Thermochimica Acta, 19 (1977) 63–68
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EFFECT OF LIGNIN CONTENT ON THERMAL DEGRADATION OF WOOD PULP

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(Received 5 July 1976)

ABSTRACT

A series of pulps containing between 3.6 and 23% of lignin was prepared by a careful delignification of a high-yield bisulfite pulp. The pulps were subjected to isothermal pyrolysis in a Perkin-Elmer TGS-1 thermobalance. The measurements were carried out at 8 different temperatures from 325 to 360°C under nitrogen atmosphere. The results obtained indicate that the effect of lignin on degradation depends strongly on temperature. Below 330°C, the rate of degradation varied only little with lignin. This variation becomes more important at temperatures above 330°C in that the rate of degradation increases with decreasing lignin content. The apparent activation energy of degradation ranges from 41.4 kcal mol^{-1} at 23% of lignin to 67.0 kcal mol^{-1} at 3.7% of lignin.

INTRODUCTION

Although thermal degradation of wood and its individual components has been studied for many years, the exact mechanism and kinetics of the occurring reactions are not yet completely clear. The recent development of modern analytical technique such as thermogravimetry (TG), differential scanning calorimetry (DSC) and others has spurred research in this field and resulted in a great number of publications dealing with the thermal properties of both natural and synthetic polymers. More often than not, however, data reported by different authors show large discrepancies, due mostly to different analytical methods used as well as to different ways of treatment of data. This can be demonstrated by the example of cellulose degradation and in particular, its apparent activation energy E_a. Using thermogravimetry, Tang and Neill[1] found $E_a = 34.2$ kcal mol^{-1} for temperatures from 240 to 310°C, and $E_a = 54.4$ kcal mol^{-1} for the interval 310–360°C. Murphy[2] obtained values of 34.0 and 29.4 kcal mol^{-1} in the range of 100 to 250°C from the rates of evolution of gaseous products. More recently, Fung[3] has found a similar value of $E_a = 35.4$ kcal mol^{-1}. On the other hand, the activation energy value found by Bryce and Greenwood[4] is lower ($E_a = 29$ kcal mol^{-1}) while those determined by Van Krevelen[5]

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and by Madorsky[6] are higher (40 and 50 kcal mol^{-1}, respectively). A higher activation energy value was also recently found by Ramiah[7]: 60±2 kcal mol^{-1} in the first stage (lower temperature) and 39 kcal mol^{-1} in the second stage (higher temperature).

Cellulose is a well-defined chemical compound which can be prepared in a relatively very pure state. This is not the case with hemicellulose and lignin, the other two principal wood components, which represent formidable structural complexity. It is therefore not surprising that data reported on the pyrolysis of these two components and of wood itself (or of its different products, such as wood pulp) would show an even greater variation. This is well demonstrated by the data compiled in the review published by Beall and Eickner[8]. Ramiah and Goring[9] have shown that the decomposition temperature T_d, defined as the temperature at which the rate of evolution of gas was 1 mm^3 h^{-1} g^{-1}, decreased in the order [cellulose → lignin → hemicellulose]. The very recent work by Hirata[10] confirmed this order of degradation. There is less agreement as far as the overall activation energy of degradation is concerned. While Ramiah and Goring[9] reported E_a values ranging between 46 kcal mol^{-1} for xylane and 150 kcal mol^{-1} for certain samples of cellulose, Hirata[10] found the values of 39.5 and 26.8 kcal mol^{-1}, respectively, for the initiation and the propagation of degradation of cellulose, and overall activation energies of 28.5 kcal mol^{-1} (220–280°C) for hemicellulose and 34.8 kcal mol^{-1} (280–300°C) for lignin.

Although different experimental techniques account for much of the variation of degradation results found in the literature, another important source of variation is the different mathematical interpretation of data. To be able to compare individual results with each other, one must not only carry out all experiments under the same conditions (i.e., experimental method, sample pre-treatment, etc.), but also interpret the data in the same fashion. In this way, a study of thermal degradation may become an important tool for material analysis and characterization.

Many currently used methods for the analysis of wood and wood pulp are cumbersome and time-consuming. The work described in this paper was undertaken to investigate the possibility of using thermogravimetry to characterize pulps with different lignin content.

EXPERIMENTAL

Thermogravimetric analysis

The degradation experiments were carried out in a Perkin-Elmer TGS-1 thermobalance under nitrogen atmosphere. Pulp samples (4–5 mg) were preconditioned by scanning the temperature to 135°C in order to remove moisture. The temperature was then decreased to 30–40°C. In an experimental run, the temperature was rapidly increased to the desired value and the weight of the sample was recorded as a function of time. All experiments were carried out in the static (isothermal) mode of operation. Mathematical model described by Cardwell and Luner[11], a short outline of which is given below, was used to analyse the thermogravimetric curves and to evaluate the overall energies of activation.

Considering a general pyrolysis reaction

$$A \rightarrow B(s)+C(g), \tag{1}$$

where A = initial reactant (solid)
B = reaction product (solid)
C = reaction product (gas),

its extent can be followed by monitoring the weight of the sample (thermogravimetry). The rate of degradation may be expressed as follows:

$$\frac{dy}{dt} = kf(y) \tag{2}$$

where y is the fraction of active material that has reacted, and $f(y)$ is a function of y. The variable y may be defined as

$$y = W/(W_0 - r) \tag{3}$$

where W = weight loss at time t
W_0 = initial weight
r = weight of inactive residue.

Combining eqn (2) with the Arrhenius equation (4):

$$k = Axe^{-E_a/RT}, \tag{4}$$

one obtains:

$$\frac{dy}{dt} = Af(y)e^{-E_a/RT} \tag{5}$$

For practical use, eqn (5) is transformed in its logarithmic form:

$$\ln[dy/dt] = \ln A + \ln f(y) - E_a/RT \tag{6}$$

Equation (6) may be used directly to evaluate the overall activation energy of degradation E_a. For this, one must stipulate that the term ($\ln f(y)$) is a constant at a given conversion y. All reaction rate data reported in this paper were taken at $y = 0.5$.

Preparation of pulps

The delignification procedure employed was described in detail in a previous publication[12]. A high-yield sodium bisulfite softwood pulp (Belgo; Consolidated-Bathurst) was used as the starting material. A total of nine pulps were prepared (including the original pulp). The pulps were characterized by standard methods of the Canadian Pulp and Paper Association. The values of lignin content were calculated from the corresponding Kappa values according to the correlation established by Lorås and Løschbrandt[13]. The results are summarized in Table 1.

TABLE 1

PROPERTIES OF PULPS PREPARED BY CHLORITE DELIGNIFICATION

Pulp	*Kappa*[a]	*Lignin* (%)	*Copper*[b] *index*	*Carboxyl*[c] *index* (*meq/100 g*)
BB-0	134	23.0	3.4	22
BB-1	114	19.5	3.5	29
BB-2	101	17.4	3.7	32
BB-3	90	15.5	4.0	32
BB-4	76	13.0	3.5	32
BB-5	65	11.1	3.5	30
BB-6	49	8.4	3.3	25
BB-7	35	6.1	2.4	22
BB-8	21	3.7	1.8	18

[a] CPPA Standard G.18. [b] CPPA Standard G.22. [c] TAPPI Standard T237 su-63.

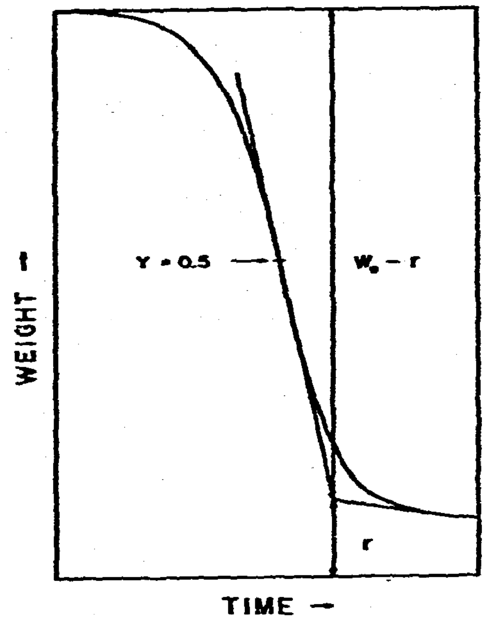
RESULTS AND DISCUSSION

The data shown in Table 1 indicate that chemical characteristics of pulp (copper index, carboxyl index) change relatively little with the degree of delignification. Previous results have shown that pulp delignification with sodium chlorite used in the present work has little effect on the molecular weight of cellulose. One can therefore assume that the lignin content is the most predominant property in the series of pulps analyzed in this work.

The pulps were subjected to isothermal pyrolysis at temperatures from 325 to 360°C at 5°C intervals. A typical curve is shown in Fig. 1. One observes that after a slow start, the degradation proceeds at a rapid rate before reaching a plateau where the weight decreases only very slowly with time. The rate of degradation (dy/dt) was evaluated as the tangent of the degradation curve at $y = 0.5$.

The rates obtained are plotted against the lignin content in the pulps in Fig. 2. One observes that the higher the temperature, the more pronounced is the dependence of degradation on lignin. The three lower temperatures (325–335°C) show little or no influence of the lignin content on the degradation rate. At 340°C, one can already observe a distinct decrease in the degradation rate with growing lignin content. This dependence becomes more pronounced as the temperature increases, and assumes an almost straight-line character above 350°C. The slope of the straight line increases with rising temperature.

On the basis of the data shown in Fig. 2, it would appear that isothermal thermogravimetry could be employed for the determination of the lignin content in pulp. One must not forget, however, that other factors which may have effect on degradation were not considered in this work. Such factors include wood species, the degree of carbohydrate degradation after pulping, and in particular, the hemicellulose content. The influence of these factors would also have to be evaluated before attempting to use the thermogravimetric technique for the analysis of lignin in pulps



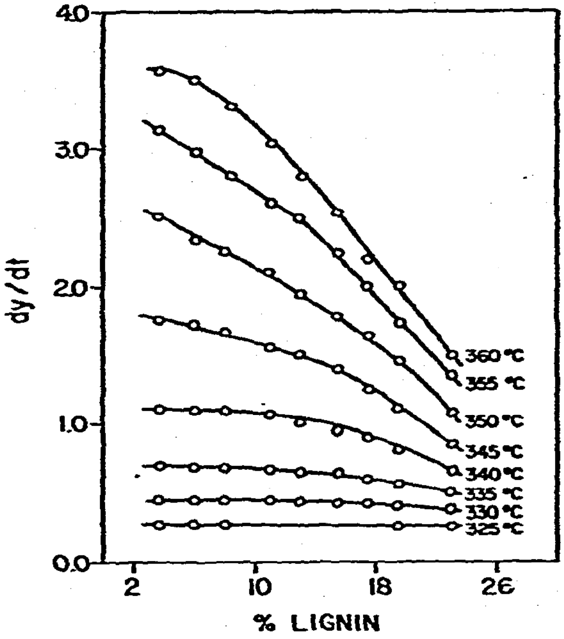
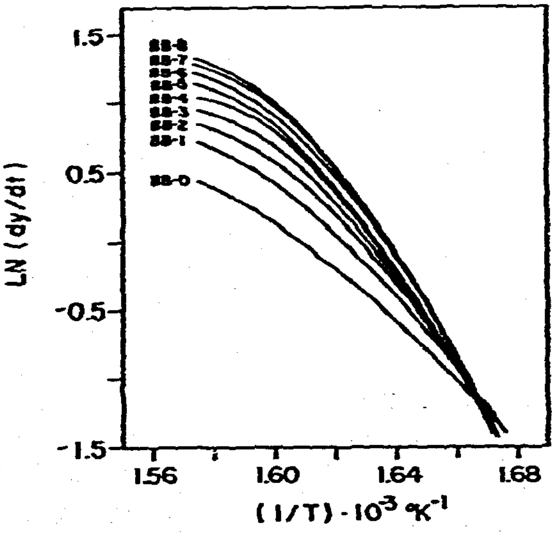


Fig. 1. A typical TG curve.

Fig. 2. Dependence of degradation rate on pulp lignin content.



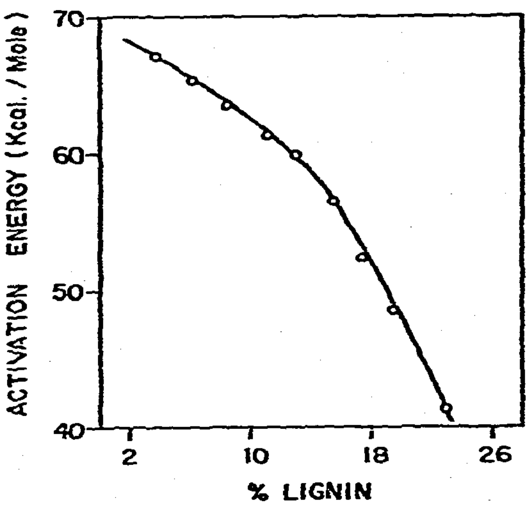


Fig. 3. Plot of ln (dy/dt) vs. $1/T$.

Fig. 4. Dependence of overall activation energy on lignin content.

of different origin. Using a suitable calibration, however, the dependence shown in Fig. 2 may be employed for the analysis of pulps which do not differ much from each other (e.g., pulp process control).

Figure 3 shows a plot of the logarithm of the rate of degradation ($\ln(\mathrm{d}y/\mathrm{d}t)$) against $1/T$ (Arrhenius plot). It is evident that the curves obtained are not rectilinear. This indicates eqn (6) is not valid in the present case and one can not evaluate an energy of activation over the whole temperature interval studied. On close look, however, most of the curvature takes place at higher temperatures ($T > 350°$). By approximating the lower parts of the curves with straight lines ($T = 325$–$345\,°\mathrm{C}$) one can obtain average overall activation energies corresponding to this temperature interval according to the following equation:

$$E_a = -(\text{slope}) \times R. \tag{7}$$

The activation energy values found by using eqn (7) are plotted against the lignin content in Fig. 4. The graph demonstrates that the overall activation energy of degradation depends quite strongly on the lignin content in the pulp and rises with decreasing lignin content from 41.4 kcal mol^{-1} at 23% to 67.0 kcal mol^{-1} at 3.7% of lignin. It is interesting to note that the 41.4 kcal mol^{-1} activation energy observed in the case of the crude pulp (BB-O; 23% of lignin) is very close to the value of $E_a = 42$ kcal mol^{-1} found in the same laboratory by Law et al.[14] for different samples of mechanical pulp (~26% of lignin).

ACKNOWLEDGMENTS

The authors wish to acknowledge with thanks the technical assistance of Mr. A. R. Plourde in bleaching and analysing the pulps. The subject matter treated in this paper forms part of the general research program of the Groupe de Recherche en Pâtes et Papiers at this University.

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