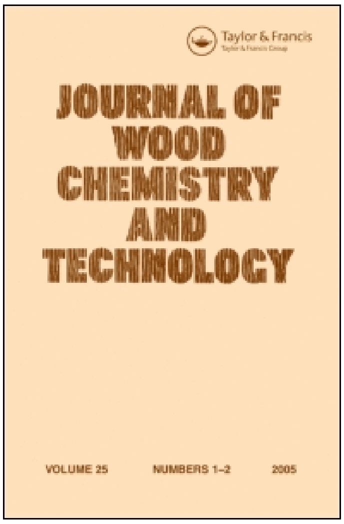

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Thermal Decomposition Study of Isolated Lignin Using Temperature Modulated TGA

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Abstract: Temperature modulated TGA (MTGA) was utilized to study the kinetics of lignin pyrolysis. Three industrial lignin preparations were investigated: softwood kraft lignin, hardwood kraft lignin, and Alcell lignin. Unlike conventional TGA, MTGA provides apparent activation energy (E_a) distribution curve using a single experimental run in a relatively short experimental time. Under Hi-Res conditions using a dynamic heating rate, the activation energies were higher than those determined using a constant heating rate. Likewise, small sample masses provided higher activation energies than those run with large sample mass. These effects can be eliminated by using a relatively large sample mass, >10 mg. In this study, we discuss the effect of MTGA conditions on calculating E_a distribution curves for lignin pyrolysis.

Keywords: Activation energy, hi-resolution TGA, lignin pyrolysis, modulated TGA

INTRODUCTION

Increasing global concerns over the stability and sustainability of fossil fuels is leading the way for biomass utilization, and the replacement of the current petrochemical-based economy. Numerous methods have been reported for the conversion of biomass into products such as fuels, chemicals, and materials.[1–3] The majority of these efforts have focused on the utilization of the carbohydrate components, for example, paper products, cellulose derivatives, and bioethanol production. The main carbohydrate component of woody biomass

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is cellulose.[4] Cellulose has a relatively simple chemical structure. It is a linear threodisyndiotactic homopolymer consisting of β-D-anhydroglucopyranose moieties linked via β(1–4) glycosidic bonds. By contrast, lignin, another principle wood component, has an extremely complex molecular structure. Lignins are complex racemic aromatic heteropolymers derived primarily from p-hydroxycinnamyl alcohol units, which due to their biosynthesis have a large variety of inter-unit linkages.[5] Further, depending on the type and length of chemical processing, the lignins will vary in molecular weight, functional groups present, degree of condensation, types of intermonomeric linkages, and types and ratios of monomeric units.[6] Due to this inherent chemical and molecular weight inhomogeneity, lignin and lignin derivatives have limited utility in applications demanding a constant well-defined feedstock. In fact, less than 2% of the total available isolated lignin is reportedly being used in higher value products.[6] However, as biomass is increasingly utilized in the development of renewable and sustainable energy, the development and utilization of lignin will become increasingly important.[7]

An enormous amount of work has been reported on the conversion of isolated lignins into value-added products.[6] One area that has been extensively studied is lignin pyrolysis. Various materials are derived from lignin pyrolysis, carbonaceous materials,[7–10] bio-pitch[11] can be converted into molded materials and functional carbonaceous materials, such as carbon and activated carbon fiber,[12] and various fine chemicals such as phenols.[13,14] The mechanism of lignin pyrolysis is very complex,[15,16] and if it is to be effectively and efficiently utilized a comprehensive understanding of the kinetics and mechanisms of the thermal reactions is needed. Furthermore, owing to the inherently complex structure of lignin, a rapid kinetic analysis method is required.

Several new techniques exist to study the thermal decomposition of multiple component systems.[17] High-resolution (Hi-Res) thermogravimetric analysis (TGA) is an established and useful technique wherein a dynamic heating rate is applied in response to mass loss.[18] This dramatically increases resolution and decreases experimental time. Modulated TGA (MTGA) is a relatively new method to estimate E_a in temperature- dependent systems.[19,20] In MTGA a sinusoidal temperature wave is applied to a sample to calculate and display the kinetic parameters of decomposition on a continuous and real-time basis. In this study, we report the effectiveness of Hi-Res TGA and MTGA on studying the thermal decomposition of three technical lignins.

MATERIALS AND METHODS

Materials

Three technical lignins, one softwood lignin (softwood kraft lignin, SKL) and two hardwood lignins (hardwood kraft lignin, HKL, and organosolv lignin, Alcell) were used in this study. The kraft lignins (Westvaco Corp.) were repeatedly washed with dilute HCl, pH 2 (Aldrich Chemicals) to remove inorganic impurities. The organosolv lignin (Repap Enterprises Inc.) was used as received. All lignin was then extracted with CH_2Cl_2/methanol (2/8) (Aldrich Chemicals) to separate the insoluble carbohydrate impurities, and precipitated in ten parts diethyl ether (Aldrich Chemicals) to remove volatile low molecular mass fractions. Lignin was recovered by filtration with a filter crucible (pore size: fine) and ground into a fine powder. Cellulose powder was purchased from Sigma-Aldrich and used as received. All samples were completely vacuum-dried over P_2O_5 (Aldrich Chemicals) before TGA analysis.

Thermogravimetric Analysis (TGA)

All TGA runs were performed on a TA-Instrument TA-Q500 TGA using a temperature range of 30–600°C and a UHP grade nitrogen flow rate of 60 mL/min. For the non-modulated Hi-Res TGA experiments an initial heating rate of 30°C/min was used with a sensitivity value of 1.00 and a resolution of 4.00. Both linear and Hi-Res heating rates were used for the MTGA analyses. In the Hi-Res MTGA experiments, the initial heating rate was 2°C/min with modulation amplitude of ±5.00°C, modulation period of 200 s, sensitivity value of 1.00 and resolution of 6.00.

Estimation of Apparent Activation Energy, E_a

The E_a for lignin pyrolysis was estimated using two different methods: (i) MTGA and (ii) Flynn and Wall and Ozawa method. The reaction rate, ν, of solid state chemical reactions can be described by

$$\nu = (d\alpha/dt) = k(T)f(\alpha) \tag{1}$$

where α is degree of conversion, t is the time, T is the temperature and $k(T)$ is a temperature-dependent constant and $f(\alpha)$ is the reaction model. $k(T)$ is normally approximated by the Arrhenius equation,[21]

$$k(T) = A\exp(-E_a/RT) \tag{2}$$

where A is the frequency factor and R is gas constant (8.314 J/mol K). In non-isothermal conditions with a linear heating rate of $\beta = dT/dt$, Eq. (2) can be written as

$$(d\alpha/dT) = (A/\beta)f(\alpha)\exp(-E_a/RT) \tag{3}$$

MTGA

In MTGA experiments, oscillation temperature is overlaid on the conventional linear heating rate. Therefore, the ratio of reaction rates, between adjacent peaks (p) and valleys (v) can be written as follows using Eq. (3):

$$\frac{(d\alpha_p/dT)}{(d\alpha_v/dT)} = \frac{f(\alpha_p)\exp(-E_a/RT_p)}{f(\alpha_v)\exp(-E_a/RT_v)} \tag{4}$$

If the reacted fraction does not change significantly between adjacent half-cycles, $f(\alpha_p) \approx f(\alpha_v)$, and their ratio approaches unity, Eq. (4) may be simplified and solved for E_a to yield Eq. (5).

$$E_a = \frac{RT_pT_v \ln(d\alpha_p/d\alpha_v)}{T_p - T_v} \tag{5}$$

In MTGA, the oscillatory temperature forcing function is defined by an average temperature T, the temperature amplitude a and its period or frequency. Because $T_p = T + a$ and $T_v = T - a$, Eq. (5) may be rewritten as follows:[19]

$$E_a = \frac{R\left(T^2 - a^2\right)L}{2a} \tag{6}$$

where $L = \ln(d\alpha_p/d\alpha_v)$, thereby enabling E_a to be calculated continuously.

Non-isothermal TGA using a linear heating rate, Flynn and Wall[22,23] and Ozawa.[24] method

Integration of Eq. (3) leads to Eq. (7).

$$g(\alpha) = \int_0^{\alpha} (d\alpha/f(\alpha)) = (A/\beta)\int_{T_0}^{T} \exp(-E_a/RT)dT \tag{7}$$

where T_0 is the temperature at the onset of the reaction. No conversion occurs beforeT_0; therefore, T_0 can bet set equal to zero for convenience.[25] By setting $x = E_a/RT$

$$g(\alpha) = (AE_a/\beta R)\int_x^{\infty} [\exp(-x)/x^2]dx = (AE_a/\beta R)p(x) \tag{8}$$

and taking the logarithm produces

$$\log(g(\alpha)) = \log(AE_a/R) - \log\beta + \log p(x) \tag{9}$$

Applying Doyle's approximation, $\log p(x) \cong -2.315 - 0.4567x$, allows Eq. (9) to be written as

$$\log\beta \cong -0.4567(E_a/RT) + [\log(AE_a/R) - \log(g(\alpha)) - 2.315] \qquad (10)$$

and $\log\beta + 0.4567(E_a/RT)$ takes a constant value as a constant α leads to a constant $\log(g(\alpha))$. The E_a is calculated from the slope of a plot of $\log\beta$ versus 1/T. The sample mass was constant at 10 mg for all TGA kinetic experiments using this method.

RESULTS AND DISCUSSION

Comparison of Conventional and Hi-Res TGA of Lignin

Lignin pyrolysis involves complex multi-step reactions that occur over a wide temperature range. For this reason it is very difficult to deconvolute the individual reaction steps. In the conventional TGA curve, main weight loss starts around 250°C and continues to 600°C (Figure 1). An inflection point of the main degradation step, indicated as a peak in the first derivative (DTGA) curve, appears at 382, 365, and 362°C for SKL, HKL and Alcell, respectively. The softwood lignin shows a ~20°C higher inflection temperature than the hardwood lignins. Unfortunately, other reaction steps and the corresponding temperature cannot clearly be seen in the conventional TGA profiles (Figure 1 left). All of the lignin preparations show a broad DTGA curve with shoulders around 300°C and 430°C.

In the Hi-Res TGA experiments the heating rate is continuously varied from ~25°C, in the low temperature region where no significant weight loss occurred, to 4.4°C, in the region of fast weight loss. Analysis of the Hi-Res DTGA curves indicates the peak temperature for the main decomposition is 366, 345, and 347°C for SKL, HKL, and Alcell, respectively. These temperature values are lower than those observed in the conventional TGA experiments. This would be due to the slower heating rate of the Hi-Res TGA as compared to the conventional TGA at the main degradation step. However, the highest inflection temperature was still observed for SKL, which was ~20°C higher than that observed for the HKL or Alcell. This occurred despite the heating rate around the inflection temperature being slightly different between the lignins, 4.7, 4.4, and 5.0 for SKL, HKL, and Alcell, respectively. As expected the Hi-Res TGA has clearly improved resolution as compared to conventional TGA. The higher temperature shoulder observed around 430°C on the DTGA curve of the hardwood lignin samples in conventional TGA are separated from the main peak in the Hi-res TGA, and appears at 418°C and 411°C for HKL and Alcell, respectively. However, at the lower temperature range of the TGA

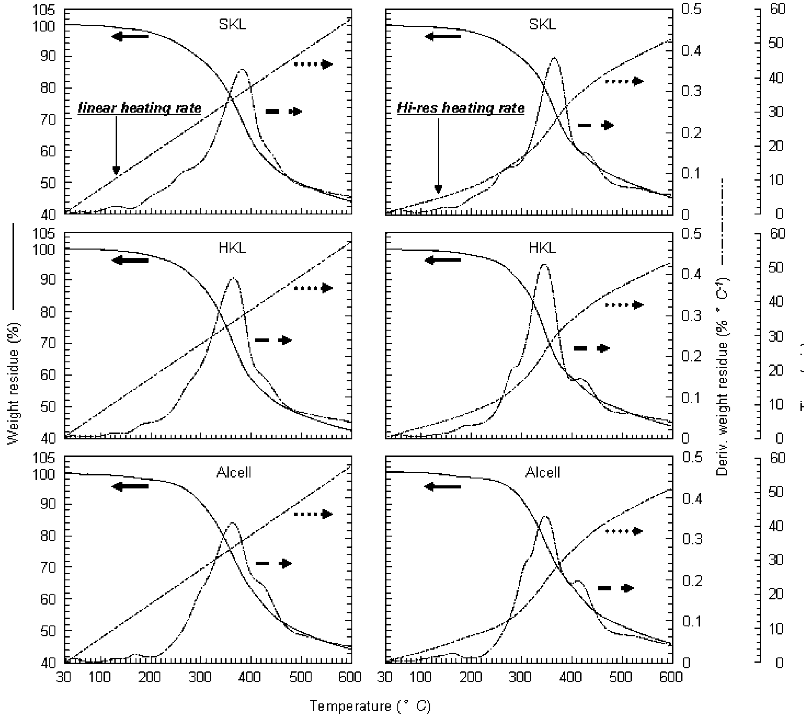

Figure 1. Conventional (left) and Hi-Res (right) TGA analysis of isolated lignin preparations. Heating rate: Conventional TGA = 10°C min^{-1}; Hi-Res TGA = dynamic heating rate, (sample mass = 10 mg).

curves, the shoulder at around 300°C on the DTGA curves in the conventional TGA still overlap with main decomposition peak in the Hi-Res TGA, although the resolution of these shoulders seems to be slightly improved. These results indicate that better resolution of the thermal events in lignin can be obtained through use of Hi-Res TGA.

E_a Estimation by Temperature Modulated TGA (MTGA)

MTGA analysis of the lignin preparations was conducted using the Hi-Res method, at a slow heating rate of 2°C/min to provide enough modulation cycles for each reaction step. The MTGA curves of three lignin preparations are shown in Figure 2. Unlike in the Hi-Res TGA method, the MTGA method temperature is modulated (±5.00°C). This combined with the slower heating rate leads to enhanced resolution. Comparison of the SKL Hi-Res TGA curve (Figure 1 right—SKL) with that obtained using the MTGA method shows the broad lower temperature peak is clearly resolved in the MTGA curve (peak a

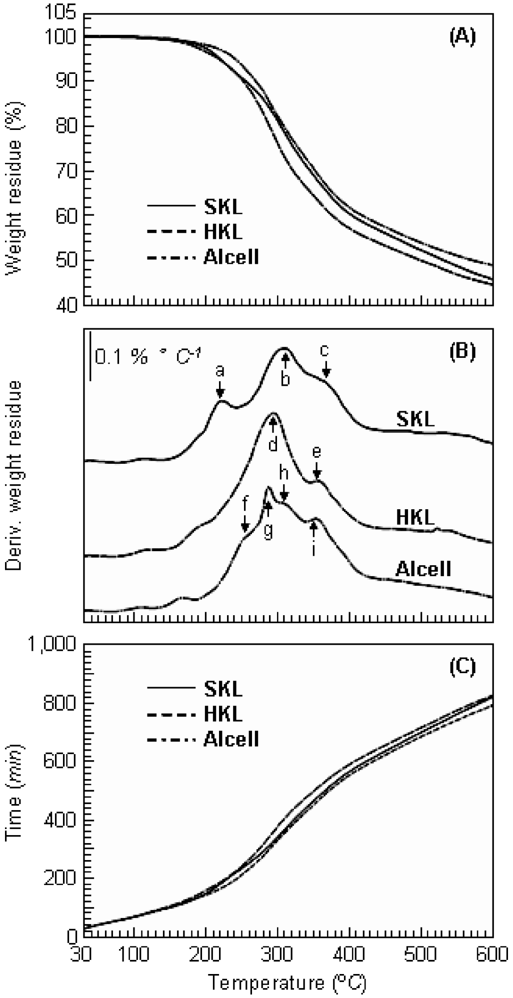

Figure 2. Temperature modulated TGA analysis of isolated lignin preparations measured with dynamic heating rates (sample mass = 5 mg), (A); TGA, (B); DTGA, (C) heating profile.

in Figure 2(B)). Likewise, the main reaction step in the Alcell lignin Hi-Res TGA (large, broad peak at 347°C) is further separated into a sharp peak and shoulder in the DMTGA curve shown in Figure 2(B) (g and h, respectively).

Activation energy (E_a) distribution curves calculated by MTGA are shown in Figure 3. Although lignin pyrolysis involves multi-step reactions, in most cases the E_a for lignin decomposition is reported as a temperature independent parameter.[26] However, MTGA can calculate the E_a for each deconvoluted

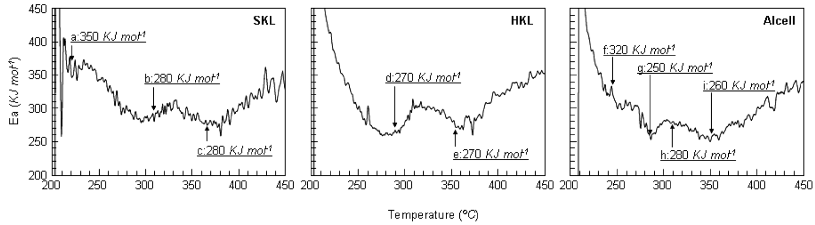

Figure 3. E_a distribution curves of isolated lignin preparations measured by MTGA.

reaction step in a single experimental run, saving on material and time. Experimental periods for all lignin samples are ~800 min (Figure 2(C)). The arrows in Figure 3 show where the calculated E_a values for the corresponding peak tops and shoulders appeared on the DMTGA curves in Figure 2(B). All of the E_a distribution curves showed roughly the same profile, but the E_a values calculated for the main and high temperature pyrolysis were slightly higher in the softwood lignin (~280 KJ mol^{-1} for b and c) than hardwood lignins, HKL (~270 KJ mol^{-1} for d and e) and Alcell (~250 and ~260 KJ mol^{-1} for g and i, respectively). These E_a values are higher than those previously reported using conventional TGA. For example, Ferdous et al.[27] calculated the activation energy for Alcell pyrolysis to be 129–361 kJ/mol in temperature range of 272–532°C and that of kraft lignin pyrolysis to be 80–158 kJ/mol in temperature range of 234–503°C using the distributed activation energy model. The lignin samples used in this research were purified using a solvent extraction method, in which low molecular mass ether soluble fractions were removed. It has been reported that the thermal degradation of lignin fractions is depended on its molecular weight.[28] Therefore, the purification process, and the removal of low molecular mass fractions likely affected the E_a values. To determine if the higher than reported E_a values were due to the purification process or due to the difference in resolution between MTGA and traditional TGA, E_a values of the three lignin preparations were determined by the traditional Flynn and Wall,[22,23] and Ozawa[24] method using conventional TGA.

Figure 4 shows the conventional TGA curves obtained for the various lignin preparations over a range of heating rates (0.3–20°C min^{-1}). As expected, decreasing heating rate led to more rapid decomposition. Using the method of Flynn and Wall, and Ozawa, E_a distribution curves (Figure 5(A)) were calculated for each degree of conversion from a plot of log β versus 1/T (data not shown). For all lignin preparations log β showed a linear relationship to 1/T, $R^2 > 0.999$, for all data points. The E_a distribution curves showed roughly the same tendency as that reported by Ferdous et al.[27] However, the E_a values for our lignin preparations calculated by Flynn and Wall,[22,23] and Ozawa[24] method are higher than those reported using the distributed activation energy model.[27] Figure 5 shows the E_a values determined for

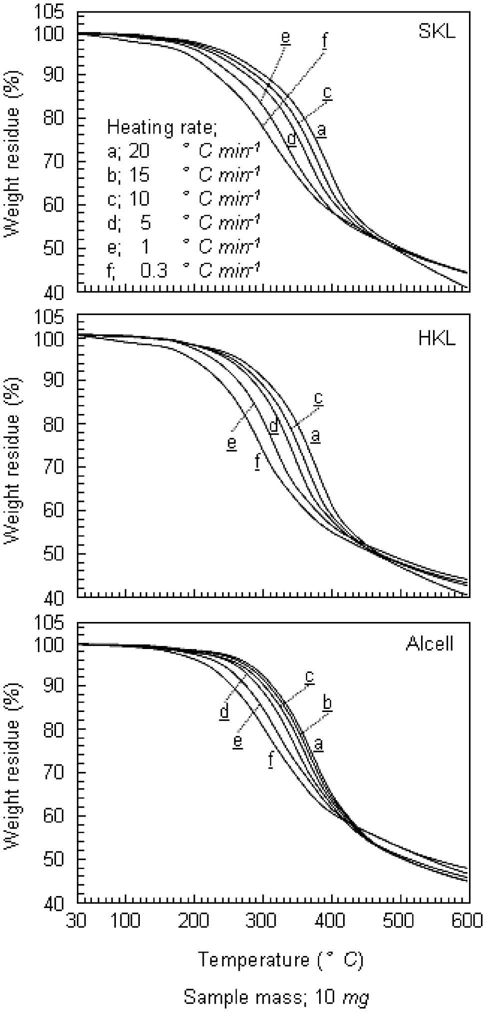

Figure 4. Conventional TGA curves of isolated lignin preparations measured under different heating rates (sample mass = 10 mg).

the main degradation process as a function of degree of conversion (5–35%) calculated by conventional TGA using the Flynn and Wall, and Ozawa method (Figure 5(A)) and MTGA (Figure 5(B)).

Effect of Sample Mass on the E_a Distribution Curves Calculated by MTGA

During pyrolysis, volatile compounds are generated, consumed, and released. Volatiles created by the thermal reactions on the surface of the material will

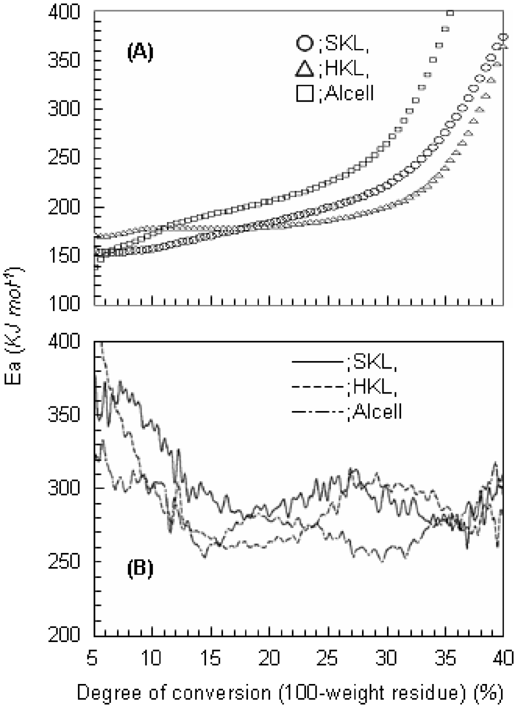

Figure 5. E_a distribution curves of isolated lignin preparations measured by Flynn and Wall, and Ozawa method (A) and (B) MTGA (shown as the function of degree of conversion).

be removed much more easily than those formed inside the bulk of the sample. Volatiles created inside the bulk will react with other volatiles and/or recombine with the solid residues. The materials created by these sub-reactions will also pyrolyze during the TGA run. Therefore, diffusion and its effect on mass transfer of gaseous materials will affect the observed E_a. Activation energy distribution curves calculated using different sample masses are shown in Figure 6. (Note: The experimental time for all of the MTGA runs for each lignin in this figure are essentially the same. The effect of experimental time on E_a will be discussed in the next section.) Usually, the E_a distribution curves obtained from MTGA are reproducible, showing very little variation between replicate runs even for small sample masses. However, the E_a was found to change with sample mass. Increasing sample mass resulted in a decrease in the calculated E_a for both kraft lignins. As shown in Figure 7, this tendency can also be observed for other biomass components, for example, cellulose.[26]

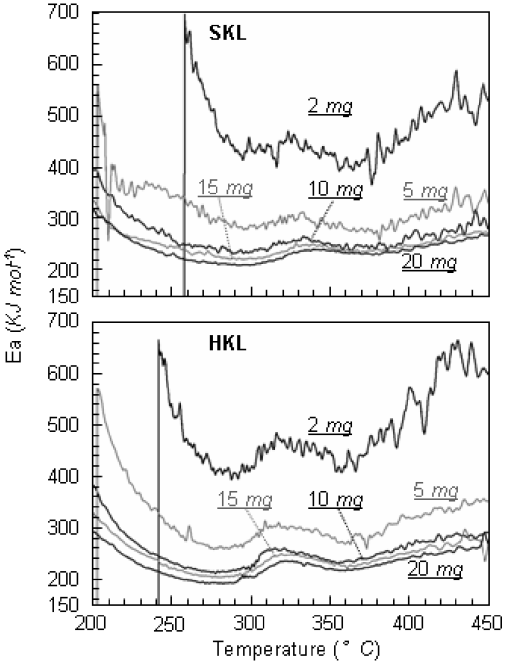

Figure 6. Effect of sample mass on E_a distribution curve of kraft lignin preparations measured by MTGA with dynamic heating rates.

Sub-reactions will take place more extensively in high volume samples, that is, large sample masses, than in small sample masses. In this case, calculated E_a values for small sample masses will be lower than that with large sample masses. Diffusion of heat will also affect TGA results, by retarding the thermal conductivity in high volume samples. However, the heating rate used

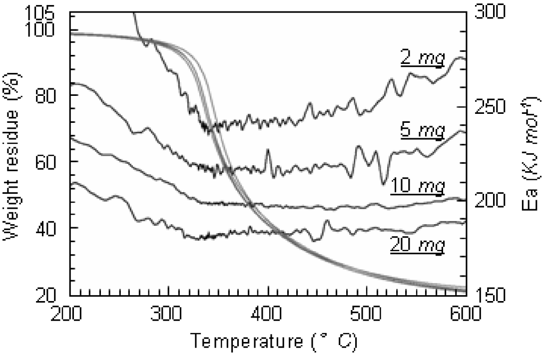

Figure 7. Effect of sample mass on E_a distribution curve of cellulose powder estimated by MTGA with dynamic heating rates.

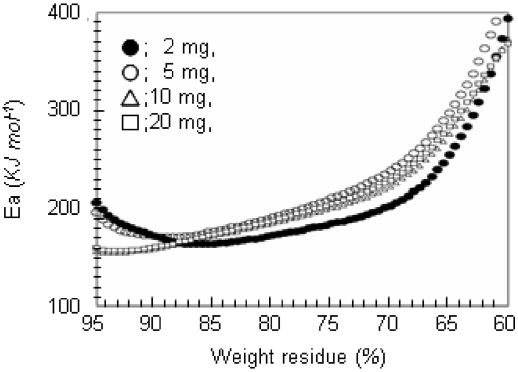

Figure 8. Effect of sample mass on E_a distribution curve of lignin preparations calculated by the Flynn and Wall, and Ozawa method.

for these analyses was very slow, and it can be seen that the TGA curves for the different mass samples are almost identical. In fact,E_a distribution curves calculated for SKL with different sample masses (5–20 mg) using the Flynn and Wall and Ozawa method, again show almost the same E_a distribution profiles (Figure 8). However, as expected the low mass sample, 2 mg, has a slightly lower E_a value, in agreement with the above speculation, but in contrast to that obtained from MTGA.

Effect of Temperature Conditions on the E_a Distribution Curves Calculated by MTGA

One typical difference between modulated and traditional TGA used in our study is heating rate. In the MTGA analysis, the Hi-Res method was utilized (heating rate was varied from ~1.8°C min^{-1} at the low temperature regions where no significant weight loss occurred, to ~0.35°C min^{-1}, at regions where the fastest weight loss occurred). This dynamic heating rate may affect E_a values. Therefore, E_a was calculated by MTGA without Hi-Res at a constant average heating rate. In these experiments, care was taken to use a slow enough heating rate, 1°C min^{-1}, to ensure collection of enough modulation cycles to be comparable to that of the Hi-Res runs. However, the constant heating rate (1°C min^{-1}) resulted in shorter experimental times, 600 min (Figure 9). It can be seen that the resolution of DTGA shown in Figure 9 decreased as compared to that of the Hi-Res method (Figure 2). This is due to the higher heating rate (1°C min^{-1} vs. ~0.35°C min^{-1} during the main decomposition step. With the constant heating rate the calculated E_a for the main reaction step decreased to ~230, ~210, and ~240 kJ/mol for SKL, HKL, and Alcell, respectively. These E_a values were slightly lower than those obtained with the Hi-Res

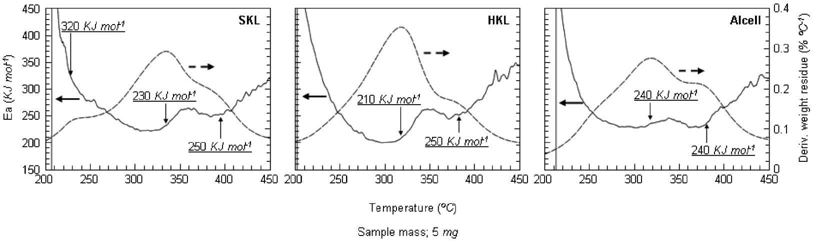

Figure 9. Temperature modulated TGA analysis of lignin preparations measured with a constant heating rate of 1°C min^{-1}. (sample mass; 5 mg)

method; ~50, 60, and 40 KJ mol^{-1} lower than corresponding Hi-Res values for SKL, HKL, and Alcell, respectively. Although technical lignins exhibit a glass transition at relatively low temperature ranges, at high temperature, they undergo condensation reactions, comparable to a thermosetting material, which would affect the E_a values calculated for lignin pyrolysis. As discussed earlier, slow heating rates reduce the thermal decomposition temperature of a sample by prolonging the exposure time of a sample to a given temperature. This would significantly affect the extent of sub-reactions, including condensation reactions, and may be one reason for the higher E_a values obtained from the Hi-Res method. To examine this, MTGA was conducted at the slowest heating rate used during the Hi-Res experiments, 0.3°C min^{-1}. Under these conditions, E_a values for the main degradation process (degree of conversion = 5–35%) were calculated to be 270 and 240 KJ mol^{-1} for SKL and HKL, respectively (Figure 10). These values are higher than those calculated using a heating rate of 1.0°C min^{-1}, and the E_a value for SKL was close to that calculated in the Hi-Res experiment, although the sample mass used for Figure 9, 10 mg, is bigger than that for Figure 3, 5 mg. These results support the effect of sub-reactions on the E_a distribution curve.

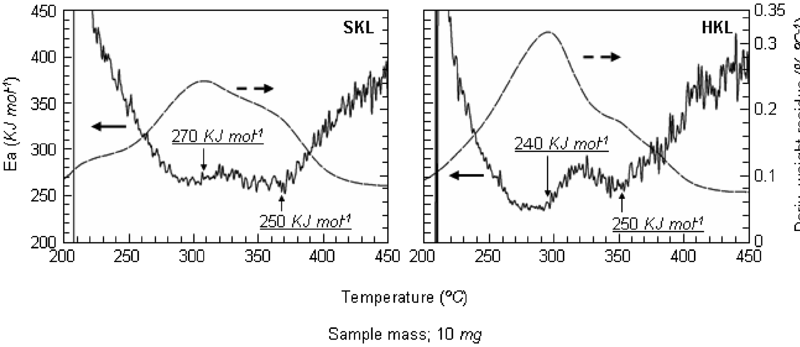

Figure 10. Temperature modulated TGA analysis of kraft lignin preparations measured with a constant heating rate of 0.3°C min^{-1} (sample mass; 10 mg).

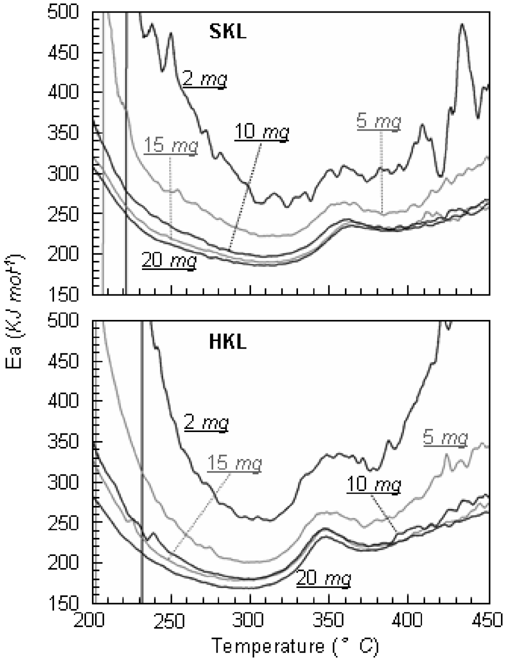

Figure 11. Effect of sample mass on Eα distribution curve of kraft lignin preparations measured by MTGA with a constant heating rate of 1°C min^{-1}.

Finally, the effect of sample mass on the E_a values calculated by MTGA with a constant heating rate (1.0°C min^{-1}) is shown in Figure 11. Under these conditions the effect of sample mass on E_a value is reduced, but still observed. Thus, this phenomenon is not due solely to the dynamic average heating rate; E_a values comparable to those determined by traditional kinetic analysis can be obtained using a linear heating rate of ~1.0°C min^{-1} and a relatively large sample mass, >10 mg.

CONCLUSIONS

Temperature modulated TGA (MTGA) was utilized to study the kinetics of lignin pyrolysis. As expected high resolution (Hi-Res) MTGA provided better resolution and separation of the multi-step reactions in lignin pyrolysis as compared to conventional TGA. Using MTGA reproducible apparent activation energy, E_a, distribution curves could be calculated for the reactions occurring during lignin pyrolysis with a single experimental run. However, the E_a values calculated by Hi-Res MTGA were higher than those determined by traditional TGA. This discrepancy can be reduced by using a constant heating rate, which can also lead to reduced experimental times. The short experimental time at temperature further reduces the extent of sub-reactions that occur when the sample is exposed to high temperature for a prolonged period of time. Using MTGA with a constant heating rate, E_a values for the main reaction step in lignin pyrolysis were calculated at ∼230, ∼210, and ∼220 kJ/mol for SKL, HKL, and Alcell, respectively. These values are comparable to those estimated by the traditional TGA with Flynn and Wall and Ozawa method. Therefore, a constant heating rate may be the better choice for lignin to compare E_a distribution between different samples by MTGA. Sample mass also appeared to have an impact on the calculated E_a values, with smaller sample masses producing larger E_a values, but can be eliminated by use of >10 mg of sample mass. Overall, MTGA is a convenient method to estimate the E_a of lignin when suitable experimental conditions are adopted.

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