

THERMAL BEHAVIOUR OF LIGNINS EXTRACTED FROM DIFFERENT RAW MATERIALS

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ABSTRACT

The thermal degradation of lignins extracted from bagasse, rice straw, corn stalk and cotton stalk, have been investigated using the techniques of thermogravimetric analysis (TG) and differential thermal analysis (DTA), between room temperature and 600°C. The actual pyrolysis of all samples starts above 200°C and is slow. The results calculated from TG curves indicated that the activation energy, E , for thermal degradation for different lignins lies in the range 7.949–8.087 kJ mol⁻¹. The DTA of all studied lignins showed an endothermic tendency around 100°C. In the active pyrolysis temperature range, thermal degradation occurred via two exothermic process at about 320 and 480°C, and a large endothermic pyrolysis region between 375 and 450°C. The first exothermic peak represents the main oxidation and decomposition reaction, the endothermic effect represents completion of the decomposition and the final exothermic peak represents charring.

INTRODUCTION

It is well known that combustion of wood, cellulose and lignin is preceded by pyrolysis, during which process gases and vapours are formed, as well as a solid residue of charcoal. Much has been published on the pyrolysis and carbonization of untreated wood, cellulose, hemicellulose, and lignin [1–5], with particular reference to the products formed and temperatures of pyrolysis under specified conditions. The chemistry of the pyrolysis of wood and its components was reviewed in 1958 by Browne [6]. TG measurements can be employed to determine temperatures and rates of pyrolysis, while DTA curves show the endothermic or exothermic nature of the reactions that accompany pyrolysis and combustion. Such information is very valuable in assessing the chemistry of the thermal decomposition of different products. Activation energies (derived from the Arrhenius equation) and volatilization rates for cellulose and cellulosic materials were determined in 1956 by Madorsky et al. [7]. Many workers [4,8] noted first-order kinetic relationships for the pyrolysis.

Thermogravimetric analysis of celluloses obtained from different sources

was investigated by Sefain and El-Kalyoubi [9]. Sefain et al. [10], reported on the thermal behaviour of holo- and hemicelluloses obtained from agricultural sources. El-Shinnawy and El-Kalyoubi [11], studied thermogravimetric and differential thermal analyses of carbomoyl ethylated and cyanoethylated wood pulp.

The aim of the present work is to study the thermal behaviour of lignins extracted from bagasse, rice straw, corn stalk and cotton stalk, by thermogravimetry (TG) and differential thermal analysis (DTA) techniques. Also, to calculate the kinetic energy for the degradation reaction.

EXPERIMENTAL

Klason lignin prepared by digesting bagasse, rice straw, corn stalk, and cotton stalk with 72% sulphuric acid [12] was tested for thermogravimetry (TG) and differential thermal analysis (DTA), using a Netzsch automatic thermobalance (No. 348 472 C). The furnace was programmed to increase the temperature by $5^{\circ}\text{C min}^{-1}$, and the heating was continued until a constant weight was attained, in a constant stream of air.

RESULTS AND DISCUSSION

Chemical analysis of the lignin samples is given in Table 1.

It is clear from Table 1 that lignin extracted from rice straw possesses the highest ash content, while cotton stalk lignin has the lowest ash content.

Thermogravimetric analysis

Thermogravimetric curves of the four samples are shown in Fig. 1. One can note that, after the initial loss of moisture at about 100°C , loss of weight attributed to actual pyrolysis begins by a minor decomposition reaction at about 250°C , and the major decomposition proceeds at a slow rate up to 500°C . At 400°C about 50% of the lignin is still unvolatilized. The slow

TABLE 1
Analysis of the different lignins

Source of lignin	Lignin %	Ash %
(a) Bagasse	72.4	27.55
(b) Rice straw	63.1	36.80
(c) Corn stalk	85.3	14.70
(d) Cotton stalk	90.65	9.30

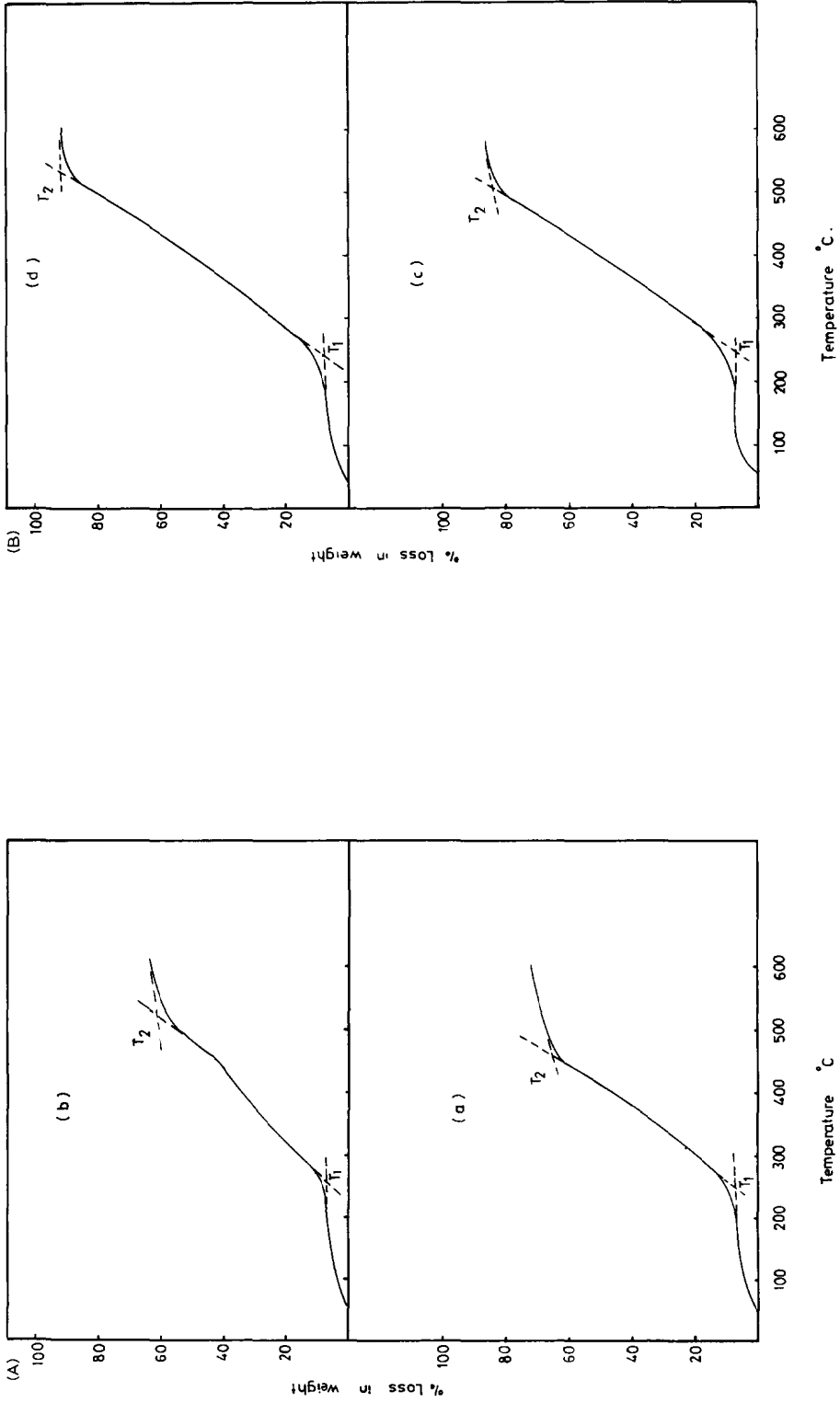


Fig. 1. TG curves: (a) bagasse lignin; (b) rice straw lignin; (c) corn stalk lignin; (d) cotton stalk lignin.

TABLE 2

Initial and charring temperatures of different lignins

Source of lignin	T_1 (°C)	T_2 (°C)
(a) Bagasse	250	455
(b) Rice straw	258	520
(c) Corn stalk	248	505
(d) Cotton stalk	240	530

disintegration of lignin over a wide temperature range can probably be explained on the basis of the nature of its macromolecules, which is intricate, consisting of aromatic nuclei connected by straight-chain links.

Table 2 summarises the initial and charring temperatures of the active decomposition reaction which are represented by T_1 and T_2 , respectively.

Generally, the active decomposition temperature is lower in the case of bagasse lignin as it chars at 455°C. Cotton stalk decomposes at the highest temperature and it chars at 530°C.

Figure 1b shows that rice straw lignin yields more char than the other samples due to the high ash content present in it.

Calculation of the activation energy

The data obtained by TG were analysed by the differential method used by Tang [13]. Assuming a first-order reaction for thermal degradation, the reaction rate constant, K , and the activation energy, E , in the main decomposition temperature region (300–400°C) were calculated from the relation

$$-dc/dt = KC$$

Where C is the concentration of the reactant, t is the time and K is the rate constant. If the concentration is replaced by the observed weight, W_t , then

$$d(W_0 - W_t)/dt = K[W_0 - (W_0 - W_t)] = KW_t$$

Where W_0 is the original weight before heating, W_t the weight after heating for a time t , then

$$-\ln[W_0 - (W_0 - W_t)] = -\ln W_t = Kt + \text{constant}$$

but at $t = 0$, $(W_0 - W_t) = 0$, hence, the constant is equal to $-\ln W_0$, and, therefore, $\ln(W_0/W_t) = Kt$. If the amount of ash at the end of the heating is considered, then

$$\ln[(W_0 - W_\infty)/(W_t - W_\infty)] = Kt$$

Where W_∞ is the weight at the end of heating (ash). Plots of $\ln(W_0 - W_\infty/W_t - W_\infty)$ against t give straight lines (Fig. 2), indicating that the degradation follows a first-order reaction.

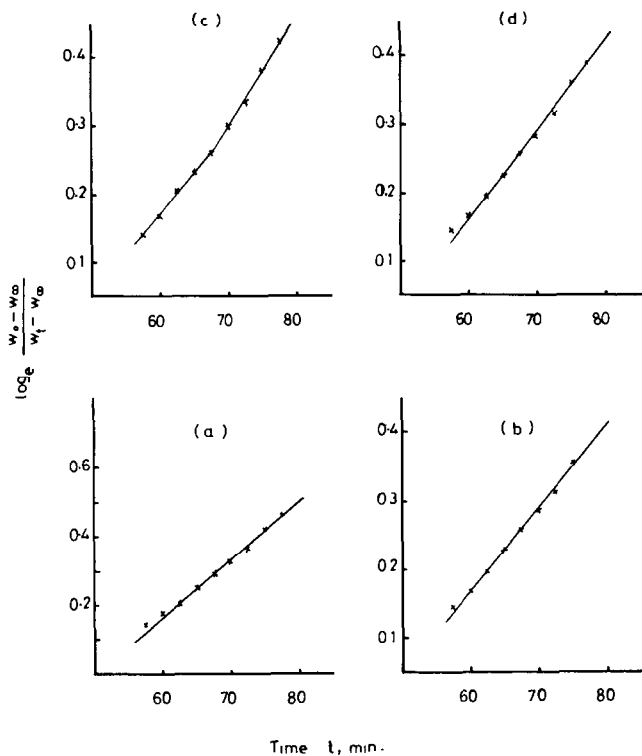


Fig. 2. Plots of $\ln[(W_0 - W_\infty)/(W_t - W_\infty)]$ against t for the four samples studied: (a) bagasse lignin; (b) rice straw lignin; (c) corn stalk lignin; (d) cotton stalk lignin.

The activation energy was calculated by applying the Arrhenius equation [14] where

$$\ln K = -E/RT$$

that is

$$-E = \ln KRT$$

Where E is the activation energy, R is the gas constant and T is the absolute temperature.

Table 3 shows the values of the reaction rate constant, K , and the activation energy, E , of the samples studied.

TABLE 3

Reaction rate constant (K) and activation energy (E) for different lignins

Source of lignin	K (min^{-1})	E (kJ mol^{-1})
(a) Bagasse	0.04025	8.087
(b) Rice straw	0.02875	7.634
(c) Corn stalk	0.03105	7.738
(d) Cotton stalk	0.0368	7.949

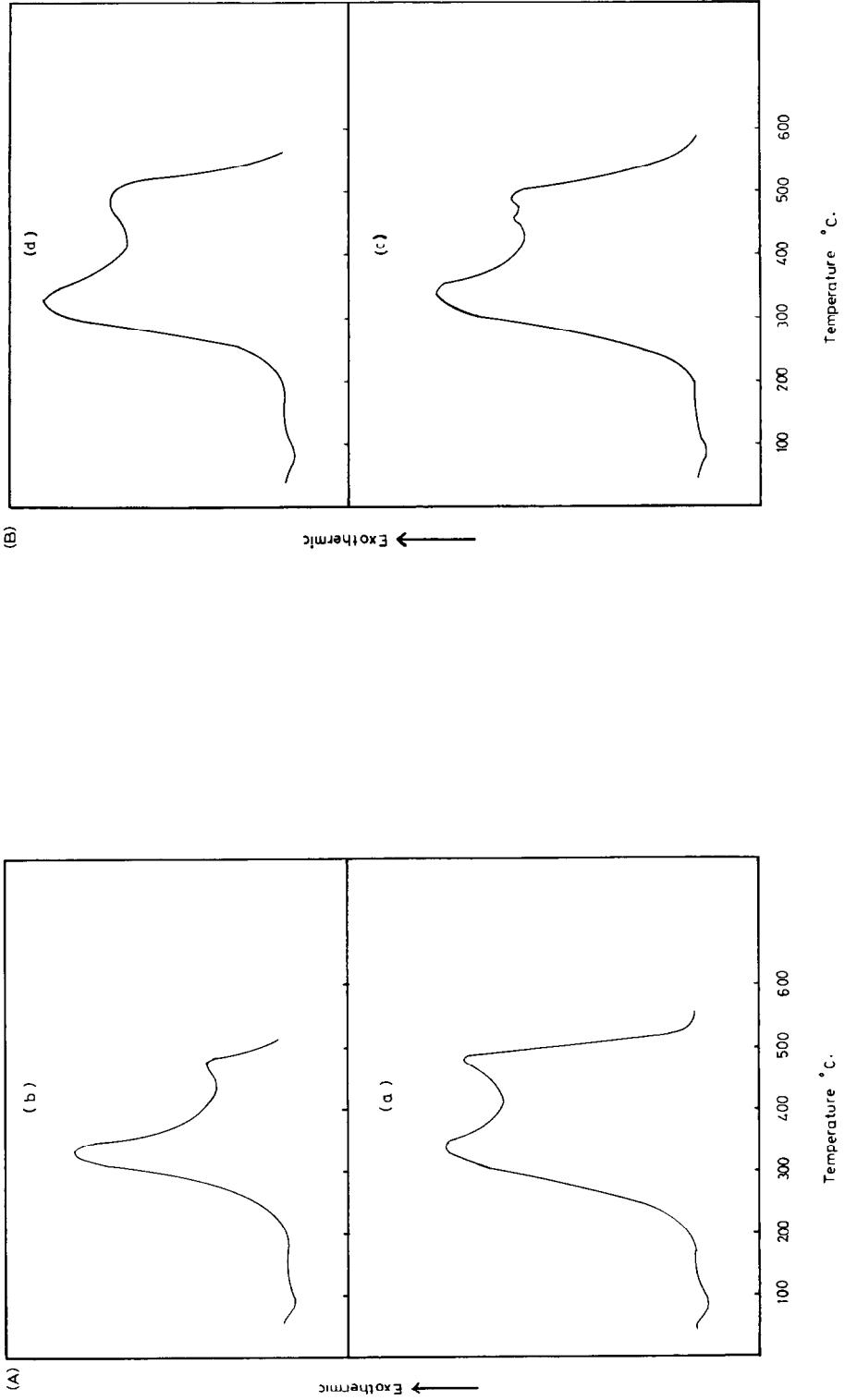


Fig. 3. DTA curves: (a) bagasse lignin; (b) rice straw lignin; (c) corn stalk lignin; (d) cotton stalk lignin.

From Table 3 it is clear that the values of the activation energy for the different samples ranged between 7.634 and 8.087 kJ mol⁻¹. The small difference observed in the activation energy may be due to different chemical degradation by sulphuric acid during extraction, as some depolymerization of the lignin molecules had probably occurred before thermal examination. The purity and the different ash content of the samples may also be capable of the variation in the activation energy.

Differential thermal analysis

It is well known that the four reaction mechanisms occurring during the pyrolysis (namely dehydration, depolymerization, decomposition and condensation, i.e., secondary polymerization and aromatization) compete with each other, and thermochemical data derived from DTA results represent the net effect from the four types of reaction. The amount contributed by each process to the net effect depends on the conditions under which pyrolysis occurs. The DTA curves in Fig. 3 demonstrate these effects for the lignin samples tested.

On the DTA curves, the first endothermic peak at about 100°C essentially represents the loss of moisture and desorption of gases, and only above 200°C does active pyrolysis occur. Since the lignin samples had been treated with sulphuric acid during extraction, some depolymerization and fragmentation had probably occurred before thermal examination. The shallow nature of the peaks on the DTA curves (Fig. 3) and the slow rate of weight loss in the TG curves (Fig. 1) may consequently reflect the effect of sulphuric acid treatment.

The exothermic peak between 300 and 375°C, represents the main oxidation and decomposition reaction. The endothermic effect between 375 and 450°C, represents completion of the decomposition of lignin (corresponding to the range from the commencement to maximum rate of weight loss in the TG curves, Fig. 1); in this range oxidation is weakly exothermic. The weight loss on pyrolysis continues above 450°C until the weight becomes constant, and the associated reaction is exothermic representing the recombination of smaller fragmentary molecules to form a char. This process is similar to that postulated for cellulose, but for lignin the endothermic fragmentation is masked by the exothermic process of char formation.

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