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THERMOGRAVIMETRIC STUDY ON TYPHA (TYPHA ANGUSTIFOLIA L.)

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Thermogravimetric analysis, was employed to study the thermal behaviour of typha, a naturally growing plant in the marshes of the south of Iraq, and its main components, holocellulose, hemicellulose and cellulose. The overall TG signal of typha appeared as the sum of those of hemicellulose and cellulose. The conditions of holocellulose fractionation, and particularly the nitrogen purging, affected the nature of the cellulose and hemicellulose, as could be concluded from the shapes of the TG curves of these fractions. The thermal behaviour of typha is greatly influenced by the stage of maturity of the plant.

Cellulose and hemicellulose are the most abundant renewable organic materials in the world. They are present in comparable amounts in land plants [1]. Early interest in the thermal degradation of cellulose was started by the discussions of the origin of bituminous coal: whether it is derived from the lignin or carbohydrate constituents of wood [2]. The deterioration and degradation of cellulosic materials are of concern to the industries using them at elevated temperatures, e.g. for the making of paper and textiles, where the general problem of the processing and drying of cellulosic materials remains to be discussed. Many authors have reported on the thermal degradation of cellulosic materials and other carbohydrates for specific purposes [3–5]. Typha is one of two wild non-woody plants that grow naturally in the marshes in the southern region of Iraq. It has not been fully utilized in industry, but it could be of value when it has been fully studied. Typha was earlier evaluated as a candidate biomass material via thermochemical means, and was found to be superior to wood [6, 7]. The thermal decomposition of typha is affected by the heating rate and atmosphere and can be catalysed by potassium carbonate [5].

In the present work, green and dry typha are evaluated in terms of the chemical constituents, and thermogravimetrically investigated in order to gain further information about the related properties of the original natural product.

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Experimental

Plant material

Typha (Typha Angustifolia L.) was collected from the marshes in Misan Province, Iraq. The green plant was directly boiled in ethanol for 2 h, to deactivate the enzymes and to minimize any biological changes. It was then air-dried, and milled to pass through 1 mm sieves. Naturally, dry old plant material was milled without any preliminary treatment.

Preparation of holocellulose

Samples (ca. 10 g) of milled material were delignified using sodium chlorite and acetic acid at 70° [8].

Fractionation of holocellulose

The holocellulose content of each sample was fractionated into cellulose and hemicellulose by successive treatments with 5% and 24% KOH under nitrogen. A separate sample of holocellulose derived from green typha was treated with the alkali without nitrogen purging.

Samples of each plant material were analysed for lignin [9], ash [10] and water solubility [11].

Sugar analysis of hemicellulose

About 20 g of the hemicellulose material was hydrolysed, and the sugars in the hydrolysate were converted into alditol acetate [12] and examined by gas chromatography, on a Pye–Unicam 204 chromatograph, using a flame ionization detector. The separation was performed with a glass column, 2.3 m in length and 4 mm i.d., packed with 3% OV–225 supported by suppelcoport 80–100 mesh, and operated at 190°.

Thermogravimetric analysis

The thermogravimetric (TG) and derivative thermogravimetric (DTG) measurements were carried out simultaneously on a Stanton Redcroft TG 760 thermobalance equipped with a three pen recorder. Samples weighing 3–5 mg were heated in platinum dishes at a rate of 20 deg min^{-1} under nitrogen gas dynamic atmosphere (25 ml min^{-1}). The TG and DTG curves involved dehydration and thermal decomposition of the materials. The dehydration part, however, was not significantly different for the various materials and hence they will not be included in the curves shown in the figures and only given as percentages within the text. The thermal decomposition part will be displayed as extents of reaction rather than percentage of the whole material weight.

Results and discussion

Samples of green and dry typha were analysed to determine the percentages of the cell-wall components (Table 1). The differences in the composition are attributed to the enzymatic and microbial degradation of the macromolecules present in the cell wall [13].

Table 1 Approximate analysis of green and dry typha

Component	Green typha	Dry typha
Water solubility, %	13.45	16.22
Lignin, %	25.32	23.68
Holocellulose, %	71.89	70.06
Cellulose, %	41.09	40.60
Hemicellulose, %	30.91	29.80
Ash, %	2.87	5.04

The results of the hydrolysis of the hemicellulosic polysaccharides (Table 2) indicate the domination of xylan of the type commonly present in non-endospermic tissues, i.e. containing a very low proportion of arabinose. Glucuronic acid and its 4-0-methyl ether were indicated from the detection of its degradation products (4-deoxyhexitol) [12]. The 1% galactose is derived from the xylan and not from independent polysaccharides [14]. The other polysaccharides are non-cellulosic 1 →4 and 1 →3 heterolinked glucans, which represent about 2.9 and 3.6% in dry and green typha, respectively. Generally, the hemicellulose of typha contained two

Table 2 Sugar analysis of the hemicellulose polysaccharides of green and dry typha

Sugar	Retention time, min	Green typha	Dry typha
Arabinose, %	1.37	7.0	6.3
Xylose, %	1.76	84.7	83.1
4DH[a], %	2.2	0.9	2.2
4DH[a], %	2.4	2.3	5.1
Galactose, %	3.95	1.0	1.0
Glucose, %	4.3	3.6	2.9

[a] 4DH = 4-O-deoxyhexitol (2 peaks)

polysaccharides, predominantly a xylan (acidic galactoarabinoxylan) and a low proportion of glucan.

Thermal behaviour of green typha

The TG and DTG curves of green typha and its three components, holocellulose, hemicellulose and cellulose, are shown in Fig. 1. Green typha dehydrates between 50 and 130°, losing about 7.0% of the weight. The main decomposition reaction commenced at 185°, attained a maximum rate (DTG peak) at 315°, and ended at 380°. The DTG signal was broad and revealed the occurrence of overlapping decomposition reactions. The decomposition of the holocellulose was identical to that of the typha, indicating that the action of lignin on the degradation is a minor one. The thermal curves of cellulose and hemicellulose were significantly different from each other and from those of the mother material. Hemicellulose lost 8.3% by weight on dehydration and decomposed between 170 and 330°, with a maximum rate of weight loss at 250°. The dehydration of cellulose involved the loss of 11.9% of the material and the main decomposition reaction started at 221°, attained a maximum rate at 342°, and ended at 380°. Thus, hemicellulose represents the low thermal stability component of typha, and cellulose is the high thermal stability component.

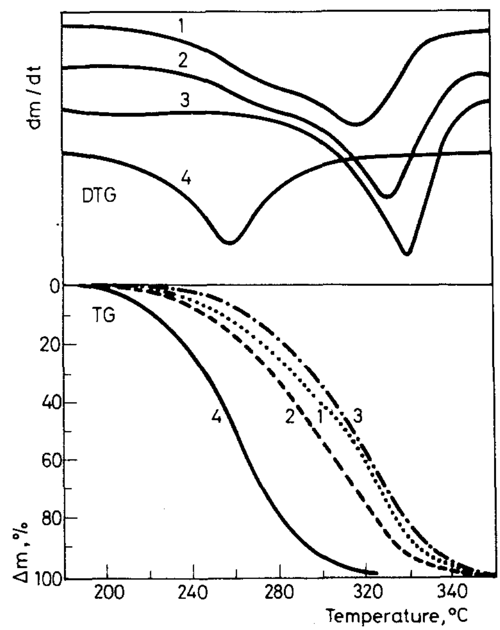

Fig. 1 TG and DTG curves of green typha, 1; holocellulose, 2; cellulose, 3; and hemicellulose, 4

The fractionation of holocellulose with alkali is a very important step in determining the percentages of cellulose and hemicellulose. The extraction on a laboratory scale is usually performed under a N_2 atmosphere. In industry, e.g. pulp and paper making, the alkali pulping, which is a common process, is usually performed atmospherically in the presence of oxygen. Figure 2 shows the DTG

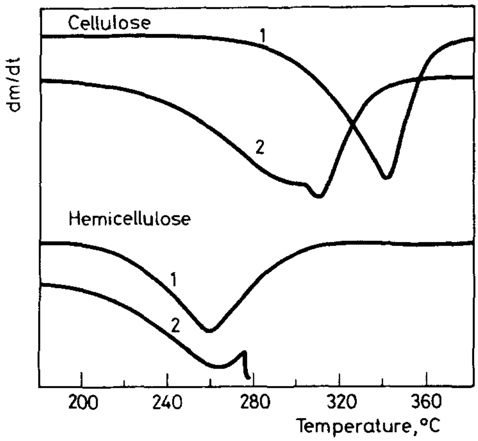

Fig. 2 DTG curves of cellulose and hemicellulose separated under nitrogen, 1 and ambient atmosphere, 2

curves of the cellulose and hemicellulose extracted under nitrogen and ambient atmospheres. The curves of cellulose differed significantly from each other, as the latter case showed not only the usual cellulose peak, but also another peak which represented almost 35% (DTG peak area basis) of the total sample, a material with lower thermal stability. Hence, the material is a degradation product of cellulose, which was formed in the alkaline medium in the presence of oxygen. Hemicellulose was more sensitive towards oxidation than cellulose, due to the difference in the rigidity of its structure, and a fusable material was obtained, which swelled on heating beyond 280°. Therefore, TG could be a rapid technique to determine the properties of cellulose and also the efficiency of the extraction process.

The TG and DTG curves of dry typha are shown in Fig. 3, superimposed on those of green typha for comparison. The dehydration step was identical for both materials with respect to the temperature interval and extent of weight loss. The initial decomposition temperature was 207°, about 20 deg higher than that for green typha. This could be due to the higher degree of polymerization, DP, of cellulose and other cell-wall polysaccharides, resulting from the differences in maturity; naturally, dry typha is definitely more mature than green typha. The natural degradation of the hemicellulosic materials during the long-term drying led to a lower content in comparison with other cell-wall components and this may also account for some of the difference in thermal stability. On the other hand, the temperature of maximum rate of weight loss was lower than that of green typha by 5 deg. The details of the decomposition differed significantly for the two materials. Two distinct steps can be observed in the DTG curve of dry typha, at 207–275° and

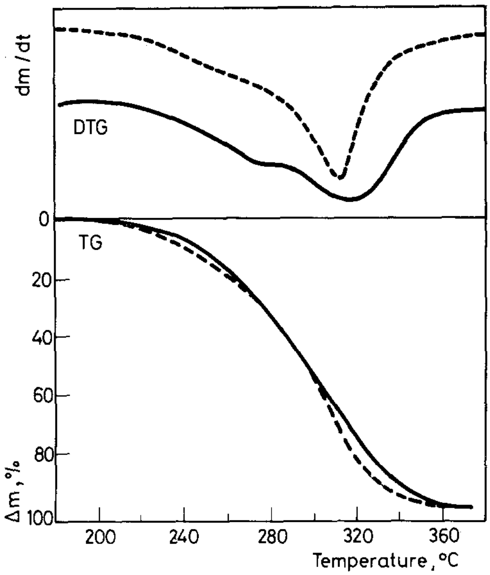

Fig. 3 TG and DTG curves of dry (– – –) and green (——) typha

275–350°, with a sharp difference in the rate of decomposition. Quantitatively, green typha lost 23.5% of its weight up to the end of the first step, whilst dry typha lost only 17.3% of its weight up to the end of this step, i.e. dry typha favoured the high thermal stability components more than green typha, in which the low thermal stability components (hemicellulose) were more abundant (Table 1). The two steps, however, refer to the decomposition of hemicellulose and cellulose, respectively [5]. Additionally, the lignin content of dry typha is lower than that of green typha, which can also play a role in the distinction of the two decomposition steps in dry typha in comparison with green typha.

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Zusammenfassung — Mittels thermogravimetrischer Analyse, TG, wurde das thermische Verhalten von Typha, einer Wildpflanze aus den Sümpfen des Südirak und deren Hauptkomponenten, Holozellulose, Hemizellulose und Zellulose untersucht. Das TG Gesamtsignal von Typha erscheint als Summe der Einzelsignale von Hemizellulose und Zellulose. Wie aus dem Verlauf der TG Kurven der einzelnen Fraktionen ersichtlich war, haben die Bedingungen bei der Fraktionierung von Holozellulose einen entscheidenden Einfluß auf die Art von Zellulose und Hemizellulose. Das thermische Verhalten von Typha wird natürlich auch wesentlich von der Reife der Pflanze beeinflußt.

Резюме — Методом ТГ изучено термическое поведение растения тифа, растущего на болотах южного Ирака, и его таких главных компонентов, как целлюлоза, голо- и гемицеллюлоза. Полный ТГ сигнал тифа представляет собой сумму сигналов гемицеллюлозы и целлюлозы. Условия фракционирования голоцеллюлозы и особенно продувка азотом, затрагивают природу целлюлозы и гемицеллюлозы. Это заключение сделано исходя из формы кривых ТГ соответствующих фракций. Термическое поведение растения в значительной степени обусловлено стадией созревания растения.