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Thermogravimetric Analysis of Lignins

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Thermogravimetric analysis of lignins isolated from *Ailanthus excelsa, Cassia siamea, Delonix regia, Moringa oleifera* and *Vitex negundo* have been carried out. An attempt has also been made to determine other thermodynamic parameters like activation energy (E_a) and enthalpy of activation (ΔH) by using Sharp-Wentworth method. The data obtained confirmed the validity of Arrhenius equation.

INTRODUCTION

Lignin is an important constituent of plant material and second most abundant renewable polymeric component of biomass. Over 95% of lignin is used presently as an energy source or displayed off as waste. On the other hand it seems to be an attractive material for modification and use for purposes that increase environmental sustainability. It can provide a number of aromatic chemicals for use in paints, food industry and agriculture[1]. A number of organic compounds were isolated from *Ailanthus excelsa, Cassia Siamea, Delonix regia, Moringa oleifera* and *Vitex negundo*. An exhaustive literature survey showed that lignins from these plants have not been isolated and also the thermogravimetric study has not been made so far.

EXPERIMENTAL

Preparation of sample[2]: A log of fully grown (in the month of September) plant was selected and after removing its bark, it was cut into chips of 2–3 in length. These chips were dried in an oven at 105°C for 24 h. These dried chips were then subjected to a pulverizer to convert it into powder and then passed through 40–60 mesh sieves. The 40–60 mesh fractions were used for analysis and those above 60 mesh were used for isolation of lignin from *Ailanthus excelsa, Cassia siamea, Delonix regia, Moringa oleifera* and *Vitex negundo*.

Isolation of lignins: The isolation and purification of alkali lignin (AL), organosolv lignin (OSL) and sulphonated lignin (SL) was achieved by following the earlier methods.[2–4]

The thermograms of all lignins were recorded using Mettler Tornado Star System over a temperature range of 329–1173 K with a heating rate of 20°C/min.

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Thermal studies

Kinetic studies are very useful in elucidating the mechanism of chemical processes. Several methods have been proposed for the estimation of kinetic parameters.[5–8] All methods involve two important assumptions that thermal and diffusion barriers are negligible and Arrhenius equation is valid.

The decomposition rate of TG curve can be defined as dc/dt, where c is the fraction of initial compound undergoing reaction. In isothermal condition it may be presumed that the reaction rate is dependent only on the fraction reacted $-dc/dt = KC^n$ where n is the order of reaction and K the specific rate constant.

The specific rate constant depends upon the temperature by the expression

$$K = Ae^{-E_a/RT}$$

where A is the pre-exponential factor, E_a the activation energy and R the universal gas constant.

RESULTS AND DISCUSSION

Chemical kinetics is benefical for determining the role of different factors and the mechanism of chemical reactions. Accordingly the data obtained for lignins, isolated from angiosperm plants, have been used to evaluate activation energy (E_a) by Sharp-Wentworth method and enthalpy of activation (ΔH)[9]. These values are computed in Table-1.

TABLE-1
THERMODYNAMIC PARAMETERS OF LIGNINS

Sr. No.	Lignins	Activation energy, E_a (kcal mol^{-1})	Enthalpy of activation, ΔH (kcal mol^{-1})
1.	AAL	1.9678	1.3757
2.	CAL	2.6085	2.0164
3.	DAL	2.2424	1.6503
4.	MAL	4.8966	4.3045
5.	VAL	8.8779	8.2858
6.	AOSL	13.6813	13.0909
7.	COSL	5.2627	4.6705
8.	DOSL	4.3475	3.7553
9.	MOSL	3.7526	3.1605
10.	VOSL	3.9814	3.3892
11.	ASL	1.0525	0.4604
12.	CSL	2.2881	1.6959
13.	DSL	1.8305	1.2384
14.	MSL	3.7526	3.1605
15.	VSL	7.5050	6.9129

When $\log\left[\frac{dc/dt}{1-c}\right]$ is plotted against $\frac{1}{T} \times 10^3$ K, a linear plot is obtained which confirms the validity of Arrhenius equation.

The similarities in thermodynamic parameters suggest the common thermal behaviour.

Thermograms of Ailanthus Alkali Lignin (AAL): The TGA and DTA of this lignin (Fig. 1) depict four decomposition steps in the range of 70–950°C and one exotherm with peak maxima at 138°C. The first decomposition zone explains slow decomposition at 70–230°C with a corresponding weight loss of 6.7%, which may be due to loss of moisture. The second decomposition with weight loss of 23% at 241–375°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH etc. The third step of gradual decomposition starts from 375–700°C with a corresponding loss of aromatic nucleus like phenols, guaiacyl, methoxy phenols, etc. The fourth step of decomposition at 700–950°C represents the removal of all side chains of lignins and consequently having a residue with weight loss of about 48%, which may be ascribed to coke cor'taining inorganic materials.

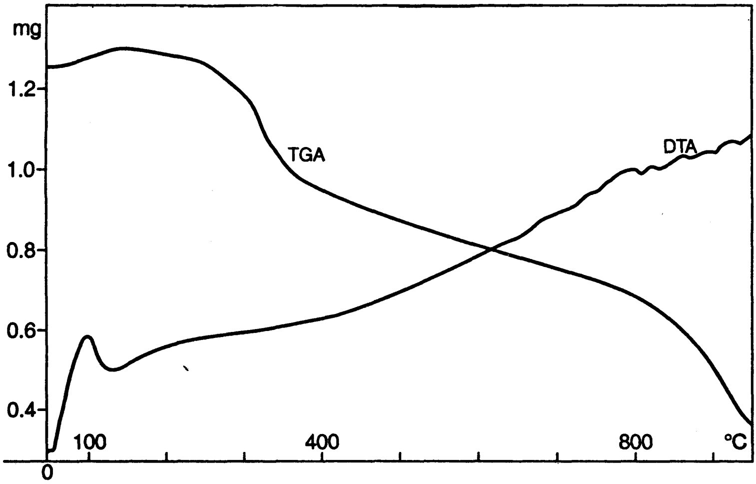

Fig. 1 TG and DT plot of a representative Lignin AAL

Thermograms of Ailanthus Organosolv Lignin (AOSL): The TGA and DTA of this lignin depict three decomposition steps in the range of 70–800°C and one endotherm with peak maxima at 153°C. The first decomposition zone indicates slow decomposition at 70–230°C with a corresponding 12% weight loss, which may be due to loss of moisture. The second decomposition with weight loss of 81.7% at 230–409°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc. The third step of gradual decomposition at 409–800°C with a corresponding loss of aromatic nucleus and all side chains of lignins and consequently having a residue with weight loss of about 18.2%, which may be ascribed to coke containing inorganic materials.

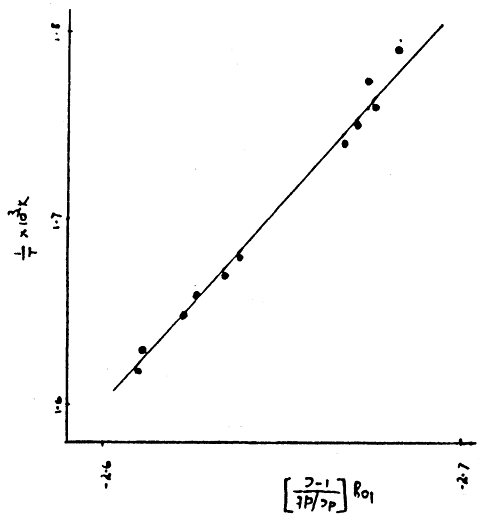

Fig. 2 Sharp-Wentworth plot for AAL

Thermograms of Ailanthus Sulphonated Lignin (ASL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–890°C and one endotherm with peak maxima at 152°C. The first decomposition zone reveals slow decomposition at 70–230°C with a corresponding 9.6% weight loss, which may be due to loss of moisture. The second decomposition with weight loss of 23.4% at 230–400°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc. The third step of gradual decomposition takes place at 400–600°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that account for 13.64% weight loss.

The fourth step of decomposition at 600–890°C represents the removal of all side chains of lignins and consequently having a residue with weight loss of about 35.33% which may be a ascribed to coke containing inorganic materials.

Thermograms of Cassia Lignin (CAL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–950°C and one endotherm with peak maxima at 152°C. The first decomposition zone shows slows decomposition at 70–230°C with a corresponding 14% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 57.5% at 230–500°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc.

The third step of gradual decomposition takes place at 500–600°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that account for 13.73% weight loss.

The fourth step of decomposition at 600–950°C represents the removal of all side chains of lignins and consequently having a residue of about 38.6% which may be ascribed to coke containing inorganic materials.

Thermograms of Cassia Organosolv Lignin (COSL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–900°C and one exotherm with peak maxima at 111°C. The first decomposition zone indicates slow decomposition at 70–230°C with a corresponding 11% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 64.56% at 230–500°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc.

The third step of gradual decomposition takes place at 500–620°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that account for 14.29% weight loss.

The fourth step of decomposition in the range of 620–900°C represents the removal of all side chains of lignin and consequently having a residue of about 37.5% which may be ascribed to coke containing inorganic materials.

Thermograms of Cassia Sulphonated Lignin (CSL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–950°C and three exotherms with peak maxima at 100, 220 and 700°C. The first decomposition zone shows slow decomposition at 70–230°C with a corresponding 8.04% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 52.29% at 230–500°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc.

The third step of gradual decomposition takes place at 500–800°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that accounts for 37.35% weight loss.

The fourth step of decomposition takes place at 800–950°C represents the removal of all side chains of lignins and consequently having a residue with weight loss of about 7.69% which may be a ascribed to coke containing inorganic materials.

Thermograms of Delonix Alkali Lignin (DAL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–850°C and one endotherm with peak maxima at 152°C. The first decomposition zone shows slow decomposition at 70–230°C with a corresponding 7% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 63.67% at 230–500°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc.

The third step of gradual decomposition takes place at 500–850°C wtih a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that represents the removal of all side chains of lignins and consequently having a residue of about 46.39% which may be ascribed to coke containing inorganic materials.

Thermograms of Delonix Organosolv Lignin (DOSL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–900°C and one endotherm with peak maxima at 153°C. The first decomposition zone shows slow decomposition at 70–212°C with a corresponding 7.67% weight loss, which may be due to loss of moisture. The second decomposition with weight loss of 50.56% at 212–370°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc.

The third step of gradual decomposition takes place at 370–550°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that accounts for 28.07% weight loss.

The fourth step of decomposition takes place at 550–900°C represent the removal of all side chains of lignins and consequently having a residue with weight loss of about 36.58% which may be ascribed to coke containing inorganic materials.

Thermograms of Delonix Sulphonated Lignin (DSL): The TGA and DTA of this lignin depict three decomposition steps in the range of 70–850°C and one exotherm and one endotherm with peak maxima at 100 and 816°C. The first decomposition zone shows slow decomposition at 70–230°C with a corresponding 4% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 26.38% at 230–600°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc.

The third step of gradual decomposition takes place at 600–850°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that represents the removal of all side chains of lignins and consequently having a residue with a weight loss of about 46.39% which may be ascribed to coke containing inorganic materials.

Thermograms of Moringa Alkali Lignin (MAL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–900°C and one endotherm with peak maxima at 152°C. The first decomposition zone shows slow decomposition at 70–230°C with a corresponding 15% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 67.32% at 230–500°C represents degradation of side chains attached to aromatic nucleus like methane, ethane, formaldehyde and phenolic —OH, etc.

The third step of gradual decomposition takes place at 500–700°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that account for 33.33% weight loss.

The fourth step of decomposition at 700–900°C represents the removal of all side chains of lignins and consequently having a residue with a weight loss of about 20% which may be ascribed to coke containing inorganic materials.

Thermograms of Moringa Organosolv Lignin (MOSL): The TGA and DTA of this lignin depict three decomposition steps in the range of 70–850°C and two endotherms with peak maxima at 134 and 380°C. The first decomposition zone shows slow decomposition at 70–230°C with a corresponding 7.8% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 68.63% at 230–550°C represents degradation of side chains attached to aromatic nucleus like methane, ethane, formaldehyde and phenolic —OH, etc.

The third step of gradual decomposition takes place at 500–700°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that account for 12.5% weight loss.

The fourth step of decomposition at 700–850°C represents the removal of all side chains of lignins and consequently having a residue with a weight loss of about 52.38% which may be ascribed to coke containing inorganic materials.

Thermograms of Moringa Sulphonated Lignin (MSL): The TGA and DTA of this lignin depict four decomposition steps in the range of 70–850°C and five endotherms with peak maxima at 214, 251, 479, 733 and 778°C. The first decomposition zone shows slow decomposition at 70–230°C with a corresponding 4.7% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 5.14% at 230–400°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde and phenolic —OH, etc.

The third step of gradual decomposition takes place at 400–600°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that account for 5.42% weight loss.

The fourth step of decomposition at 600–850°C represents the removal of all side chains of lignins and consequently having a residue of about 6.4% which may be ascribed to coke containing inorganic materials.

Thermograms of Vitex Alkali Lignin (VAL): The TGA and DTA of this lignin clearly indicate only two decomposition zones in the range of 70–400°C and exotherms at 371 and 583°C. The first decomposition zone shows slow decomposition with 10.26% weight loss from 70–230°C. The second decomposition zone shows gradual decomposition from 200–400°C corresponding 52.38% weight loss which represents elimination of gases, phenolic moieties, etc.

Thermograms of Vitex Organosolv Lignin (VOSL): The TGA and DTA of this lignin show three decomposition steps in the range of 70–800°C and three endotherms and one exotherm with peak maxima at 222, 721, 754 and 552°C respectively. The first decomposition zone shows slow decomposition at 70–280°C with a corresponding 24.08% weight loss, which may be due to loss of moisture. The second decomposition with a weight loss of 20.20% at 300–420°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde and phenolic —OH, etc.

The third step of gradual decomposition takes place at 420–800°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that represents the removal of all side chains of lignins and consequently having a residue with a weight loss of about 86.08% which may be ascribed to coke containing inorganic materials.

Thermograms of Vitex Sulphonated Lignin (VSL): The TGA and DTA of this lignin show three decomposition steps in the range of 70–650°C and one endotherm with peak maxima at 419°C. The first decomposition zone shows slow decomposition with 70–120°C with a corresponding 1.4% weight loss, which may be due to loss of moisture. The second decomposition with weight loss of 21% at 120–400°C represents degradation of side chains attached to aromatic nuclei like methane, ethane, formaldehyde, phenolic —OH, etc.

The third step of gradual decomposition takes place at 401–650°C with a corresponding loss of aromatic nuclei like phenols, guaiacyl, methoxy phenols, etc. that represents the removal of all side chains of lignins and consequently having a residue with 11% weight loss which may be ascribed to coke containing inorganic materials.

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