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THERMAL ANALYSIS OF EUCALPTUS CAMALDULENSIS AND COTTON STALKS AT DIFFERENT HEATING RATES

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The thermal decomposition of Eucalptus Camaldulensis and Cotton Stalks at different heating rates showed three exothermic peaks. The heating rate is the factor that affects their sharpness and position. The peaks are sharp at low heating rates. IR spectra of pyrolized residue at different temperature were also studied.

Combustion of wood, cellulose, and lignin is preceded by pyrolysis where gaseous and liquid products are formed as well as a solid residue of charcoal. Some of the gases and liquids, when mixed with air, burn with a flame, whereas the charcoal burns in air by glowing without flame. Controlled pyrolysis of wood, bark and wood waste is an important means for the production of gaseous or solid fuel or a source of raw materials for chemical synthesis.

Wood pyrolysis is performed through a complex series of simultaneous and consecutive reactions. Neither the nature nor the extent of individual reactions are known, the yield of pyrolytic products, such as gases, tar and char is highly influenced by the physical and chemical conditions under which the pyrolysis process occurs. Thermal degradation of wood material involves the exothermic reactions in wood [1] defined three phase points:

1. Flame point, 225° to 260°, at which decomposition gases will burn if an ignition source is present.
2. Burning point, 26° to 290°, at which burning occurs with a steady flame. (The decomposition becomes exothermic during the burning point and causes a self-induced flash.)
3. Flash point, 330° to 470°, the range of spontaneous ignition.

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Gillet and Urlings [2] in studied the decomposition of wood between 105° and 505°. Using isothermal heating in a nitrogen atmosphere, found active pyrolysis occurred near 250° to 260°. In a subsequent study [3, 4], they concluded that the pyrolysis products of wood and of a cellulose-lignin mixture were the same above 450°.

Hawley [5] defined the ignition temperature of wood as that temperature at which ignitable volatiles are produced even if a higher temperature is required for ignition. The concept of a series of degradation zones was originated by Hawley and later modified by Browne [6].

Amy [7] describes the general course of pyrolysis of lignocellulosic materials. After the last traces of water are removed, which requires a temperature of about 140°, four classes of products are produced by wood carbonization: Noncondensable gases (carbon monoxide, carbon dioxide, hydrogen, methane).

Pyroligneous products (condensable contain more than 50% moisture). Tar (moisture-free condensable). Charcoal. Gases are evolved at temperatures between 200° and 400° to 45°, with a maximum at about 350° to 400°. The rate of production of pyroligneous material passes through a maximum between 250° and 300° virtually ceases at about 350°. Tar forms between about 300° 400° to 450°. Some gases primarily hydrogen, continue to be evolved above 400°. Charcoal which contains practically all the original ash is not completely carbonized even at 1500°.

The main objective of this study to investigate the thermal degradation of two species of wood at inert atmosphere and flow at different heating rates using thermogravimetric analysis (TG) and differential thermal analysis DTA techniques. IR spectra and X-ray diffraction were also studied.

Experimental

Preparation of sample

Eucalptus Camaldulensis are obtained from the faculty of Agriculture Experiment Station at Abis, Egypt. E. camaldulensis and Cotton Stalks were chipped and converted into dust (40 mesh). The dust was exhaustively extracted with a mixture of ethanol and benzene (1:2 *v/v*). The extracted dust was washed with hot water and dried in a vacuum oven.

Analysis of wood

The percentage of carbon and hydrogen was determined by using the normal combustion method. The percent of oxygen was obtained by difference. The analysis have been carried out in the Microanalytical Laboratory National Research Centre.

TG measurement

Thermal gravimetric analysis and differential thermal analysis were performed using automatic thermobalance of type NETZSCH Geretebua Gmbh Selb Bestell-Nr. 348 472°. The temperature range of 20-600°. First in the nitrogen flow at heating rate 15 deg/min second in an inert atmosphere flow at different heating rates varies from 1-12 deg/minute. The thermal treatment was carried out at the same conditions.

Infrared spectra

The infrared absorption spectra of prepared samples were determined using Beckman IR spectrophotometer 4220 using KBr discs.

X-ray analyses

X-ray diffraction pattern were studied on the Siemens D 500 diffractometer from Bragg angle 5 to 35°. Powder samples were used directly for recording the diffraction patterns. The diffraction area of a sample was 2x1 cm^2. The crystallinity of samples was obtained use of the method devised by Jayme and Knolle [8].

Results and discussion

The result of the elemental analysis moisture and ash are shown in Table 1.

Typical dynamic TG-DTG and DTA curves obtained by decomposition of two species of wood between 25 and 600° are shown in Fig. 1. The TG curves obtained for two species exhibited a moisture weight loss between 5.1 and 5.8% from 50-130° Fig. 1. As expected for the loss of water, an endothermic peak can be observed in the corresponding zone of the DTA-curve. This initial loss of weight is followed by a plateau between approximately 130 and 200°.

Table 1 Chemical analysis of raw materials

	E-Camaldulensis	Cotton stalks
Moisture weight %	5.8	5.1
Ash, weight %	2.40	2.10
Elemental analysis weight %		
Carbon	62.30	59.85
Hydrogen	6.20	6.02
Oxygen	31.30	34.2

In the TG curve after the plateau region and up to the end of the process a continuous weight loss is observed, while in the DTG curve a change in the mass loss rate occurs. These peaks appear from 220 to 230^0 approximately. There, the conversion varies from 23% on the initial mass for the E. camaldulensis to 29% to the cotton stalks. Correspondingly the DTA curves show a region of exothermic reaction with its maxima temperature varying from 270^0 for the cotton stalks to 300^0 for E. camaldulensis. The next zone shows a sharp peak in DTG curve, with a maximum temp. 335^0 for E.camaldulensis.

Considering the DTA curve in the above mentioned region, it shows a exothermic process except E. camaldulensis where an endothermic peak is observed. In general, there is an acceptable concordance in the behaviour observed in the TG-DTG and DTA curves for two species under observa-

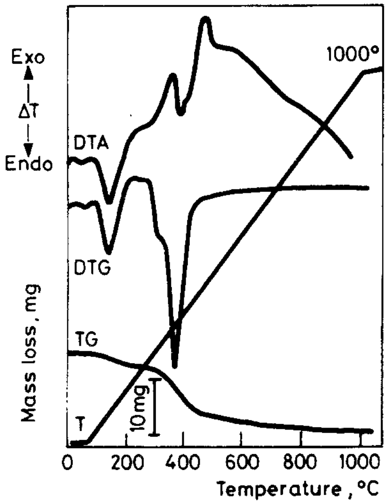

Fig. 1 TG, DTG and DTA curves for *E*.camaldulensis

tion. The moisture loss and the corresponding endothermal evolution in the first zone are the common characteristics of two species.

The TG and DTG curves between 200° and 330° shown a weight loss of 25% approximately for two species and the exothermic reaction from the DTA curve could be attributed to the hemicellulose decomposition. These observations are similar to those [9] who found in a thermogravimetric study of hemicellulose obtained from hardwood, the major percentage of weight loss occurs between 200° and 300°. Such observations are also similar to Kosik *et al.* [10].

The next zone in DTG curve would correspond to cellulose to lignin decomposition these components according to the above mentioned author, are decomposed between 240° and 350° approximately for cellulose. For the lignin, the observed decomposition between 300° and 500° includes exothermic process. However, the process observed for cellulose is first endothermic and then exothermic.

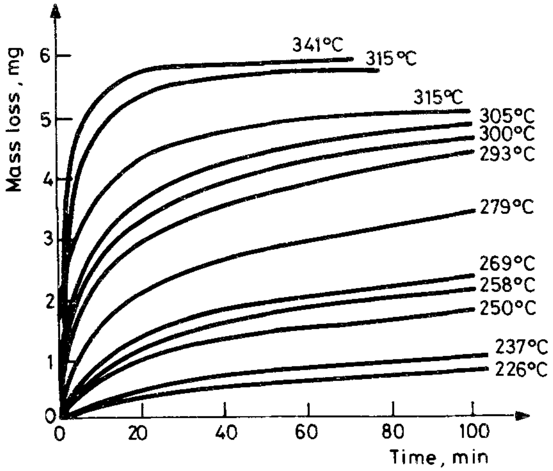

Fig. 2 Isothermal decomposition of Cotton stalks

Concerning the above, an endothermic peak is observed at 355° in E.camaldulensis, it is supposed that such a peak corresponds to cellulose decomposition. The exothermic reaction of the hemicellulose and the incipient decomposition of lignin could contribute to alter the endothermic peak in the other species. Sandermann and Augustin [11] showed, that a mixture of isolated components in the same amounts as they are present in wood, results in a thermogram which is very similar to that of the corresponding wood.

The isothermal measurements were carried out for two species in dry nitrogen at temperature 220 and 340° approximately. Curves in Fig. 2 shown the isothermal behaviour corresponding to cotton stalks being similar for two species. The final weight loss of a sample of any temperature which is very difficult to determine, was obtained by graphic extrapolation from a plot of weight loss *vs.* reciprocal line as it was described by Dollimore [12]. Domansky and Rendos [13] compared the DTA curves of different lignin preparations in vacuo and concluded that the degradation pattern was virtually the same for each. An endotherm extended from about 100 to 180° and was followed by an exotherm at about 400° [14].

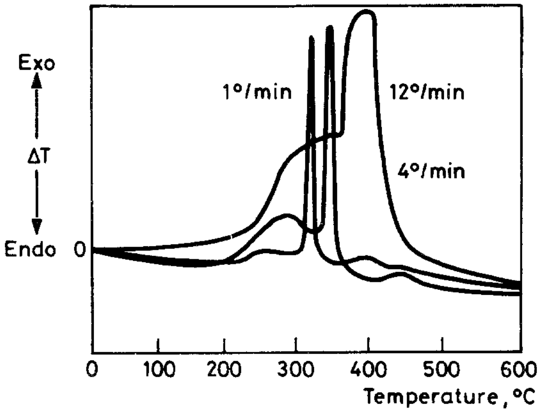

Fig. 3 DTA thermograms of E-camaldulensis at inert atmosphere with different heating rates

On changing the heating rate from 1.0 to 12 deg/min sharp peaks appeared in the curve Fig. 3. Detailed studies of DTA curves Fig. 3 show that the endothermic reactions start at about 50° and end at about 200° with a little shifting to lower temperature as the heating rate is increased (170° for 1.0 deg/min; 130° for 4 deg/min and 100° for 12 deg/ min). The exothermic reactions appear as three peaks. The first exothermic peak is low and broad and shifts to a higher temperature as the heating rate is increased. The peaks are situated between 200 and 290° for 1.0 deg/min and between 220 and 320° for 4 deg/min. The peak for both heating rates is at about 280°, while at 12 deg/min heating rate the exothermic peak starts at 150° and ends at 470°. The first exothermic peak is attributed to the exothermic reactions due to the basic decomposition of hemicellulose and the cleavage of the glucosidic linkages of cellulose by the same authors [15]. The second exothermic peak is sharp and shifts to higher temperature at increased heating rate. At a heating rate 1.0 deg/min, the second peak is very sharp at 320°. At 4 deg/min, the second peak is well defined in a very narrow temperature ranges, 330-340°, and a third peak can also be seen at 450°. At the faster heating rate (12 deg/min), there is only one broad exothermic peak obscuring all the forementioned peaks. It starts at 360° and ends at 460°, nearly in the same range found by Domburgs [15].

Infrared spectra

Infrared spectra of wood at different temperatures are shown in Fig. 4. It seems that the endothermic peak is due not only to driving off moisture and absorbed gases but may be related to the softening and melting of lignin. The lignin is softening point is about 170°. Generally, at the end of endothermic period at about 190°, the lignin powder becomes one mass. There is no major change in the IR spectrum of lignin on heating to 190°.

Thermal softening of moisted wood at temperatures below 180° is more physical than chemical in nature. The softening can be attributed to the plasticization by water, thereby accelerating the reduction of hydrogen bonding and promoting the rearrangement of the chemical components under pressure. These thermal motions, therefore, may not relate to crystalline structure but to the relative motions of mass in the amorphous region of materials.

The thermal reaction of wood at more than the 180° transition may be classified in two ways. One is the degradation reaction that caused depolymerization or modification of the chemical components. The degradation may include reactions, such as the dehydration of macromolecules and conversion of heat sensitive functional groups. Further, degradation of the crystallinity, shortening of the chain length of cellulosic materials, and formation of levoglucosan may also occur.

The spectral changes of heated woods can be observed from the shift of band maxima for OH and carbonyl absorptions. In all cases examined, wood hydroxyl absorbed at about 3390 - 3400 cm^{-1} at 25°. These band shifted to a lower wave number after 200° and decreased in intensity on healing. It is well known that the infrared band at 3000 to 3600 cm^{-1} of wood is the superposition of many hydroxyl groups absorbing at different states of hydrogen bonding the 3400 cm^{-1} absorption was assigned to the intermolecular hydrogen bonded hydroxyl groups in the 101 plane, while the 3350 cm^{-1}

band is the absorption of intra-molecular hydrogen bonded hydroxyl groups in cellulose [16]. Therefore, the shift of the hydroxyl absorption maxima to a lower wave number may indicate the loss of intermolecularly bonded hydroxyl groups to form anhydrocellulose or the other macromolecular components of wood [14]. On further heating of the wood to temperature higher than 300°, the loss of overall hydroxyl band intensity suggests degradation of intermolecular-bonded hydroxyl groups. This agrees with the results of X-ray crystallinity data as shown in Fig. 5.

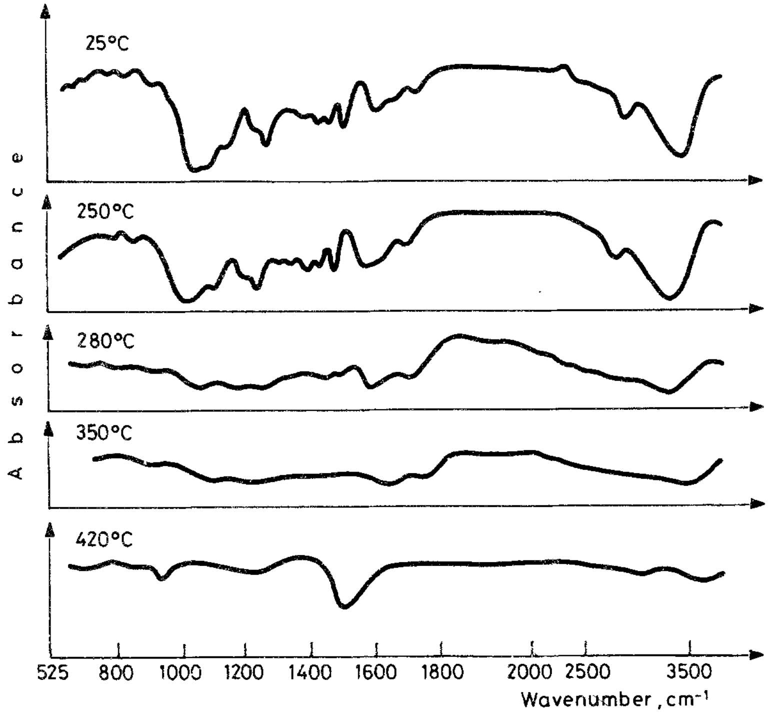

Fig. 4 Infra-red spectra of E.camaldulensis and its pyrolized residues at different temperatures

Generally there are three exothermic DTA peaks (at 280°). The IR spectra of E.camaldulensis Fig. 4 of the pyrolyzed residue shows a disappearance of the absorption bands at wave-numbers 1670, 1380 and 1100-1020 cm^{-1} and a diminishing of the band at 2980 cm^{-1}, this suggest that the aliphatic parts in pyrolyzed residue are the starting point for the thermal decomposition, this included scission of the C-H groups between the adjacent aromatic rings (decrease in the absorption band at wave number 820 cm^{-1}).

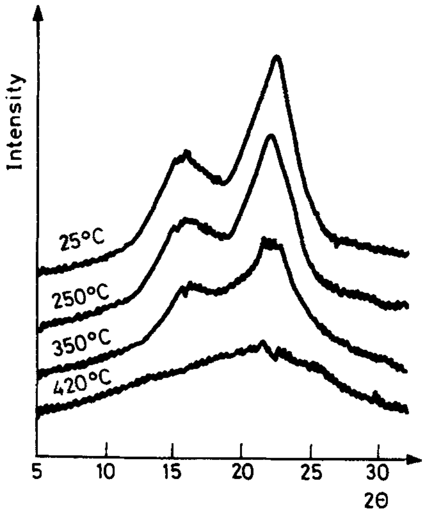

Fig. 5 X-ray diffraction pattern of E.camaldulensis Wood with increasing temperature treatment

The peak of DTA for the second exothermic reaction is sharp at 320° at the slow heating rate. The IR spectrum (Fig. 4) of the residue at 380° shows the disappearance of more absorption bands 1370, 1520, 1470 and 1230 cm^{-1}. This suggest that, as heating is continued and the thermal decomposition of aromatic rings begins. The third peak in the DTA curve is about 420°. It is probably related to the evolution of hydrogen gas when condensed of the residue carbon in the char into a graphite like ring occurs [17].

The IR spectrum shows that no functional groups have remained except the OH group at wave number 3-400 cm^{-1}. New absorption bands appeared at wave number 1540 and 880 cm^{-1} which are assigned as alkane linkage [18], they are probably generated during pyrolysis of wood. The temperatures of DTA peaks are in good agreement with the findings of Kudo and Yoshida [19]. They found that, on the analysis of the methoxyl groups after isothermal heating of dry distilled wood, lignin decomposition begins at about 280° with a maximum rate occurring between 350 and 450° and the completion of the reaction at 450 and 500°. These three temperature ranges correspond to the first, second and third peaks of this present work.

X-ray diffraction

The X-ray diffraction pattern of E.camaldulensis are similar in addition to the relatively poorly resolved (002) plane diffraction at 22 degrees and (101 + 101) plane diffraction at 15-16 degrees.

The calculated crystallinity of E.camaldulensis at room temperature was 41%. In practice, hardwood may be considered as a completely amorphous substance. Upon heat treatment of wood the crystallinity starts to decrease at a temperature of about 200°, this temperature coinciding with the observed small exothermic reaction in DTA curve and the initial softening temperature of the substances. This suggests that the exothermic reaction takes place not only in the amorphous region, but also in the crystalline region of cellulose, when heated to higher temperature, all woods lost almost all crystallinity and produced an amorphous diffraction at 240° and 350°, respectively.

The glass transition temperature for oven dry wood occurs in the vicinity of 180-200°. At this temperature, the thermal expansion coefficient of material undergoes a discontinuity [20], while the configurational rearrangement of polymer chain backbones takes place. At temperatures higher than the transition temperature, the free volume of a material increases and its heat capacity and compressibility change [21]. This 180 to 200° transitional temperature is thus meaningful for setting suitable conditions for wood composite - board production.

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Zusammenfassung — Bei der thermischen Zersetzung von Eucalptus Camaldulensis und Baumwollstengeln bei verschiedenen Aufheizgeschwindigkeiten zeigen sich drei exotherme Peaks. Ihre Breite und Lage wird durch die Aufheizgeschwindigkeit beeinflußt. Bei niedrigen Aufheizgeschwindigkeiten ergeben sich scharfe Peaks. IR-Spektren des pyrolisierten Rückstandes wurden bei verschiedenen Temperaturen ebenfalls untersucht.