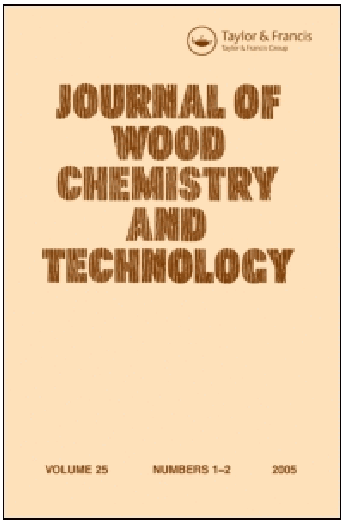

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Gaugler, Marc and Grigsby, Warren J.(2009) 'Thermal Degradation of Condensed Tannins from Radiata Pine Bark', Journal of Wood Chemistry and Technology, 29: 4, 305 — 321

To link to this Article: DOI: 10.1080/02773810903165671

URL: http://dx.doi.org/10.1080/02773810903165671

Journal of Wood Chemistry and Technology, 29: 305–321, 2009
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ISSN: 0277-3813 print / 1532-2319 online
DOI: 10.1080/02773810903165671

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Thermal Degradation of Condensed Tannins from Radiata Pine Bark

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Abstract: In order to understand the influence of the inherent chemistry on the relative thermal stability of condensed tannins, the thermal degradation behaviors of various radiata pine bark extracts have been investigated using thermogravimetric analysis (TGA). Generally, results suggest pine bark extract fractions may be readily processed at temperatures below 200°C if co-extracted polysaccharides contents are minimized. Those extracts possessing greater carbohydrate content and lower tannin purity tend to have decreased thermal stability. The initial onset temperature for degradation of relatively crude extracts with high proportions of carbohydrate contents were relatively low (*ca.* 150°C), whereas extract purification to <5% carbohydrate content gave increases in thermal stability of at least 50°C. The complicity of the carbohydrate content in the degradation of the tannin samples was also supported by calculated Ozawa activation energies and modulated TGA experiments. While no increase in the thermal stability was gained by acetylating the pendant hydroxyl groups of the pine bark tannin extract, chemical variations such as sulfonation have a large effect on thermal degradation, promoting lower degradation temperatures.

Keywords: Condensed tannins, decomposition, DSC, polyphenolics, TGA, thermal analysis

INTRODUCTION

Globally there is growing awareness and interest in the use of renewable feedstocks and chemicals as alternatives to petrochemicals. This interest is being driven by a number of factors including an emerging industrial biotechnology sector that is based on a number of differing bioresources.[1] While

The authors are grateful to the Biopolymer Network Ltd. for financial support of this work. The Biopolymer Network Ltd. is funded through the New Zealand Foundation of Research, Science and Technology. The authors also extend their thanks to Dr. K. Torr for assistance with ^{1}H NMR analysis.

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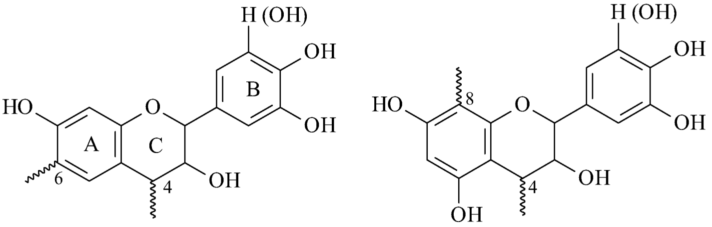

Figure 1. Typical structures of condensed tannins. Resorcinolic type with 4-6 interflavanyl linkage such as found in profisetinidin containing quebracho extracts (left) and phloroglucinolic type with 4–8 interflavanyl linkage such as found in radiata pine bark extracts (right).

currently not prominent, one class of bio-derived materials, termed condensed tannins, offers a potential synthetic utility in a range of industrial applications. Condensed tannins are polyphenolic flavanyl oligomers which can be extracted from several sources including the heartwood and bark of trees.[2] Moreover, condensed tannins can be obtained from purpose grown crops or residue wastes from pulp and paper or lumber processing. While the constituent chemistry of extracts can vary substantially, condensed tannins have the general oligomeric structures shown in Figure 1 and are commonly bonded by interflavanyl linkages through either C4-C6 or C4-C8.[3] Although a range of other uses have been explored, historically these polyphenolic materials have primarily found industrial application in tanning leather, adhesives or as flow modifiers in cements and drilling fluids.[4] Currently tannins are extracted in commercial quantities from Acacia and Quebracho species for such applications, although they can be obtained from other species including spruce or pine.

We have been investigating the extraction, characterization, and utilization of condensed tannins in a range of potential applications.[5] Primarily this has been with radiata pine bark tannins, evaluating the chemical constituents, molecular weight profiles and chemistry of extracts as well as separation technologies and extract refinement for functionalizing, chemical conversion or synthetic application. Condensed tannins from pine bark are generally phloroglucinolic tannins having two meta-orientated hydroxyls on the A ring (Figure 1).[6] In one emerging application, there is potential to incorporate modified pine bark tannin extracts directly into structural adhesive formulations for use in bonding wood.[7] In this application the tannin substitutes for resorcinol, a more expensive component in the adhesive formulation. Similarly, as renewable, biobased materials, tannins offer potential to substitute in part or full for other synthetic petrochemical materials in a variety of applications where phenolic derivatives are used such as in plastics, adhesives, resins, and coatings.[8]

In some industrial applications, the processing and formulation of chemical intermediates and products will require the condensed tannins exhibit relatively high thermal stability where processing temperatures may range or exceed

150–200°C. Potential examples include plastic processing and chemical modification as in polyester synthesis. This will require demonstration of thermal stability beyond temperatures of more traditional applications of tannins.[2,3] Relative to other biomaterials, little is known about condensed tannin stability at temperatures $>100°C$. Other bioderived materials such as cellulose, wood components, starch, and proteins have a number of investigations reporting their relative thermal stabilities and degradation onset temperatures of the materials in native and modified forms.[9–12] In the case of condensed tannins only a few products incorporating tannin extracts have had their thermal stability evaluated. This is usually to confirm chemical reactivity or adhesive cure, with differential scanning calorimetry (DSC) the predominant thermal analysis technique used.[13]

In the current study, we report evaluations of the relative thermal stability of various pine bark tannin extracts varying in degree of purity, refinement, and chemical conversion using thermal gravimetric analysis (TGA). These condensed tannin extracts have been fractionated and differ in polysaccharide content. Chemical modification was by sulfite treatment or acetylation and are typical condensed tannin modifications. TGA was used to evaluate thermal degradation profiles primarily investigating the onset and activation energies for the processes of degradation. DSC was also used to corroborate decomposition processes such as volatiles loss or charring. The results of this analysis contributed to determining the suitability and further use of the condensed tannins in high temperature processing applications.

METHODS AND MATERIALS

Various condensed tannins were investigated and include crude pine bark extracts containing polysaccharides co-extracted with the tannins, fractioned bark extracts having a high degree of tannin purity and extracts produced with differing chemistries due to source, extraction conditions, or post-treatment (Table 1). The pine bark tannin was obtained directly from extracting radiata pine bark as outlined below. Colatan GT100, a unmodified quebracho extract product obtained as a spray dried powder, was sourced from Unitán S.A.I.C.A. (Buenos Aires, Argentina). Catechin was obtained as the dihydrate form from Sigma Aldrich.

Pine Bark Extraction

Generally, to obtain crude pine bark tannin, dried radiata pine bark from 26 year old pulp logs was hammer milled (<2 mm) and extracted into hot water (95°C) before being filter pressed. This process was continued until the filtrate was sufficiently concentrated and the liquor then passed through a spray

Table 1. Description of tannin samples with NMR estimated carbohydrate content

	Name	Description	Carbohydrate content (%)
1	Catechin	Model compound with monomeric tannin structure	—
2	HW Crude	Hot water extract of pine bark	15
3	Sulfited Tannin	Pine bark extracted with sodium sulfite	12
4	Ultrafiltered HW	HW pine bark extract ultrafiltered	5
5	Purified HW	HW extract purified by a novel fractionation process	<1
6	Carbohydrate rich HW	A carbohydrate rich HW extract	30
7	Quebracho Tannin	Commercial extract from Quebracho	n/a
8	Tannin Acetate	Acetylated pine bark tannin	0

drier operating a 300°C/120°C temperature regime.[7] The isolated spray dried extract obtained was the HW Crude pine bark extract (2, Table 1). Similarly, sodium sulfite (2% w/w on bark) was used to extract the bark and the resulting spray dried extract was the Sulfited Tannin (3, Table 1).

Pine Bark Extract Refinement

The HW Crude extract was further refined by processing the reconstituted extract through a 5000 kDa ultrafiltration membrane.[14] The retentate from this ultrafiltration was isolated and freeze dried as the Ultrafiltered HW (4, Table 1) and the permeate discarded. The reconstituted HW Crude extract was also fractionated by partitioning through use of a proprietary method to give two fractions that were purified and carbohydrate rich fractions, labelled Purified HW and Carbohydrate rich HW, respectively (5 and 6, Table 1).

Preparation of Tannin Acetate

Acetylated tannin was prepared by treating HW Crude pine bark extract (5 g) with neat acetic anhydride (12 mL) and 1-methylimidazole (5% w/w) as catalyst. The mixture was heated at 65°C for 4 h before carefully pouring into iced water. The precipitated product was further washed with portions of water and filtered until the filtrate water was >pH 4. The pale brown product was isolated in 75% yield and the fully esterified product confirmed by ^{1}H NMR analysis.[15]

^{1}H NMR Analysis

A Bruker Avance 400 NMR instrument was used to obtain ^{1}H NMR spectra. Samples were dissolved into a mixture of deuterated acetone and D_2O and a spectrum acquired using standard acquisition parameters and a spectral width of 20 ppm. The carbohydrate contents of each fraction were then estimated by integrating the aryl proton region (7.5–5.5 ppm) with respect to the carbohydrate region (ca. 3.2–4.2 ppm) using a calibration curve generated from known polysaccharide contents.

Thermogravimetric Analysis (TGA)

TGA experiments were performed using a Thermal Analysis Instruments Q500 TGA. The furnace and balance were continuously purged with nitrogen at 60 and 40 ml/min, respectively. Sample size was 16 ± 1 mg. The temperature ranged from 25 to 900°C with heating rates of 2, 5, 10, 15, and 20°C/min. The resulting degradation profiles were plotted as %weight loss and its first time derivative. Activation energies were calculated using Ozawa plots determined over a range of heating rates (2, 5, 10, 15, 20°C/min) or by the Kissinger method using standard routines.

High Resolution Modulated TGA (MTGA)

The sample size was 16 ± 1 mg. The TGA temperature was modulated at an amplitude of ±5°C for all experiments. The modulation period was 200 s and the average heating rate was 4°C/min at a resolution of 6 and sensitivity of 1 for all experiments.

Differential Scanning Calorimetry (DSC)

DSC was conducted on a Thermal Analysis Instruments Q1000 DSC under a nitrogen purge. A standard heating rate of 10°C/min was employed from room temperature to 400°C. A sample size of 4–6 mg was placed in an encapsulated pan and then the lid pierced with a pin before heating samples.

RESULTS

In order to understand the thermal degradation profiles of fractionated extracts, the carbohydrate contents of the various radiata pine bark extract fractions were first determined using ^{1}H NMR analysis (Table 1). By quantifying the integral ratios of the aryl protons with those attributed to carbohydrate in the ^{1}H NMR spectra, the carbohydrate content of the samples was estimated.[5] The crude pine bark extract had 15% carbohydrate, consistent with literature where the carbohydrate content can range between 12 and 20% depending on the bark source, tree height and extraction conditions used.[2,3,16] Ultrafiltration with a 5000 kDa membrane gave a pine bark fraction with a reduced carbohydrate content of 5%. Partitioning the crude extract into two fractions produced a relatively purified tannin fraction with <1% carbohydrate content and a carbohydrate rich fraction containing some 30% carbohydrate.

Thermal Degradation Profiles

Shown in Figure 2 are the thermal degradation profiles for hot water pine bark tannin extract (Crude HW), the corresponding tannin material extracted with sodium sulfite and the flavanyl monomer catechin, whose structure is that of the monomeric phloroglucinolic unit in Figure 1. A heating rate of 10°C/min under nitrogen was used. Each weight loss curve is plotted from 100°C to 800°C and normalized by omitting any initial weight loss due to evaporation

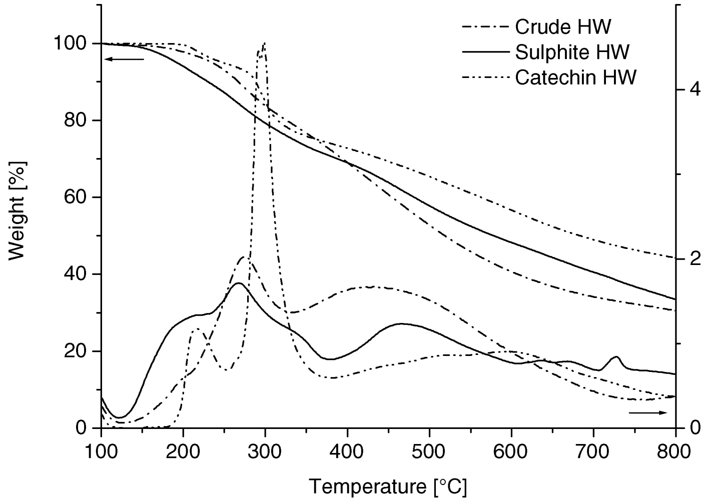

Figure 2. Thermal gravimetric analysis profiles of catechin, HW Crude, and Sulfite Tannin samples.

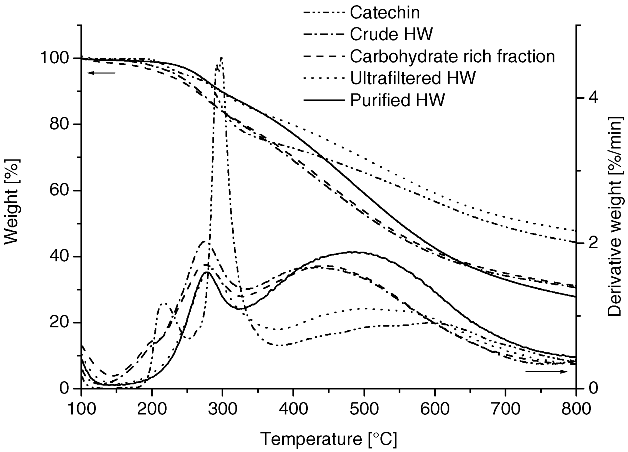

Figure 3. TGA of tannin extracts and fractions having varying carbohydrate composition.

of adsorbed water from the sample. This was due to the hygroscopicity of the samples which variously adsorbed water prior to analysis. Catechin had two distinct degradation processes with maxima at 230 and 310°C, while the pine bark samples have much broader profiles with maxima at ca. 280°C and ca. 450°C. For catechin, the thermogram shows minimal weight loss below 200°C, at which point there was an initial weight loss (ca. 5%) then a further, greater weight loss from 250 to 315°C (ca. 20%) after which there was a gradual decrease in sample weight on further heating which led to a total loss in weight of ca. 60% at 800°C. Although they differ, the weight loss profiles for the Crude HW and Sulfite Tannin were relatively similar when compared with catechin. However, the three samples displayed differing onset temperatures for initial sample degradation which ranged from 150 to 200°C as determined by changes in the first derivative weight loss curve (%/min).

Shown in Figure 3 are thermograms of pine bark extracts having varying carbohydrate content. The weight loss curves show two distinct profiles for this series of pine bark samples as described for Figure 2. A comparison of weight derivative curves revealed the two samples with relatively higher carbohydrate content, Crude HW and Carbohydrate rich HW, had lower onset temperatures (ca. 150°C) compared to extracts relatively free of carbohydrate. The two refined extracts, Purified HW and Ultrafiltered HW, had higher onset temperatures which were comparable to catechin. Furthermore, as well as differing onset temperatures, there were also differences in the profile of the weight derivative curves which could be attributed to the presence of carbohydrate. Both Crude HW and Carbohydrate rich HW weight derivative curves exhibit a defined shoulder to the broad, major degradation of the sample that

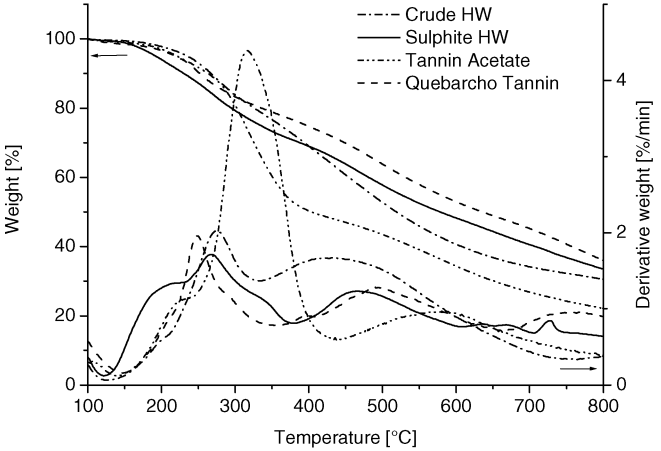

Figure 4. TGA of tannin samples from differing sources or chemistry.

had a common maximum (ca. 280°C) with the purified samples. While values for oligomeric polysaccharide decomposition are reportedly greater than 200°C,[17] it was apparent this initial degradation of samples having significant carbohydrate content (>10%) was attributable to polysaccharide decomposition.

A comparison of tannin extracts having differing chemistry is shown in Figure 4. The Sulfited Tannin had a differing weight loss profile to that of the Crude HW. The degradation onset temperature (130°C) of Sulfited Tannin was ca. 30°C lower than the Crude HW. The profile of the weight derivative curve was also broader for the Sulfite HW sample, though the maximum of this curve was 275°C which was comparable to HW Crude (280°C). In the case of the acetylated tannin, a similar degradation onset temperature (160°C) was observed as that of the Crude HW, but this material has a different weight loss profile with some 50% weight loss by 400°C. This was almost twice that of the tannin extracts at this temperature. For the Quebracho Tannin sample that has a high proportion of the resorcinolic flavanyl structure (Figure 1),[2,6] the initial onset and degradation profile was similar to the pine bark extract samples, although the maxima for this process (240°C) was ca. 40°C lower than the Crude HW.

Analysis of the differing tannin chemistries revealed that two typical treatments of condensed tannins led to lower thermal stability than the crude radiata pine bark tannin sample (Figure 4). The partial sulfitation of the tannin which results in a sulfonate group at the 4 position (Figure 1) *via* cleavage of the 4-8 interflavanyl linkage[2,3,6] has promoted thermal instability, with a distinctly lower decomposition onset. This was not unexpected as pyrolysis of condensed tannins results in catechol generation through cleavage of the pyranyl ring and phenyl B-ring liberation.[18] The presence of a sulfonate group on the pyranyl ring (4-position) likely promotes this pyrolytic decomposition.[19] In the case of full esterification of pine bark tannin by acetylation, similar thermal stability as the Crude HW was apparent, despite the absence of any carbohydrate species in this sample. Below 400°C the thermal decomposition of tannin acetate was dominated by relatively high weight loss (50%), which was probably due to acetyl group loss. For the quebracho-derived sample GT100, the relatively lower thermal stability of this extract with a weight loss maximum at 240°C may have been promoted by the differing hydroxylation pattern of this polyphenol. The lower number of hydroxyls and substitution pattern on the A-ring has been implicated in pyrolysis at lower temperatures.[18]

Calculated Degradation Activation Energies

Ozawa plots were produced for each tannin sample using differing heating rates ranging from 5 to 15°C/min to determine decomposition temperatures and the activation energies for these processes (Figure 5).[20] The activation energies (Ea) for initial decomposition were calculated for weight losses ranging between 5 and 22.5% using the slopes of these curves. Above weight losses of 25%, the samples tend to show self-sustained thermal degradation, which generally occurred at temperatures >300°C (Figures 2 and 3).

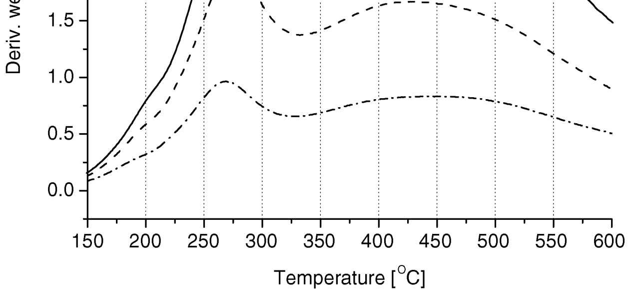

Figure 5. TGA profiles of Crude HW with differing heating rates used to calculate activation energy values using the Ozawa method.

Table 2. Degradation temperatures and activation energies by the Ozawa method

	Peak	
Sample	Temp. (°C)	Ea (kJ/mol)
Catechin	197	242
HW Crude	228	401
Ultrafiltered HW	238	357
Purified HW	241	307
Carbohydrate rich HW	182	673
Sulfited Tannin	159	277
Tannin Acetate	189	214
Quebracho Tannin	217	259

Table 2 shows the Ozawa calculated activation energies for peak temperatures between 180–240°C up to the maximum for the initial weight loss (22.5%) using different heating rates (Figure 5). Comparison of the hot water extracted tannin fractions show the Ozawa calculated activation energies (Ea) ranged between 240 and 670 kJ/mol and were dependent on the relative carbohydrate contents of the samples. Higher peak temperatures and lower activation energies were evident for samples with increasing purity. The relative carbohydrate content was found to strongly correlate with both the peak degradation temperature ($R^2 = 0.92$) and Ozawa activation energies ($R^2 = 0.93$, Figure 6). For samples with differing tannin chemistry such as Sulfite Tannin and Tannin Acetate there were lower peak temperatures and activation energy values of ca. 250 kJ/mol.

Activation energies are dependent on the type of chemical bond being cleaved.[21] Given the relationship of extract purity with degradation onset temperatures and kinetics calculated by the Ozawa method (Table 2), activation energy values were also calculated by the Kissinger method (Table 3).[22] With the Kissinger method the activation energy values were obtained from the slope of $\ln(\beta/T_p^2)$ versus $1/T_p$ plot. This method differs from the Ozawa method, which utilized weight loss in determining Ea values and therefore was sensitive to the influence of carbohydrate.[20] Kissinger Ea values ranged from 308 and 205 kJ/mol for the different tannin chemistries with the Sulfited Tannin the highest and Quebracho Tannin the lowest. The Crude HW and Tannin Acetate had Ea values of 257 and 226 kJ/mol, respectively.

Modulated TGA

Given tannin purity impacted on the onset temperatures and activation energy values (Table 2), high resolution modulated TGA (MTGA^{TM}) was utilized to determine whether there were any further distinctions in the

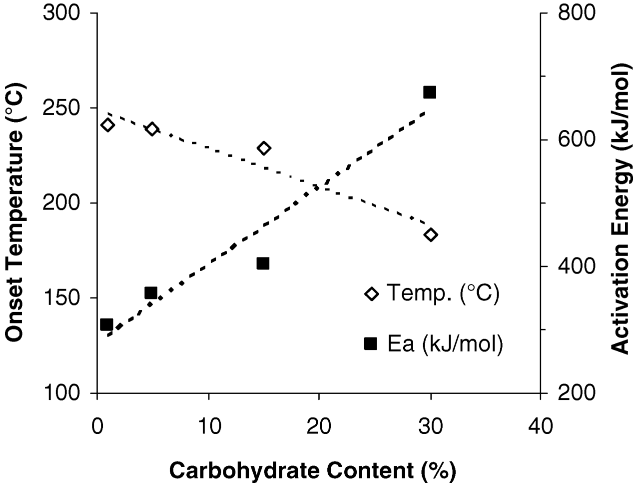

Figure 6. Comparison of Ozawa activation energy values with sample carbohydrate content.

thermal degradation profiles between tannin samples (Figure 7). In applying MTGA, differences in profiles were evident with samples exhibiting differing decomposition kinetics.[23] Evident with the MTGA profiles were Ea values consistent with those calculated by the Kissinger method (Table 3). The activation energy profiles for the Carbohydrate rich HW sample exhibited a change in activation energy with weight loss conversion. Therefore the decomposition of this fraction is thought to be autocatalytic rather than a first order reaction. In contrast, both the Purified HW and Ultrafiltered samples had an initial decrease in Ea values up to 10–15% conversion followed by a relatively flat profile above 25% conversion indicative of autocatalytic decomposition.[23]

Table 3. Degradation temperatures and activation energies calculated by the Kissinger method

Sample	T_P (°C)	Activation energy Kissinger method (kJ/mol)
Catechin	217 (295)	176 (121)
HW Crude	275	256
Ultrafiltered HW	274	161
Purified HW	284	211
Carbohydrate rich HW	279	247
Sulfited Tannin	266	308
Tannin Acetate	314	226
Quebracho Tannin	247	205

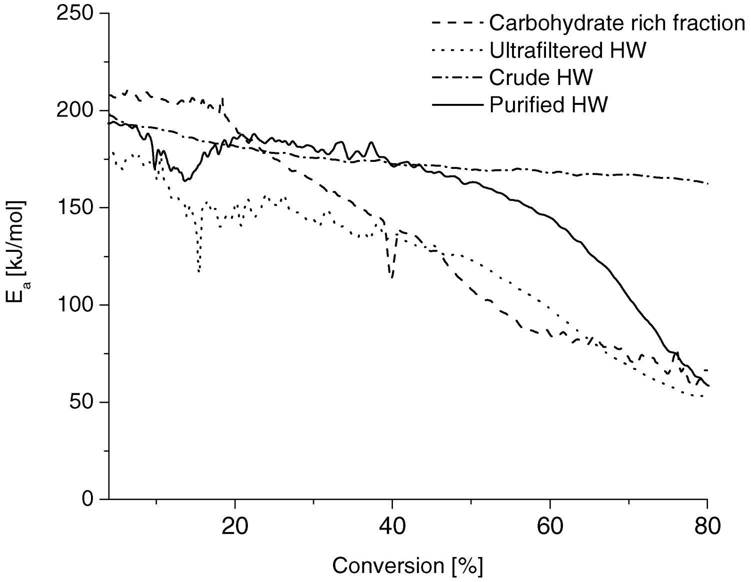

Figure 7. Thermograms from Hi-Res^{TM}MTGA^{TM}analysis of selected tannin samples.

The contrasting activation energy curves between samples was confirmation the presence of higher carbohydrate contents led to differing decomposition kinetics compared to those samples relatively low in carbohydrate. The HW Crude showed intermediate behavior between these samples, which resulted in a relatively flat, smooth profile of Ea values through the entire 60% weight loss on heating. With MTGA, it is anticipated one decomposition process is finished first, before the next.[21] However, while the HW Crude sample indicates a single decomposition mechanism where the Ea was independent of the weight loss, the results collectively suggest that carbohydrate and tannin may “interact” when decomposing, rather than decompose independently.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was undertaken on relevant samples to further assess the nature of sample decomposition (Figure 8). By conducting DSC it was anticipated relative heat flow behaviors of samples would indicate whether decomposition processes were through loss of volatiles or by charring. Analysis of extracts containing varying proportions of carbohydrate show similar trends on heating through to 400°C. On heating through to 100°C all samples initially show a broad endotherm attributable to loss of adsorbed water. On further heating the processes of degradation were apparent with all

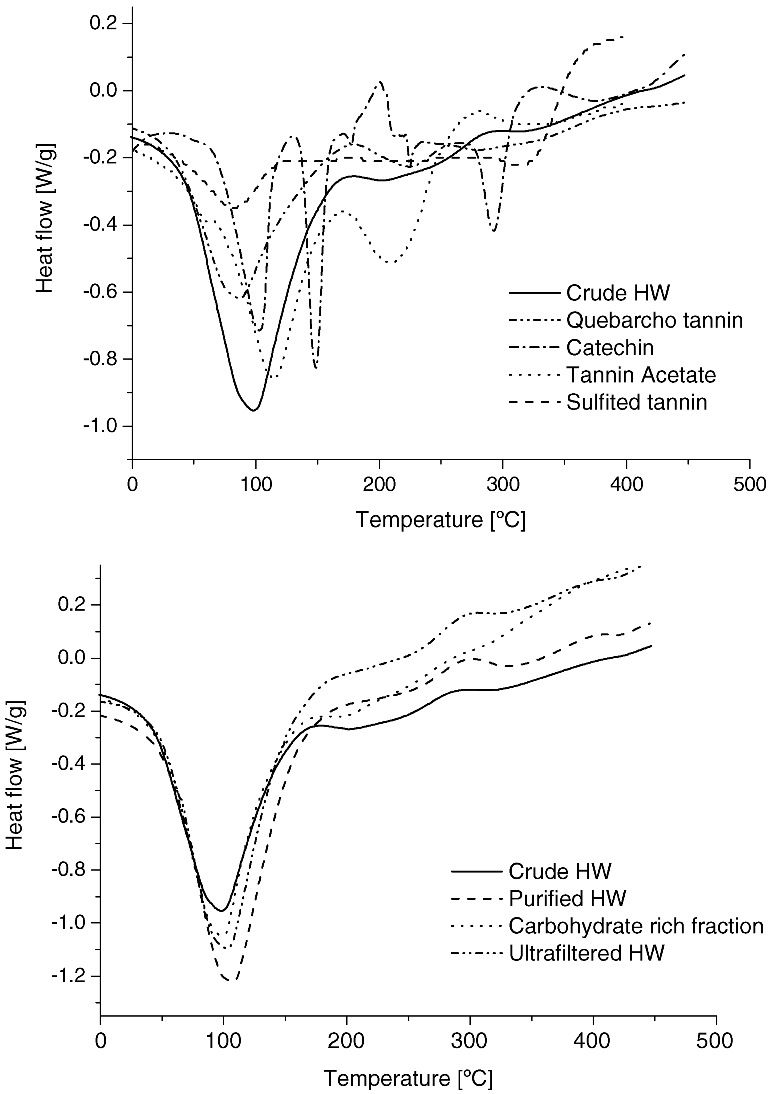

Figure 8. Differential scanning calorimetry thermograms for various tannin samples.

samples exhibiting a general exothermic increase upon heating above the onset temperatures for degradation established by TGA. The DSC thermograms were also distinguished by an exotherm between 250 and 320°C. Figure 8 also shows the Purified HW and ultrafiltered HW samples had exothermic behaviors initiating at relatively higher temperatures than the Carbohydrate rich fraction and Crude HW samples, consistent with TGA (Figure 3). Evident with this exothermic behavior was a likelihood samples were charring rather than decomposing through loss of volatiles. Given the polyphenolic nature of tannins, this would be expected from the nature of the pyrolytic decomposition of tannins as assessed by pyrolysis GCMS.[18]

DSC analysis of those tannin samples having differing chemistry showed some contrasting behaviors between samples (Figure 8). The Quebracho sample had a relatively similar DSC profile as that for Crude HW. The Quebracho sample showed the same initial endotherm attributable to water loss, then a second, minor endothermic feature consistent with onset of degradation (Figure 4), which was followed by exothermic heat flow on further heating. As a comparison, catechin, a flavonoid monomer, showed two endothermic features at 100°C and 150°C consistent with losses of associated water. On further heating, there was both an exothermic (200°C) and endothermic peak attributable to catechin degradation.[24] The Sulfited Tannin DSC thermogram shows initial water loss, but above 100°C was characterized by a single, sharp exothermic increase above 300°C. This DSC behavior of the Sulfited Tannin above 100°C could be considered inconsistent with the relatively low degradation onset observed in thermogravimetric analysis (Figure 4). In the case of Tannin Acetate, this sample was characterized by a broad endothermic feature at 200°C followed by an exotherm (250°C), consistent with the onset of degradation and the observed high weight loss, respectively (Figure 4).

SUMMARY

Thermal degradation behaviors have been assessed for a range of radiata pine bark tannin samples using thermogravimetric analysis. With similar degradation profiles, there was a trend for increased thermal stability of samples with progressively lower carbohydrate contents and greater tannin purity. This increase in thermal stability was significant. Initial onset temperatures for degradation of crude extracts having high proportions of carbohydrate contents were relatively lower (ca. 150°C). Purification of the pine bark extract to <5% carbohydrate content led to a degradation onset ca. 200°C, an increase in thermal stability of at least 50°C. Furthermore, the calculated Ozawa activation energies for this initial degradation process were dependent on the extract carbohydrate content. The complicity of the carbohydrate content in the degradation of the tannin samples was also supported by modulated TGA experiments that established differences in degradation kinetics for those samples with varying carbohydrate content. In contrast, analysis using DSC did not readily distinguish differences in exothermic behaviors for initial degradation of those relatively purified tannin samples.

Analysis of samples with inherently differing tannin chemistry suggests the chemical variations have a large effect on thermal degradation. The presence of a sulfonate group on the tannin pyranyl ring promoted degradation at a lower temperature than the corresponding tannin sample extracted in hot water only. Esterification via acetylation of pendant hydroxyl groups did not increase the thermal stability of the tannin sample. A similar degradation onset temperature as the Crude HW sample was evident for the acetylated tannin, which was further distinguished by a relatively high weight loss attributed to loss of acetyl groups. In the case of the resorcinolic quebracho tannin sample, this was found to have relatively lower thermal stability than the crude pine bark extract.

In general, the results suggest condensed tannins from radiata pine may be readily processed at temperatures below 200°C if co-extracted polysaccharide contents are minimized. Such temperatures may allow tannins to be used in various processing applications that employ these temperatures. However, the relative purity and inherent chemistry of tannin-based materials will need to be considered if attempting to process tannin-based materials at temperatures up to 230°C. It now remains to further investigate the thermal stability of other condensed tannin fractions and substitution chemistries to further establish degradation behaviors of tannin materials.

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