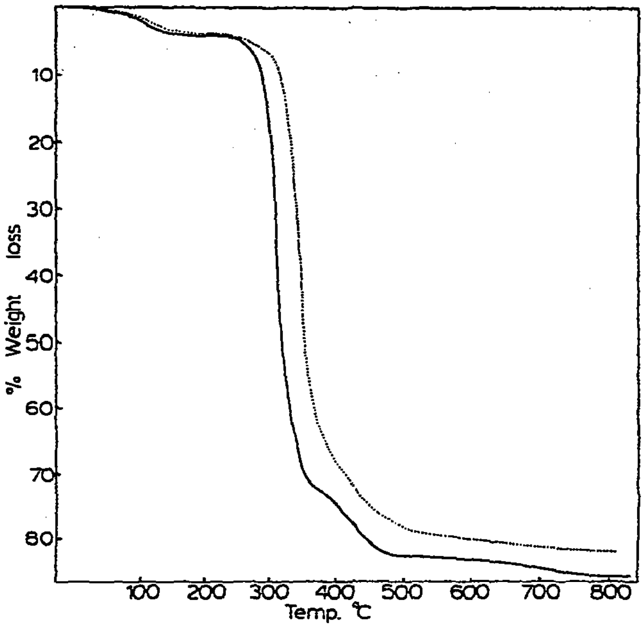

Fig. 3. The effect of bleaching on the thermal stability of reed pulps. ······, bleached soda (reed); ————, unbleached soda (reed).

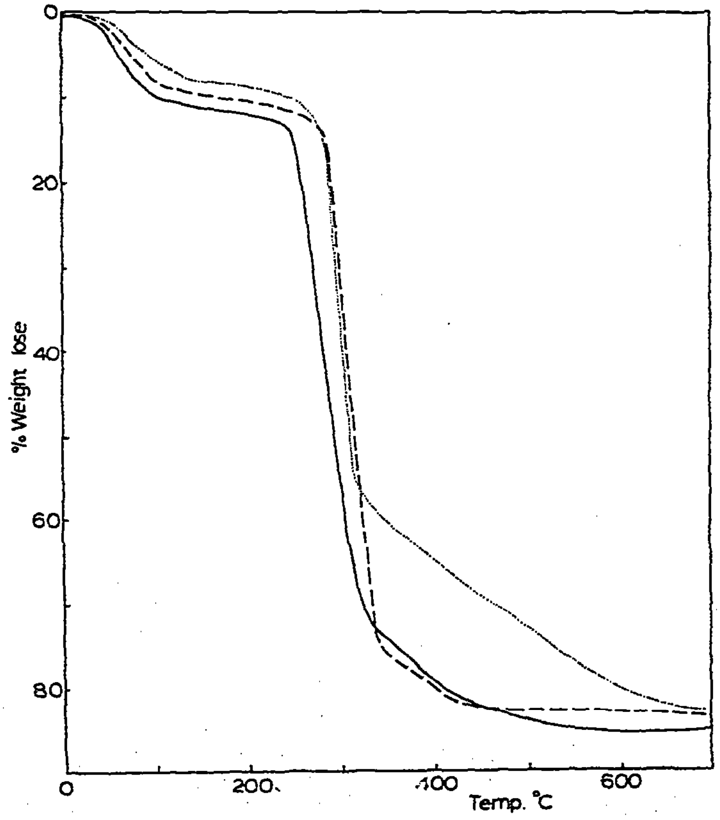

Fig. 4. The thermogravimetric curves of pulps obtained from hardwood and softwood. ————, Bleached kraft (mixed hardwood); — — —, bleached sulfite (mixed softwood); ······, bleached kraft (mixed softwood).

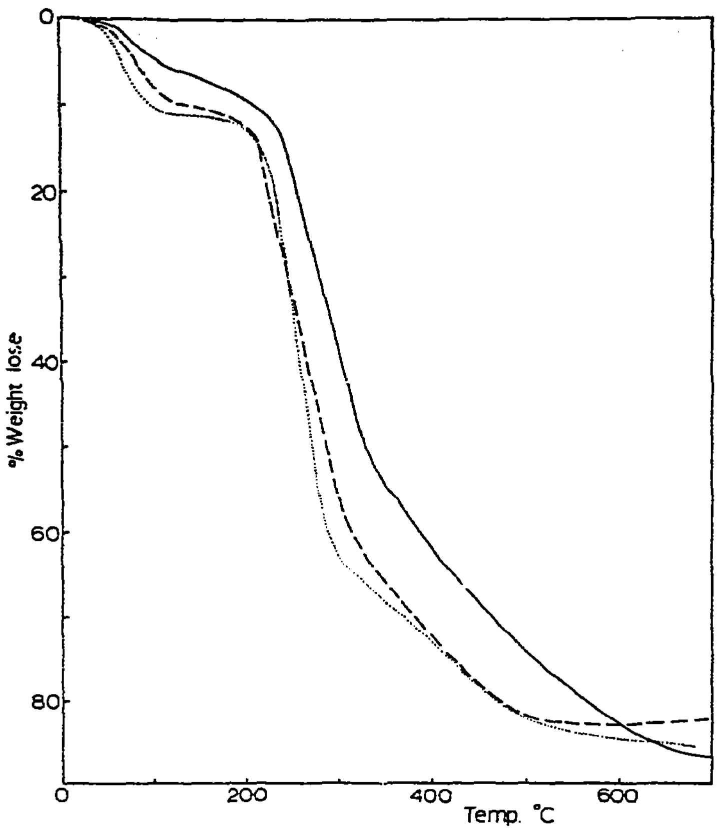

Fig. 5. The thermogravimetric curves of raw materials. ———, Reed stalk: — — —, *Glycyrrhiza glabra* L.: · · · · · ·, kenaf bark.

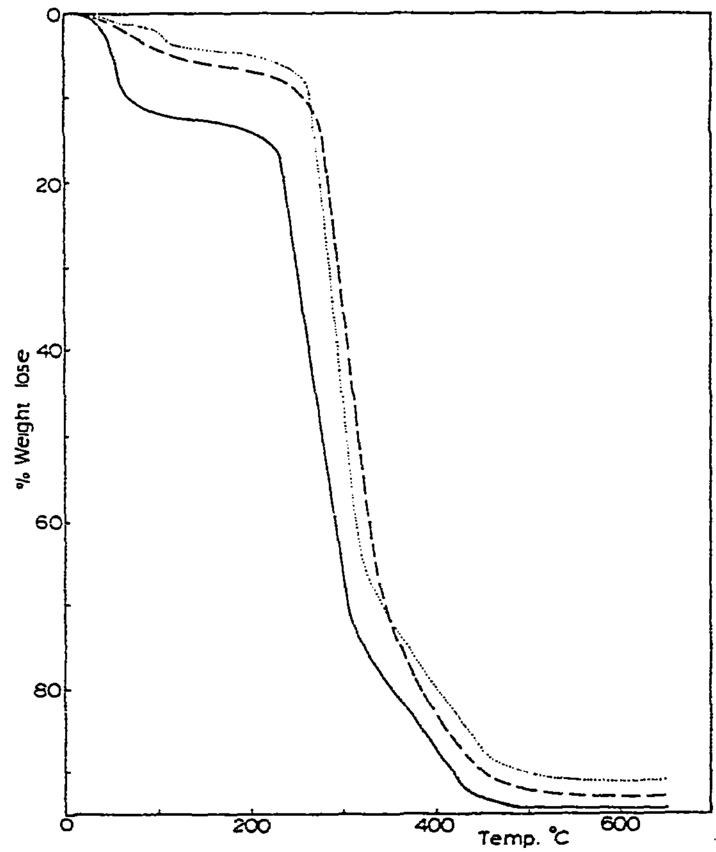

Fig. 6. The effect of anthraquinone concentration used in the pulp preparation on the thermal stability of the product. ———, Soda (AQ free); · · · · · ·, soda–AQ (0.02% AQ); — — —, soda–AQ (0.1% AQ).

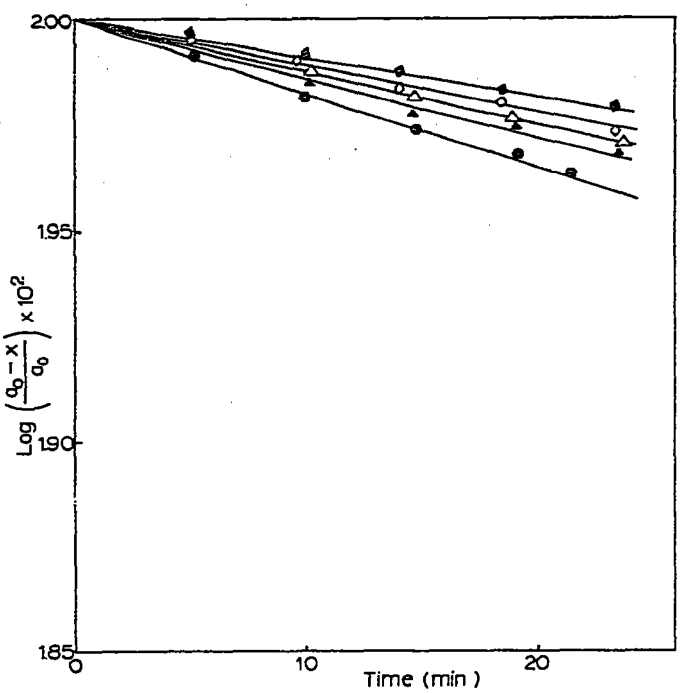

Fig. 7. The isothermal weight loss at 210°C for different pulps. ◆, Unbleached kraft (reed); ◇, soda–anthraquinone (0.05% AQ); ▲, unbleached soda (reed); ●, bleached kraft (mixed hardwood); △, bleached kraft (mixed softwood).

have higher resistance towards decomposition than *Glycyrrihrza glablra* and kenaf. Typical thermograms for these different raw materials are shown in Fig. 5.

The thermogravimetry of soda–anthraquinone pulps of reed show that the thermal stability of the pulp increases with the increase in the percentage of AQ used in the treatment, which in fact affects the kappa number of the product, i.e. the kappa number decreases with the increase in percentage of AQ (Fig. 6).

The results obtained from the isothermal treatment at 210°C shown in Fig. 7 confirms the observations illustrated in Figs. 3–6.

From the instantanous slopes of the thermograms at different temperatures, the energy of activation of the decomposition process, over the initial 15–20% weight loss, was calculated. The results obtained for the different pulps are shown in Table 3. The table also contains the decomposition temperatures as estimated from the DTG thermograms, i.e. the temperature at which the maximum rate of weight loss takes place.

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